

# Synthesis and Electrical Resistivity of Diiodotetrakis(isocyanide)rhodium(III) Cation-7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ) Radical Anion Salts and X-Ray Crystal Structure of Diiodotetrakis(4-methylphenylisocyanide)rhodium(III)<sup>+</sup>–TCNQ<sup>•-</sup> Salt

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## Abstract

Four simple and two complex TCNQ<sup>•-</sup> radical anion salts with diiodotetrakis(isocyanide)rhodium(III) cations were prepared; [Rh(RNC)<sub>4</sub>I<sub>2</sub>]<sup>+</sup>TCNQ<sup>•-</sup> (R = 4-MeC<sub>6</sub>H<sub>4</sub>, 4-MeOC<sub>6</sub>H<sub>4</sub>, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, and 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) and [Rh(RNC)<sub>4</sub>I<sub>2</sub>]<sup>+</sup>(TCNQ)<sub>2</sub><sup>•-</sup> (R = C<sub>6</sub>H<sub>5</sub> and 4-MeC<sub>6</sub>H<sub>4</sub>). The complex salts exhibit relatively small electrical resistivities, 8.3 Ω cm for R = C<sub>6</sub>H<sub>5</sub> and 30 Ω cm for R = 4-MeC<sub>6</sub>H<sub>4</sub>, while resistivities of the simple salts fall in the range 5.1 × 10<sup>5</sup>–3.0 × 10<sup>6</sup> Ω cm as compacted samples at 25 °C.

Electronic absorption spectra and magnetic susceptibilities indicate that the simple salts in the solid state involve the monomeric TCNQ<sup>•-</sup> radical anion, except for [Rh(4-MeC<sub>6</sub>H<sub>4</sub>NC)<sub>4</sub>I<sub>2</sub>]<sup>+</sup>TCNQ<sup>•-</sup> in which the TCNQ<sup>•-</sup> radical anion exists in a column with a weak electronic interaction. A single-crystal X-ray analysis of [Rh(4-MeC<sub>6</sub>H<sub>4</sub>NC)<sub>4</sub>I<sub>2</sub>]<sup>+</sup>TCNQ<sup>•-</sup> revealed the columnar structure of the TCNQ<sup>•-</sup> radical anion with an equal interplanar spacing. The monoclinic crystal, space group C2/c, has cell dimensions *a* = 7.4690(8), *b* = 24.759(2), *c* = 22.875(3) Å, β = 92.95(1)°, and *Z* = 4. Least-squares refinement, based on 3299 independent reflections with |*F*<sub>o</sub>| > 3σ(*F*), produced an *R* factor of 0.054.

## Introduction

It is well known that the partial oxidation of K<sub>2</sub>Pt(CN)<sub>4</sub> with halogen leads to the formation of K<sub>2</sub>Pt(CN)<sub>4</sub>X<sub>0.3</sub>·H<sub>2</sub>O (X = Cl, Br) [1] and that porphyrin and phthalocyanine nickel complexes (NiL) are oxidized by iodine to form NiL·I<sub>1–1.08</sub>

[2]. These partially oxidized metal complexes exhibit high conductivities. Recently, we reported the synthesis and electrical resistivity of tetrakis(isocyanide)rhodium(I) cation-7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) radical anion salts, [Rh(RNC)<sub>4</sub>]<sup>+</sup>(TCNQ)<sub>*n*</sub><sup>•-</sup> (R = alkyl or aryl group; *n* = 1, 2, or 3) [3]. It may be expected that the partial oxidation of these salts leads to more conducting materials. This idea prompted us to perform the oxidation of simple salts, [Rh(RNC)<sub>4</sub>]<sup>+</sup>TCNQ<sup>•-</sup>, by elemental iodine, where the rhodium(I) complexes are fully oxidized by iodine to give the TCNQ salts of rhodium(III) complexes without partial oxidation products.

