Inorganica Chimica Acta, 49 (1981) 79–84
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Synthesis and Electrical Resistivity of Tetrakis(isocyanide)rhodium(I) Cation–TCNQ Radical Anion Salts

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Received September 6, 1980

The following 12 simple and complex salts of the $\mathrm{TCNQ}^{\bar{\cdot}}$ *radical anion with tetrakis(alkyl- or arylisocyanide)rhodium(I) cations were prepared,* $[\mathrm{Rh(RNC)_4}]^+\mathrm{TCNQ}^{\bar{\cdot}}$ *(R = t-Bu, c-*C_6H_{11}*, 4-*MeC_6H_4*, 4-*$MeOC_6H_4$*, 2,6-*$Me_2C_6H_3$*, and 2,4,6-*$Me_3C_6H_2$*),* $[\mathrm{Rh(RNC)_4}]^+(\mathrm{TCNQ})_2^-$ *(R = c-*C_6H_{11}*, Ph, 4-*MeC_6H_4*, 2,6-*$Me_2C_6H_3$*, and 2,4,6-*$Me_3C_6H_2$*) and* $[\mathrm{Rh(4\text{-}MeC_6H_4NC)_4}]^+(\mathrm{TCNQ})_3^-$ *In addition, a novel* $\mathrm{TCNQ}^{\bar{\cdot}}$ *salt formulated as* $[\mathrm{Rh(PhNC)_4}]^+(\mathrm{TCNQ}^{\bar{\cdot}})_{2/3}(\mathrm{ClO_4^-})_{1/3}$ *also was obtained Electrical resistivities of the simple salts vary widely over the 3 0 X* 10^5*–larger than* 10^{10} *Ω cm range as compacted samples at 25 °C The variation of resistivities over a wide range was found also in the 1 2 complex salts, of which* $[\mathrm{Rh(PhNC)_4}]^+(\mathrm{TCNQ})_2^-$ *and* $[\mathrm{Rh(4\text{-}MeC_6H_4NC)_4}]^+(\mathrm{TCNQ})_2^-$ *exhibit relatively small resistivities, 9 3 and 38 Ω cm, respectively, as compacted samples at 25 °C Electronic absorption spectra and magnetic susceptibilities of the salts are discussed in terms of the stacking of the* $\mathrm{TCNQ}^{\bar{\cdot}}$ *radical anion (and also neutral TCNQ for the complex salts) in the crystalline state*

Introduction

Extensive studies have been carried out on low-dimensional organic and inorganic crystals [1] Of these the charge-transfer (CT) complexes between 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and tetrathiafulvalene (TTF) or its derivatives [2], and mixed-valence platinum complexes with planar structures, such as $K_2Pt(CN)_4Br_{0\ 3}3H_2O$ [3], are best known as highly electrical conductors in the fields of organic and inorganic chemistry, respectively Each moiety which constitutes these crystals not only adopts a planar structure but also involves hetero atoms with large polarizabilities It has already been mentioned that these two factors are of importance for obtaining complexes with high electrical conductivities [4]

In the previous papers, one of the authors reported the preparation and electrical resistivities of simple and complex salts formed between bis(dialkyldithiocarbamato)gold(III) [5] or -copper(III) [6] cations and the $\mathrm{TCNQ}^{\bar{\cdot}}$ radical anion, $[\mathrm{M(S_2CNR_2)_2}]^+(\mathrm{TCNQ})_n^-$ (M = Au, Cu, R = alkyl groups, n = 1 or 2), all of which behave as semi-conductors These works led us to the idea that cationic d^8 metal complexes with square planar structure would serve as counter moieties for obtaining conductive $\mathrm{TCNQ}^{\bar{\cdot}}$ radical anion salts Thus, it was undertaken to adopt tetrakis(isocyanide)rhodium(I) cations, $[\mathrm{Rh(RNC)_4}]^+$ (R = alkyl or aryl), as square planar d^8 metal complexes These cations are known to oligomerize even in solution [7, 8] and electrical resistivities of the salt themselves, such as chloride, perchlorate *etc* with R = Me, Et, vinyl, and Ph (compacted samples), were reported to fall in the 45–(1 4 X 10^{10}) Ω cm range at room temperature [9]