This paper reports the preparation and electrical resistivities of simple and complex salts formed between diiodotetrakis(isocyanide)rhodium(III) cations and the TCNQ<sup>•-</sup> radical anion, [Rh(RNC)<sub>4</sub>I<sub>2</sub>]<sup>+</sup>(TCNQ)<sub>*n*</sub><sup>•-</sup> (R = C<sub>6</sub>H<sub>5</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, 4-MeOC<sub>6</sub>H<sub>4</sub>, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, and 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; *n* = 1 or 2). Electronic and magnetic properties of these salts in the solid state also are discussed in terms of the interaction between the TCNQ<sup>•-</sup> radical anions or between TCNQ<sup>•-</sup> and neutral TCNQ. The X-ray crystal structure of [Rh(4-MeC<sub>6</sub>H<sub>4</sub>NC)<sub>4</sub>I<sub>2</sub>]<sup>+</sup>TCNQ<sup>•-</sup> is also described.

## Experimental

### Materials

Complex precursors, [Rh(RNC)<sub>4</sub>]<sup>+</sup>TCNQ<sup>•-</sup> (R = 4-MeC<sub>6</sub>H<sub>4</sub>, 4-MeOC<sub>6</sub>H<sub>4</sub>, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, and 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) and [Rh(C<sub>6</sub>H<sub>5</sub>NC)<sub>4</sub>]<sup>+</sup>(TCNQ<sup>•-</sup>)<sub>0.67</sub>(ClO<sub>4</sub>)<sub>0.33</sub>, were prepared as reported previously [3].

All the manipulations for preparing the TCNQ complexes were carried out under nitrogen atmosphere.

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**Preparation of Diiodotetrakis(isocyanide)rhodium-(III)-TCNQ<sup>-</sup> Simple Salts, [Rh(RNC)<sub>4</sub>I<sub>2</sub>]<sup>+</sup>TCNQ<sup>-</sup> (R = 4-MeC<sub>6</sub>H<sub>4</sub> (2a), 4-MeOC<sub>6</sub>H<sub>4</sub> (3a), 2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub> (4a), and 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (5a))**

An equimolar mixture of [Rh(4-MeC<sub>6</sub>H<sub>4</sub>NC)<sub>4</sub>]<sup>+</sup>TCNQ<sup>-</sup> (500 mg, 0.64 mmol) and molecular iodine (160 mg, 0.64 mmol) in acetonitrile (40 cm<sup>3</sup>) was refluxed for 30 min, followed by filtration on heating. The resulting solution was allowed to stand in a refrigerator overnight to give a precipitate, which was collected by filtration and recrystallized from acetonitrile, affording purple needles of **2a** in a 70% yield. Simple salts **3a–5a** were similarly obtained in 60–75% yields by the reaction of iodine and [Rh(RNC)<sub>4</sub>]<sup>+</sup>TCNQ<sup>-</sup> with an appropriate R group.

Several attempts to prepare [Rh(C<sub>6</sub>H<sub>5</sub>NC)<sub>4</sub>I<sub>2</sub>]<sup>+</sup>TCNQ<sup>-</sup> by the reaction of [Rh(C<sub>6</sub>H<sub>5</sub>NC)<sub>4</sub>]<sup>+</sup>(TCNQ<sup>-</sup>)<sub>0.67</sub>(ClO<sub>4</sub><sup>-</sup>)<sub>0.33</sub> with iodine have been unsuccessful, probably because of instability.

**Preparation of Diiodotetrakis(isocyanide)rhodium-(III)-TCNQ Complex Salts, [Rh(RNC)<sub>4</sub>I<sub>2</sub>]<sup>+</sup>(TCNQ)<sub>2</sub><sup>-</sup> (R = C<sub>6</sub>H<sub>5</sub> (1b) and 4-MeC<sub>6</sub>H<sub>4</sub> (2b))**

An acetonitrile (40 cm<sup>3</sup>) solution containing [Rh(C<sub>6</sub>H<sub>5</sub>NC)<sub>4</sub>]<sup>+</sup>(TCNQ<sup>-</sup>)<sub>0.67</sub>(ClO<sub>4</sub><sup>-</sup>)<sub>0.33</sub> (500 mg, 0.73 mmol), iodine (190 mg, 0.73 mmol), and neutral TCNQ (150 mg, 0.73 mmol) was refluxed for 1 h. The resulting green solution was filtered on heating and the filtrate was allowed to stand in a refrigerator overnight to afford **1b**, which was recrystallized from acetonitrile, 50% yield. Complex salt **2b** was similarly obtained in a 60% yield by the equimolar reaction of **2a** with TCNQ. On the other hand, **3a–5a** have only been recovered in the reactions with neutral TCNQ.

Elemental analyses and properties of the simple and complex salts obtained are listed in Table I.

#### Physical Measurements

Electrical resistivities, electronic and infrared absorption spectra, and magnetic susceptibilities were measured as described previously [3, 4].

#### X-Ray Crystal Structure Determination for Salt 2a

Preliminary oscillation and Weissenberg photographs indicated a monoclinic system and possible space groups of *C2/c* and *Cc*. The former was later proved to be correct, based on the successful analysis. Accurate cell constants were determined by the least-squares fit of the angular coordinates of 48 independent reflections with  $2\theta$  values from 30° to 35°, which were measured on a Rigaku four-circle automated diffractometer with MoK $\alpha$  ( $\lambda = 0.71069$  Å) radiation.

#### Crystal Data

C<sub>44</sub>H<sub>32</sub>N<sub>8</sub>I<sub>2</sub>Rh (**2a**), *M* = 1029.50, monoclinic, space group *C2/c*, *a* = 7.4690(8), *b* = 24.759(2), *c* = 22.875(3) Å,  $\beta = 92.95(1)^\circ$ , *V* = 4224.5(8) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* (flotation) = 1.62 g cm<sup>-3</sup>, *D<sub>c</sub>* = 1.6187(4) g cm<sup>-3</sup>, *F*(000) = 2012,  $\mu$ (Mo-K $\alpha$ ) = 19.2 cm<sup>-1</sup>.

A single crystal with approximate dimensions 0.03 × 0.18 × 0.63 mm was used for the data collection on the diffractometer. Intensities were collected by using a graphite-monochromatized Mo-K $\alpha$  radiation and the  $\omega$ - $2\theta$  scan technique at a  $2\theta$  scan rate of 4° min<sup>-1</sup>. The scan width in  $\omega$  was (1.0 + 0.34 tan  $\theta$ )° and 30 s background counts were taken either side of the every scan. No significant intensity variation was observed through the data collection. The intensities were corrected for

TABLE I. Analytical Data and Properties of the TCNQ<sup>-</sup> Salts.

No.	Salt	Crystal form	mp (dec.) (°C)	Found (Calcd) %		
				%C	%H	%N
2a	[Rh(4-MeC <sub>6</sub> H <sub>4</sub> NC) <sub>4</sub> I <sub>2</sub> ] <sup>+</sup> TCNQ <sup>-</sup>	purple needles	172–177	51.11 (51.33)	3.12 (3.13)	10.94 (10.88)
3a	[Rh(4-MeOC <sub>6</sub> H <sub>4</sub> NC) <sub>4</sub> I <sub>2</sub> ] <sup>+</sup> TCNQ <sup>-</sup>	purple needles	198–202	47.97 (48.33)	3.16 (2.95)	10.31 (10.25)
4a	[Rh(2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NC) <sub>4</sub> I <sub>2</sub> ] <sup>+</sup> TCNQ <sup>-</sup>	purple needles	228–232	53.11 (53.11)	3.86 (3.71)	10.28 (10.32)
5a	[Rh(2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> NC) <sub>4</sub> I <sub>2</sub> ] <sup>+</sup> TCNQ <sup>-</sup>	green microcrystals	202–206	54.65 (54.70)	4.44 (4.24)	9.99 (9.81)
1b	[Rh(C <sub>6</sub> H <sub>5</sub> NC) <sub>4</sub> I <sub>2</sub> ] <sup>+</sup> (TCNQ) <sub>2</sub> <sup>-</sup>	purple needles	238–241	53.34 (53.04)	2.62 (2.40)	14.38 (14.27)
2b	[Rh(4-MeC <sub>6</sub> H <sub>4</sub> NC) <sub>4</sub> I <sub>2</sub> ] <sup>+</sup> (TCNQ) <sub>2</sub> <sup>-</sup>	purple needles	213–216	54.96 (54.52)	3.17 (2.94)	13.48 (13.62)