This paper reports the preparation and electrical resistivities of a series of simple and complex salts of the $[\mathrm{Rh(RNC)_4}]^+(\mathrm{TCNQ})_n^-$ type, where R = t-Bu, c-C_6H_{11}, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 2,6-$Me_2C_6H_3$, and 2,4,6-$Me_3C_6H_2$, n = 1, 2, or 3 Electronic spectra and magnetic properties of the salts also are discussed in terms of the interaction between the $\mathrm{TCNQ}^{\bar{\cdot}}$ radical anions or between $\mathrm{TCNQ}^{\bar{\cdot}}$ and neutral TCNQ in the solid state

Experimental

Materials

Alkyl and aryl isocyanides [10, 11] used as ligands in this work and bis(1,5-cyclooctadiene)dichlorodirhodium, $[\mathrm{Rh(1,5\text{-}C_8H_{14})Cl}]_2$ [12], were prepared by the literature methods Tetrakis(isocyanide)rhodium(I) perchlorates, $[\mathrm{Rh(RNC)_4}]^+\mathrm{ClO_4^-}$ (R = t-Bu, c-C_6H_{11}, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 2,6-$Me_2C_6H_3$, and 2,4,6-$Me_3C_6H_2$) were synthesized by the

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TABLE I. Properties and Analysis of the TCNQ$^{\overline{\cdot}}$ Salts.

No.	Salt	Crystal form	Mp (dec.) °C	Found (Calcd)		
				C	H	N
1a	$[\mathrm{Rh(t\text{-}BuNC)_4}]^+\mathrm{TCNQ}^{\overline{\cdot}}$	Purple plates	130–135	59.63	6.27	17.43
				(60.09)	(6.30)	(17.52)
2a	$[\mathrm{Rh(c\text{-}C_6H_{11}NC)_4}]^+\mathrm{TCNQ}^{\overline{\cdot}}$	Dark blue plates	>107	64.09	6.51	15.06
				(64.59)	(6.50)	(15.07)
3a	$[\mathrm{Rh(PhNC)_4}]^+(\mathrm{TCNQ}^{\overline{\cdot}})_{2/3}(\mathrm{ClO_4^-})_{1/3}$*	Purple needles	>195	63.20	3.36	13.74
				(63.15)	(3.34)	(13.64)
4a	$[\mathrm{Rh(4\text{-}MeC_6H_4NC)_4}]^+\mathrm{TCNQ}^{\overline{\cdot}}$	Purple needles	195–200	68.08	4.17	14.39
				(68.13)	(4.16)	(14.45)
5a	$[\mathrm{Rh(4\text{-}MeOC_6H_4NC)_4}]^+\mathrm{TCNQ}^{\overline{\cdot}}$	Green needles	227–230	62.76	3.73	13.60
				(62.94)	(3.84)	(13.34)
6a	$[\mathrm{Rh(2,6\text{-}Me_2C_6H_3NC)_4}]^+\mathrm{TCNQ}^{\overline{\cdot}}$	Green needles	190–194	69.31	4.82	13.47
				(69.31)	(4.85)	(13.47)
7a	$[\mathrm{Rh(2,4,6\text{-}Me_3C_6H_2NC)_4}]^+\mathrm{TCNQ}^{\overline{\cdot}}$	Purple needles	208–211	70.00	5.44	12.79
				(70.34)	(5.55)	(12.62)
2b	$[\mathrm{Rh(c\text{-}C_6H_{11}NC)_4}]^+(\mathrm{TCNQ}_2^{\overline{\cdot}})$	Green microcrystals	206–209	65.33	5.26	17.62
				(65.89)	(5.53)	(17.73)
3b	$[\mathrm{Rh(PhNC)_4}]^+(\mathrm{TCNQ})_2^{\overline{\cdot}}$	Purple needles	>300	67.34	2.90	18.29
				(67.61)	(3.05)	(18.19)
4b	$[\mathrm{Rh(4\text{-}MeC_6H_4NC)_4}]^+(\mathrm{TCNQ})_2^{\overline{\cdot}}$	Purple needles	229–233	68.93	3.53	17.49
				(68.64)	(3.70)	(17.15)
6b	$[\mathrm{Rh(2,6\text{-}Me_2C_6H_3NC)_4}]^+(\mathrm{TCNQ})_2^{\overline{\cdot}}$	Purple plates	225–228	70.14	4.64	16.37
				(69.56)	(4.28)	(16.22)
7b	$[\mathrm{Rh(2,4,6\text{-}Me_3C_6H_2NC)_4}]^+(\mathrm{TCNQ})_2^{\overline{\cdot}}$	Purple plates	235–238	69.98	4.63	15.41
				(70.39)	(4.80)	(15.39)
4c	$[\mathrm{Rh(4\text{-}MeC_6H_4NC)_4}]^+(\mathrm{TCNQ})_3^{\overline{\cdot}}$	Green needles	>300	68.68	3.29	19.12
				(68.98)	(3.40)	(18.93)