the Lorentz and polarization effects, but no correction was made for absorption. Of 4857 unique reflections measured in the range of  $3^\circ < 2\theta < 55^\circ$ , 3299 had significant counts  $|F_o| > 3\sigma(F)$ , which were used in the solution and refinement of the structure.

The coordinates of all the non-hydrogen atoms were obtained by conventional Patterson and Fourier syntheses. Block-diagonal least-squares refinement with anisotropic thermal parameters for all the non-

TABLE II. Atomic Coordinates ( $\times 10^4$ ; H,  $\times 10^3$ ) for  $[Rh(4-MeC_6H_4NC)_4I_2]^+TCNQ^-$  (2a) with e.s.d.s in Parentheses.

Atom	x	y	z
Rh	0	0	0
I	2764.6(7)	616.2(2)	-287.9(3)
C(1)	686(8)	154(3)	833(3)
C(2)	1541(8)	-656(3)	75(3)
C(3)	1807(8)	349(3)	1882(3)
C(4)	2125(11)	873(3)	2050(3)
C(5)	2753(12)	981(3)	2609(3)
C(6)	3054(9)	572(3)	3018(3)
C(7)	2726(11)	55(3)	2838(3)
C(8)	2099(11)	-69(3)	2281(3)
C(9)	3695(12)	704(4)	3635(3)
C(10)	3259(8)	-1531(2)	275(3)
C(11)	3110(11)	-1737(3)	823(3)
C(12)	3878(12)	-2230(3)	949(3)
C(13)	4790(9)	-2521(3)	541(3)
C(14)	4920(10)	-2296(3)	7(4)
C(15)	4159(9)	-1796(3)	-144(3)
C(16)	5602(12)	-3064(3)	697(4)
C(17)	795(10)	2472(3)	2373(3)
C(18)	1703(10)	2962(3)	2231(3)
C(19)	811(9)	3452(3)	2373(4)
C(20)	3341(9)	2966(3)	1957(3)
C(21)	4206(10)	2484(3)	1791(3)
C(22)	4210(10)	3457(3)	1815(3)
N(1)	1174(7)	238(2)	1298(3)
N(2)	2376(7)	-1030(2)	144(2)
N(3)	4903(10)	2093(3)	1662(3)
N(4)	4929(10)	3849(3)	1702(3)
H(4)	215(9)	116(3)	177(3)
H(5)	299(11)	133(3)	273(3)
H(7)	269(8)	-23(2)	311(3)
H(8)	197(10)	-42(3)	209(3)
H(91)	281(10)	87(3)	382(3)
H(92)	366(10)	41(3)	383(3)
H(93)	453(9)	101(3)	372(3)
H(11)	250(10)	-151(3)	111(3)
H(12)	369(9)	-237(3)	131(3)
H(14)	547(9)	-246(3)	-31(3)
H(15)	432(8)	-166(2)	-57(3)
H(161)	496(12)	-327(4)	89(4)
H(162)	581(9)	-322(3)	35(3)
H(163)	672(13)	-304(4)	94(4)
H(17)	146(8)	214(3)	228(3)
H(19)	148(9)	378(3)	230(3)

hydrogen atoms led to a residual index  $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.061$ . On the basis of anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for hydrogen atoms found in a difference-Fourier map, the final four cycles of the refinement gave  $R = 0.054$  and  $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.052$ . The weighting scheme,  $1/w = \sigma^2(F_o) + 0.0003|F_o|^2$ , was used. Atomic scattering factors for all the neutral atoms were taken from the tabulation [5]. The final atomic coordinates are listed in Table II. Atomic thermal parameters and observed and calculated structure factors are available from the editor.

Calculations for the crystallographic analysis were performed on HITAC M160H computers at the Information Processing Research Center, Kwansai Gakuin University.

## Results and Discussion

### Electrical Properties

Measurements of specific resistivities ( $\rho$ ) for compacted pellets of all the simple and complex salts have indicated that they behave as typical semiconductors in the temperature (T) range measured (30–90 °C), except for 5a which decomposed above 65 °C. Specific resistivities at 25 °C ( $\rho_{25^\circ C}$ ) and activation energies ( $E_a$ ) obtained from the equation  $\rho = \rho_0 \exp(E_a/kT)$  are listed in Table III, which shows also magnetic susceptibilities ( $\chi_M$ ) in the solid state at room temperature. The  $\rho_{25^\circ C}$  values of the simple salts fall in the range of  $10^3$ – $10^6 \Omega \text{ cm}$ . These values are smaller by one or

TABLE III. Electrical Resistivity ( $\rho$ ), Activation Energy ( $E_a$ ), and Magnetic Susceptibility ( $\chi_M$ ) of the  $TCNQ^-$  Salts.

Salt	$\rho_{25^\circ C}$ ( $\Omega \text{ cm}$ )	$E_a^a$ (eV)	$\chi_M^b$ ( $\text{emu mol}^{-1}$ )
Simple salt			
2a	$5.1 \times 10^3$	0.17	$-1.5 \times 10^{-4}$
3a	$3.0 \times 10^6$	0.36	$7.6 \times 10^{-4}$
4a	$2.8 \times 10^5$	0.28	$10.0 \times 10^{-4}$
5a	$7.4 \times 10^5$	0.39	$6.7 \times 10^{-4}$
Complex salt			
1b	8.3	0.043	$2.1 \times 10^{-4}$
2b	30	0.12	$4.7 \times 10^{-4}$

<sup>a</sup>Calculated from the linear relations in the 30–85 °C range, except for 5a in which the calculation was performed in the 30–60 °C range. <sup>b</sup>Measured at room temperature.

two orders of magnitude than are those of the corresponding rhodium(I) salts,  $[\text{Rh}(\text{RNC})_4]^+\text{TCNQ}^-$  ( $\text{R} = 4\text{-MeC}_6\text{H}_4$ ,  $4\text{-MeOC}_6\text{H}_4$ ,  $2,6\text{-Me}_2\text{C}_6\text{H}_3$ , and  $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ ) [3]. In particular, the resistivity of  $[\text{Rh}(4\text{-MeC}_6\text{H}_4\text{NC})_4\text{I}_2]^+\text{TCNQ}^-$  ( $5.1 \times 10^3 \Omega \text{ cm}$ ) is much smaller than are those of  $\text{TCNQ}^-$  simple salts with relatively small resistivities reported so far [6], such as alkali metal- and ammonium- $\text{TCNQ}^-$  salts. On the other hand, the  $\rho_{25}^\circ\text{C}$  values of complex salts **1b** and **2b** are comparable with those of the rhodium(I) complex salts with corresponding isocyanide ligands.

### Crystal Structure of $[\text{Rh}(4\text{-MeC}_6\text{H}_4\text{NC})_4\text{I}_2]^+\text{TCNQ}^-$ (**2a**)

Figure 1 shows the structure of the cation moiety, together with the selected bond distances and angles. The rhodium atom is coordinated by four

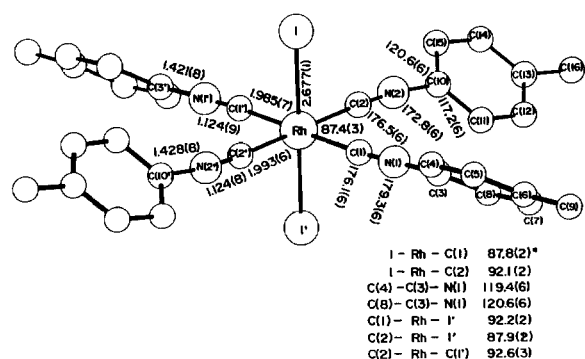


Fig. 1. The structure of the  $[\text{Rh}(4\text{-MeC}_6\text{H}_4\text{NC})_4\text{I}_2]^+$  cation together with the atom-labelling scheme and selected bond distances and angles.