*Cl: Found 1.69: Calcd 1.73.

reaction of $[\mathrm{Rh(1,5\text{-}C_8H_{14})Cl}]_2$ with an excess of the appropriate isocyanide, as described elsewhere [13].

All the synthetic reactions of TCNQ$^{\overline{\cdot}}$ radical anion salts were carried out under dry nitrogen.

*Preparation of Simple Salts, $[Rh(RNC)_4]^+TCNQ^{\overline{\cdot}}$ (R = t-Bu(*1a*), c-C_6H_{11} (*2a*), 4-MeC_6H_4(*4a*), 4-$MeOC_6H_4$ (*5a*), 2,6-$Me_2C_6H_3$ (*6a*), and 2,4,6-Me_3-C_6H_2 (*7a*))*

To a hot water/ethanol (1:1 v/v, 15 cm^3) solution of $[\mathrm{Rh(t\text{-}BuNC)_4}]^+\mathrm{ClO_4^-}$ (321 mg, 0.60 mmol) was added $\mathrm{Li^+TCNQ}^{\overline{\cdot}}$ (127 mg, 0.60 mmol) dissolved in the same mixed solvent (10 cm^3). The solution was allowed to stand in a refrigerator overnight to afford a precipitate *1a*, which was collected by filtration and dried *in vacuo*, 84% yield. The same reaction taking $[\mathrm{Rh(c\text{-}C_6H_{11}NC)_4}]^+\mathrm{ClO_4^-}$ for the t-Bu analog yielded *2a* in an 87% yield. Simple salts *4a–7a* were similarly obtained in 80–90% yields by the equimolar reaction of $\mathrm{Li^+TCNQ}^{\overline{\cdot}}$ in ethanol with the appropriate $[\mathrm{Rh(RNC)_4}]^+\mathrm{ClO_4^-}$ complex in acetonitrile.

Preparation of $[Rh(PhNC)_4]^+(TCNQ^{\overline{\cdot}})_{2/3}(ClO_4^-)_{1/3}$ (3a)

The equimolar reaction of $[\mathrm{Rh(PhNC)_4}]^+\mathrm{ClO_4^-}$ in acetonitrile with $\mathrm{Li^+TCNQ}^{\overline{\cdot}}$ in ethanol afforded a novel salt *3a* in an 85% yield.

Preparation of Complex Salts, $[Rh(RNC)_4]^+$-$(TCNQ)_2^{\overline{\cdot}}$ (R = c-C_6H_{11} (2b), Ph (3b), 4-MeC_6H_4 (4b), 2,6-$Me_2C_6H_3$ (6b), and 2,4,6-$Me_3C_6H_2$ (7b)) and $[Rh(4\text{-}MeC_6H_4NC)_4]^+(TCNQ)_3^{\overline{\cdot}}$ (4c)

To a hot acetonitrile (40 cm^3) solution of *2a* (398 mg, 0.54 mmol) was added neutral TCNQ (218 mg, 1.08 mmol) in hot acetonitrile (20 cm^3). The mixture was allowed to stand in a refrigerator overnight to afford a precipitate *2b*, which was filtered and dried *in vacuo*, 85% yield. Complex salts *3b*, *6b*, and *7b* with the composition of 1:2 were similarly obtained in 80–85% yields by the reactions of the appropriate simple salts with excess TCNQ in acetonitrile, while the reaction of *4a* with neutral TCNQ yielded the 1:3 complex salt *4c* in an 85% yield, irrespective of the excess amounts of TCNQ. On the other hand, *4b* with the composition of 1:2 was obtained by gradual cooling after refluxing an acetonitrile solution containing *4a* and neutral TCNQ (mol ratio of 1:2) for a few minutes, 90% yield.