carbon atoms of the isocyanide ligands and by two iodine atoms to assume a *trans*-octahedral geometry. Four carbons and rhodium are coplanar within  $\pm 0.028 \text{ \AA}$ , and two iodine and two carbon atoms as well as rhodium also make two planes with the maximum deviations of  $\pm 0.024 \text{ \AA}$ . The Rh-C distances (1.985(7) and 1.993(6)  $\text{ \AA}$ ) are close to those observed for  $[\text{Rh}_2\text{I}_2(4\text{-MeC}_6\text{H}_4\text{NC})_8]^{2+}(\text{PF}_6^-)_2$  (1.97–1.99  $\text{ \AA}$ ) [7],  $[\text{Rh}(\text{C}_6\text{H}_5\text{NC})_4]^+(\text{BF}_4^-)$  (1.954  $\text{ \AA}$ ) [8],  $[\text{Rh}(4\text{-FC}_6\text{H}_4\text{NC})_4]^+\text{Cl}^- \cdot \text{H}_2\text{O}$  (1.96  $\text{ \AA}$ ) [9], and  $[\text{Rh}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_4]^+\text{TCNQ}^-$  (1.96(2)  $\text{ \AA}$ , averaged) [10]. The Rh-I distance (2.677(1)  $\text{ \AA}$ ) is also close to that of  $[\text{Rh}_2\text{I}_2(4\text{-MeC}_6\text{H}_4\text{NC})_8]^{2+}(\text{PF}_6^-)_2$  (2.735(1)  $\text{ \AA}$ ) [7].

The  $\text{TCNQ}^-$  radical anion is planar with the deviation of the atoms ( $\pm 0.003 \text{ \AA}$ ) from the least-squares plane (Fig. 2). It is located on the two-fold axis (Fig. 3), and arranged along the *a* axis to form a column with an equivalent spacing (3.183  $\text{ \AA}$ ) between the  $\text{TCNQ}^-$  molecular planes. Although the molecular overlap is insufficient, this intermolecular spacing is close to that in tetrathiaful-

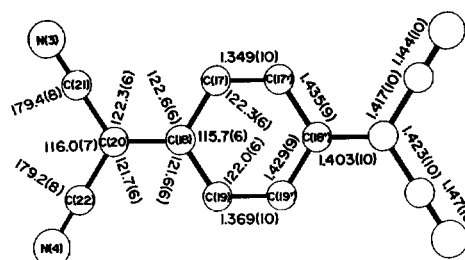


Fig. 2. The structure of the  $\text{TCNQ}^-$  radical anion together with the atom-labelling scheme and bond distances and angles.

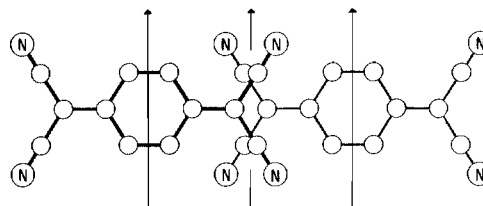


Fig. 3. The molecular overlapping scheme of the  $\text{TCNQ}^-$  radical anions.

valene- $\text{TCNQ}$  (3.17  $\text{ \AA}$ ) [11, 12] exhibiting a high conductivity. Such a  $\text{TCNQ}$  arrangement for **2a** is compatible with the relatively small resistivity as a simple salt. The negative charge on the  $\text{TCNQ}^-$  molecule has been estimated as  $0.68 e^-$  from the bond lengths of the molecule, according to the method of Flandrois and Chasseau [13]. The slightly oxidized electronic state compared with that of the  $\text{TCNQ}^-$  radical anion may contribute to a rather smaller resistivity of this salt in spite of the simple salt, as described above.