Physical Measurements

Electrical resistivities, magnetic susceptibilities, and infrared spectra were measured as described previously [14]. Electronic absorption spectra were recorded on a HITACHI 340 spectrophotometer (3850–12500 cm^{-1}) and a UNION SM-401 spectrophotometer (12500–40000 cm^{-1}).

Results and Discussion

Preparation and Characterization

The equimolar reactions of $[Rh(RNC)_4]^+ClO_4^-$ with $Li^+TCNQ^{\cdot-}$ gave simple salts, except for the Rh complex with R = Ph which afforded a novel salt $[Rh(PhNC)_4]^+(TCNQ^{\cdot-})_{2/3}(ClO_4^-)_{1/3}$ (*3a*). The composition of *3a* was determined by elemental analysis and electronic absorption spectroscopy; *3a* in MeCN exhibited splitting absorptions around 740 nm assignable to the LE_1 band of $TCNQ^{\cdot-}$ radical anion [15] and the molar extinction coefficient of the absorption maximum at 744 nm (16600 dm^3 mol^{-1} cm^{-1}) was about two-thirds of that for usual $TCNQ^{\cdot-}$ simple salts (ϵ = 24400 dm^3 mol^{-1} cm^{-1} [16]). The involvement of the ClO_4^- anion in *3a* was confirmed from the infrared spectrum in Nujol mulls, which showed a strong band at 1090 cm^{-1} characteristic of the ClO_4^- anion. Salt *3a* as well as *2a, 4a, 6a*, and *7a* reacted with neutral TCNQ to yield the corresponding 1:2 complex salts *3b, 2b, 4b, 6b*, and *7b*, respectively, and the 1:3 complex salt *4c*. On the other hand, *1a* and *5a* have only been recovered in the reactions with neutral TCNQ.

Electrical Properties

Except for *1a* and *3a* which are almost insulators, the temperature dependence of specific resistivities (ρ, compacted samples) of the salts is depicted in Fig. 1, which indicates that the salts other than *4a* behave as typical semi-conductors in the temperature range measured (20–90 °C). The log ρ *vs.* 1/T plot for *4a* deviates from a straight line in the 20–50 °C range, although there is seen a linear relation in a limited temperature range. Such a deviation from linearity of the log ρ *vs.* 1/T plots was reported for the $TCNQ^{\cdot-}$ simple or complex salts with alkali metal, quinolinium, and triethylammonium cations [17], which have been suggested either to exist in two different conduction states or to involve an extrinsic electrical conduction arising from impurities or lattice defects, resulting in discontinuity of activation energies.

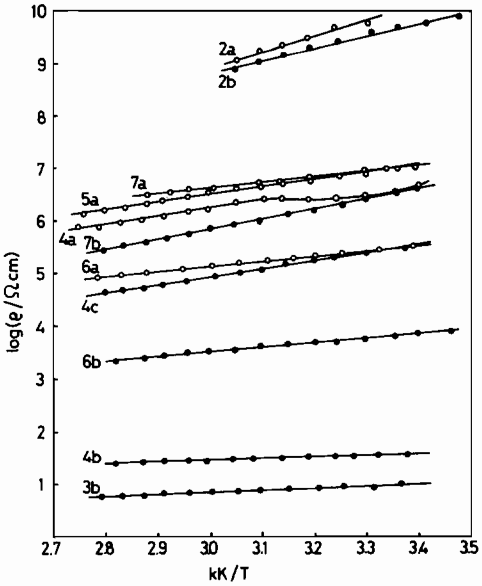

Fig. 1. Temperature dependence of the specific resistivity of the $TCNQ^{\cdot-}$ salts.

Specific resistivities at 25 °C ($\rho_{25°C}$) and the activation energies (E_a) calculated from the equation $\rho = \rho_0 \exp(E_a/kT)$ are summarized in Table II, which lists also magnetic susceptibilities (χ_M) in the solid state at room temperature. The fact that *1a* and *2a* exhibit fairly large ρ values may be related to low planarities of $[Rh(RNC)_4]^+$ (R = t-Bu and c-C_6H_{11}) arising from the R groups; such cationic moieties might prevent the $TCNQ^{\cdot-}$ radical anion from being

TABLE II. Electrical Resistivity (ρ), Activation Energy (E_a), and Magnetic Susceptibility (χ_M) of the $TCNQ^{\cdot-}$ Salts.