The crystal structure of the salt is illustrated in Fig. 4. The  $\text{TCNQ}^-$  molecules form columns along the *a* axis. The rhodium atom occupies (0, 0, 0) as well as  $(1/2, 1/2, 0)$ ,  $(1/2, 0, 1/2)$ , and  $(1/2, 1/2, 1/2)$ , and the cation moieties interact with one another along the *a* axis. The iodine atom contacts with the carbon atom of the 4-methylphenyl ring which belongs to another cation along the *a* axis, as illustrated in Fig. 5. The closeness is slightly shorter than is the sum of van der Waals radii of carbon and iodine atoms (3.85  $\text{ \AA}$ ) [14]. Furthermore, the cation moieties weakly interact with one another through the 4-methylphenyl ring. The 4-methylphenyl rings are arranged in a column along the *a* axis. The mean spacings between the rings are 3.60  $\text{ \AA}$  (I/I') and 3.55  $\text{ \AA}$  (II/III) with the carbon atom-4-methylphenyl ring plane closest distances of 3.38 and 3.33  $\text{ \AA}$ , respectively. Thus, the cation moieties are concluded to interact with one another along the *a* axis as well as the columnar arrangement of the  $\text{TCNQ}^-$  radical anions.

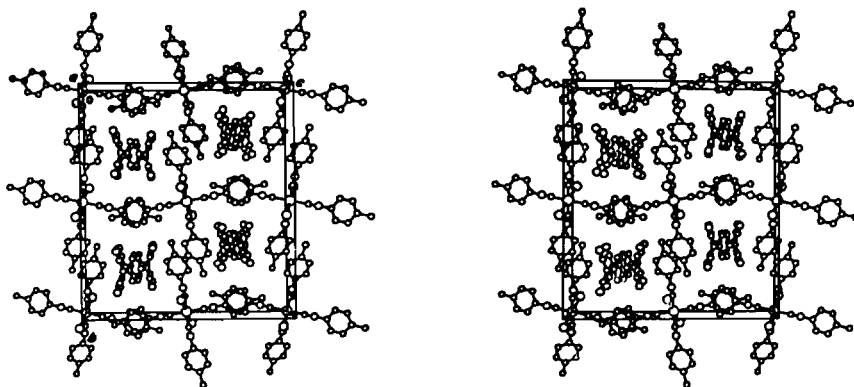


Fig. 4. A stereoview of the unit cell of  $[\text{Rh}(\text{4-MeC}_6\text{H}_4\text{NC})_4\text{I}_2]^+\text{TCNQ}^-$  (**2a**) along the  $a$  axis.

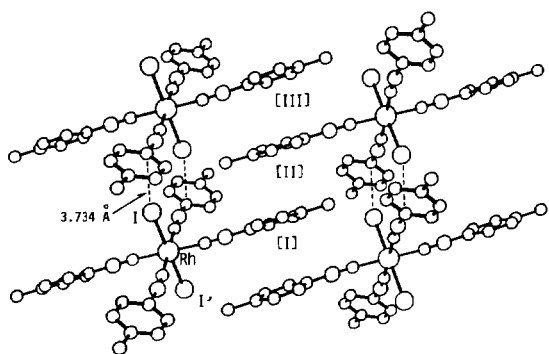


Fig. 5. A perspective view of the arrangement of the cation moieties along the  $b$  axis.

### Electronic and Magnetic Properties

An acetonitrile solution of **2a** exhibits electronic absorption bands at around 12 000, 24 000 and 40 000  $\text{cm}^{-1}$ , of which the former two are close to the wavenumbers of absorption maxima of monomeric  $\text{TCNQ}^-$  in acetonitrile [15]. The latter is due to the cationic moiety [16]. All other simple salts displayed almost the same spectra as **2a** in acetonitrile.