Salt	$\rho_{25°C}$ Ω cm	E_a eV	χ_M[a] emu mol^{-1}
1a	$>1 \times 10^{10}$	–	-2.5×10^{-4}
2a	8.7×10^9	0.55	-2.8×10^{-4}
3a	$>1 \times 10^{10}$	–	-1.2×10^{-4}
4a	3.5×10^6	0.29[b]	0.53×10^{-4}
5a	9.8×10^6	0.28	-0.11×10^{-4}
6a	3.0×10^5	0.20	-0.72×10^{-4}
7a	1.0×10^7	0.22	-1.3×10^{-4}
2b	4.5×10^9	0.47	5.6×10^{-4}
3b	9.3	0.070	7.8×10^{-4}
4b	3.8×10	0.065	3.1×10^{-4}
6b	6.5×10^3	0.17	11.6×10^{-4}
7b	3.3×10^6	0.37	6.8×10^{-4}
4c	3.1×10^5	0.32	5.6×10^{-4}

[a] Measured at room temperature. [b] Calculated from the linear relation in the 50–90 °C range.

TABLE III. Absorption Maxima[a] of the Electronic Spectra of the $\mathrm{TCNQ}^{\overline{\cdot}}$ Salts in Nujol Mulls.

Salt	Wavenumber/10^3 cm^{-1}				
1a			14.5	(23.4)	26.2
2a			14.7	(22.2)	25.3
3a		(10.0)	14.3	(22.7)	26.2
4a	6.2	11.6 (13.3)	14.9	22.9	26.9
5a	6.1	11.6 13.2	15.7	23.1	25.8
6a	6.7	11.5 (13.3)	15.6	23.2	(25.5) 26.9
7a	7.4	11.5 13.2	14.4 19.5	24.0	27.5
2b		11.5–16.0[b]		20.9 22.6	(26.3)
3b		(10.0) 11.5–13.2[b]	16.1–16.9	(22.7)	25.6 (27.6)
4b		(9.5) 11.4 13.1	17.0	(23.5)	26.3
6b		10.0 11.4	15.2	(21.0) (23.4)	(26.0) 28.2
7b		9.4 11.2	16.4	(21.7) 24.3	27.3 (29.4)
4c		(9.3) 11.5 13.2	(18.5)	23.6–25.6	

[a]Shoulders in parentheses. [b]Fine structure was observed.

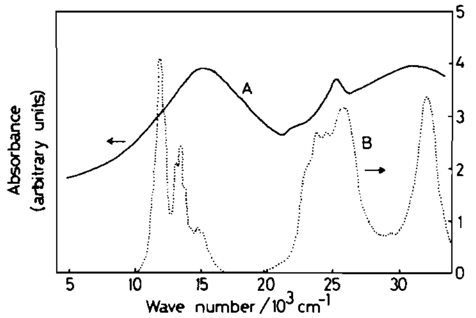

Fig. 2. Absorption spectra of *2a* in Nujol mulls (A) and in acetonitrile (B).

arranged in a columnar structure with reasonable interplanar distances. Even though the isocyanide ligand has a high planarity such as aryl isocyanides, however, the introduction of too many Me substituents on the phenyl group seems to increase the ρ value, as inferred by comparing *7a* with *4a* and *6a*. These two effects causing the increase of resistivities may still operate on the 1:2 complex salts; the resistivities of complex salts *2b* and *7b* are lowered only slightly compared with the corresponding simple salts, respectively. This is in contrast with most TCNQ complex salts, which exhibit smaller ρ values by two to six orders of magnitude than the corresponding simple salts [14, 18]. On the other hand, the resistivities of *3b* and *4b* are considerably small, the former being one of the best conductors among the $\mathrm{TCNQ}^{\overline{\cdot}}$ radical anion salts with cationic transition metal complexes reported so far [5, 6, 19].

Electronic Spectra and Magnetic Properties

Fig. 2 shows the electronic absorption spectra of *2a* in the solid state and in acetonitrile. The bands around 12000 and 24000 cm^{-1} in the solution spectrum are due to transitions to the first and second locally-excited states of $\mathrm{TCNQ}^{\overline{\cdot}}$ (LE_1 and LE_2), respectively [15], and those around 26000 and 32000 cm^{-1} to metal to ligand charge-transfer (CT) transitions in the $[\mathrm{Rh(c\text{-}C_6H_{11}NC)_4}]^+$ cation [20]. All other simple salts as well as *3a* exhibited almost the same spectra as *2a* in acetonitrile. although absorption maxima arising from the cationic moieties are somewhat shifted depending on the nature of the isocyanide ligand on the rhodium atom.

Salt *2a* shows diamagnetic property in the solid state (Table II), indicating that the $\mathrm{TCNQ}^{\overline{\cdot}}$ radical anion exists as a dimer. The solid state spectrum of *2a*, however, displays no absorption band due to CT transitions between the $\mathrm{TCNQ}^{\overline{\cdot}}$ radical anions (Fig. 2), whereas most simple salts with columnar structure exhibit the CT band in the 5000–10000 cm^{-1} range [21]. This fact may rule out any π-type interactions between the $\mathrm{TCNQ}^{\overline{\cdot}}$ radical anions in solid *2a*. Recently, X-ray structure analyses of the diamagnetic $\mathrm{TCNQ}^{\overline{\cdot}}$ salts of bis(2,2′-bipyridyl)platinum(II). $[\mathrm{Pt(bpy)_2}]^{2+}(\mathrm{TCNQ})_2^{\overline{\cdot}}$ [22], and N-ethylphenazinium [23] have demonstrated that they involve a σ-type interaction between the $\mathrm{TCNQ}^{\overline{\cdot}}$ radical anions which are linked through dicyanomethylene carbon atoms to each other. There is, however, no data on electronic spectra of these salts. Thus, we measured the solid state spectrum of $[\mathrm{Pt(bpy)_2}]^{2+}(\mathrm{TCNQ}^{\overline{\cdot}})_2$, which has shown no absorption band in the 5000–10000 cm^{-1} region at all. In view of this result, the $\mathrm{TCNQ}^{\overline{\cdot}}$ radical anions in solid *2a* also may interact with each other in a σ-type fashion. The same conclusion may be drawn for salts *1a* and *3a* on the basis of their solid state spectra quite similar to *2a* (Table III) and diamagnetisms (Table II). The very high

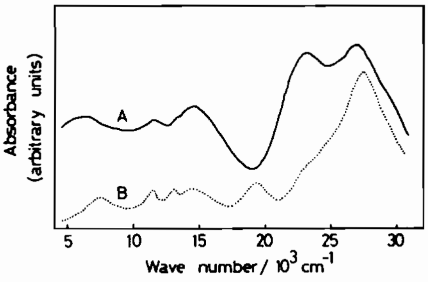

Fig. 3. Absorption spectra of *4a* (A) and *7a* (B) in Nujol mulls.

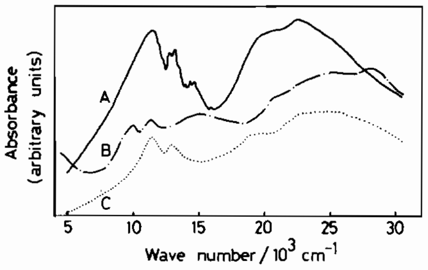

Fig. 4. Absorption spectra of *2b* (A), *6b* (B), and *4c* (C) in Nujol mulls.

resistivities of *1a–3a* are related to the absence of the CT band.

Figure 3 shows the solid state spectra of *4a* and *7a*. Although there are found somewhat complicated splittings of the absorption bands in the 10000–20000 cm^{-1} range, the spectra clearly show a band assignable to CT transitions between the TCNQ$^{\bar{\cdot}}$ radical anions around 6000 (*4a*) or 7500 cm^{-1} (*7a*). This indicates that the TCNQ$^{\bar{\cdot}}$ radical anions are coupled with each other in a columnar structure, although *4a* shows an apparent weak paramagnetism (Table II). A similar (TCNQ)$_2^{2-}$ dimer is suggested to exist in simple salts *5a* and *6a*, which exhibit almost the same spectra as *4a* (Table III) and diamagnetic susceptibilities at room temperature (Table II).