Figure 6 illustrates the electronic absorption spectra of simple salts **2a** and **3a** and complex salt **1b** in the solid state. Of the three bands observed for **2a** the lowest energy band around 8000  $\text{cm}^{-1}$  (shoulder) may be assigned to the charge transfer (CT) transition between the  $\text{TCNQ}^-$  radical anion [15], and the two higher energy bands around 11 500 and 22 200  $\text{cm}^{-1}$  to the first and second locally-excited states of the  $\text{TCNQ}^-$  moiety,  $\text{LE}_1$  and  $\text{LE}_2$ , respectively [17]. The electronic interaction between the  $\text{TCNQ}^-$  radical anions is consistent not only with the  $\text{TCNQ}^-$  radical anion column having the equal intermolecular spacing in the solid state, as revealed by the X-ray crystallography (Fig. 3), but also with the small diamagnetism of this salt.

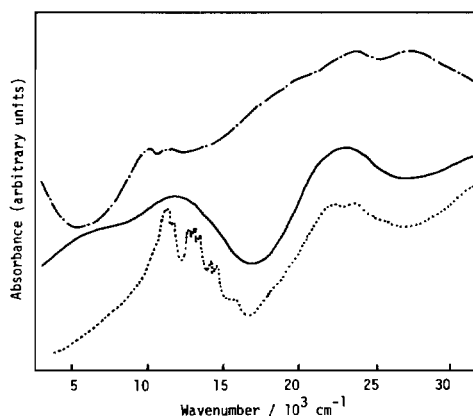


Fig. 6. Electronic absorption spectra of **2a** (—), **3a** (---), and **1b** (- · -) in Nujol mulls.

The absorption spectrum of **3a** in the solid state consists of several bands with fine structures; the appearance is similar to that of this salt in acetonitrile, suggesting the presence of monomeric  $\text{TCNQ}^-$  radical anion in solid **3a**. This is compatible with the paramagnetism and the large resistivity of this salt. The same conclusion may be drawn for salts **4a** and **5a** based on their electronic spectra (Table IV) and magnetic properties (Table III). Thus, solids **3a**–**5a** seem to constitute an alternate stacking of the cationic and anionic moieties such as  $\text{D}^+\text{A}^-\text{D}^+\text{A}^- \dots$  [18].

Although there are some intricate splittings in the solid state spectrum of **1b**, the spectrum shows four absorption maxima, 10 000, 11 500, 17 500 (shoulder), and 23 500  $\text{cm}^{-1}$ , which are characteristic of the  $\text{TCNQ}^-$  1:2 complex salts such as  $[\text{Et}_4\text{N}]^+(\text{TCNQ})_2^-$ ,  $[\text{MePh}_3\text{P}]^+(\text{TCNQ})_2^-$  [19], and  $[\text{SCH}_2\text{CH}_2\text{SC}=\text{NMe}_2]^+(\text{TCNQ})_2^-$  [4]. The former two bands are due to the monomeric  $\text{TCNQ}^-$  radical anion [19]. The latter does not contradict the fact that the salt exhibits a paramagnetic susceptibility. In addition, the infrared spectrum of **1b** displayed a very broad band in the 1600–4000

TABLE IV. Electronic Absorption Maxima<sup>a</sup> of the TCNQ<sup>•-</sup> Salts in Nujol Mulls.

Salt	Wavenumber (10 <sup>3</sup> cm <sup>-1</sup> )						
Simple salt							
2a	(8.0)	11.5			22.2		
3a		11.4	16.3 <sup>b</sup>		22.2	(23.1)	(23.9)
4a		11.5	16.3 <sup>b</sup>	(20.6)		22.9	
5a		11.5	16.3 <sup>b</sup>	(18.6)	22.4	23.3	(25.0)
Complex salt							
1b	10.0	11.5	(17.5)	(20.0)		23.5	27.5
2b	9.5	11.4	(16.7)	(20.4)		23.3	27.8

<sup>a</sup>Shoulders in parentheses. <sup>b</sup>Fine structures were observed.

cm<sup>-1</sup> range, which is ascribed to the CT transition between the TCNQ<sup>•-</sup> radical anion and neutral TCNQ [19]. Solid **2b** exhibited almost the same spectrum as **1b**. These results suggest that **1b** and **2b** involve a columnar stacking consisting of both the TCNQ<sup>•-</sup> radical anion and neutral TCNQ. This structure is consistent with low resistivities of these salts.

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