The absorption spectra of complex salts *2b, 6b,* and *4c* in the solid state are illustrated in Fig. 4. The spectrum of *2b*, despite of a complex salt, resembles well that of bis(di-*n*-propyldithiocarbamato)gold(III)–TCNQ simple salt, $[\mathrm{Au(S_2CN(n\text{-}Pr_2)_2]^+TCNQ^{\bar{\cdot}}}$ [5], which has been reported to involve an alternative stacking of the cation and the radical anion ($\mathrm{D^+A^{\bar{\cdot}}D^+A^{\bar{\cdot}}\cdots}$). This fact predicts that there is similar alternative stacking of the $[\mathrm{Rh(c\text{-}C_6H_{11}\text{-}NC)_4]^+}$ cation and the TCNQ$^{\bar{\cdot}}$ radical anion in *2b* in the crystalline state. It is, however, not obvious whether neutral TCNQ participates in the alternative stacking such as $\mathrm{D^+A^{\bar{\cdot}}AD^+A^{\bar{\cdot}}A\cdots}$ or constitutes an independent column by itself as in the TCNQ crystals [24], although the latter case is more likely since *2b* displays no band arising from the CT transition between TCNQ$^{\bar{\cdot}}$ and TCNQ in the near-infrared to infrared regions at all, which is usually observed in most TCNQ complex salts [25]. The alternative stacking of $[\mathrm{Rh(c\text{-}C_6H_{11}NC)_4]^+}$ and TCNQ$^{\bar{\cdot}}$ is consistent with the high resistivity and the paramagnetic property of *2b* at room temperature (Table II). On the other hand, the 1:2 complex salts other than *2b* exhibited a broad band in the infrared region, in addition to typical electronic spectra as complex salts in the 5000–25000 cm^{-1} region [25] (see Fig. 4 for *6b*). In particular, the infrared spectra of *3b* and *4b* showed an extremely broad CT band over the 800–4000 cm^{-1} region, superimposed with many sharp vibration bands. This is compatible with the low resistivities of *3b* and *4b*. The electronic spectrum of 1:3 complex salt *4c* is very similar to that of *4b* (see Table III), however no CT band between TCNQ$^{\bar{\cdot}}$ and TCNQ with appreciable intensities has been observed in the infrared region. This is not in conflict with the fairly large resistivity of *4c* compared with *4b*.

References

1 'Low-Dimensional Cooperative Phenomena', ed. by H. J. Keller, NATO Adv. Study Inst., *7* (1975); 'Chemistry and Physics of One-Dimensional Metals', ed. by H. J. Keller, NATO Adv. Study Inst., *25 (1977).*

2 M. Narita, C. U. Pittman, Jr., *Synthesis,* 489 (1976); E. M. Engler, *Chemtech.,* 274 (1976).

3 K. Krogmann, *Angew. Chem. Internat. Ed., 8,* 35 (1969); M. J. Minot and J. H. Perlstein, *Phys. Rev. Lett., 26,* 371 (1971).

4 A. F. Garito and A. J. Heeger, *Acc. Chem. Res., 7,* 232 (1974).

5 Y. Yumoto, F. Kato and T. Tanaka, *Bull. Chem. Soc. Jpn., 52,* 1072 (1979).

6 Y. Yumoto and T. Tanaka, *Bull. Chem. Soc. Jpn., 52,* 3457 (1979).

7 K. Kawakami, M. Okajima and T. Tanaka, *Bull. Chem. Soc. Jpn., 51,* 2327 (1978).

8 K. R. Mann, N. S. Lewis, R. M. Williams, H. B. Gray and J. G. Gordon II, *Inorg. Chem., 17,* 828 (1978).

9 'Synthesis and Properties of Low-Dimensional Materials, ed. by J. S. Miller, *Annals of New York Academy of Science, 313,* 580 (1978).

10 I. Ugi and R. Meyr, *Org. Synth., 41,* 13 101 (1962).

11 M. Makosza and A. Jonczyk, *Org. Synth., 55,* 96 (1976).

12 J. Chatt and L. M. Venanzi, *J. Chem. Soc.,* 4753 (1957).

13 R. Kuwae and T. Tanaka, *Bull. Chem. Soc. Jpn., 52,* 1067 (1979).

14 S. Araki, H. Ishida and T. Tanaka, *Bull. Chem. Soc. Jpn., 51,* 407 (1978).

15 J. Tanaka, M. Tanaka, T. Kawai, T. Takabe and O. Maki, *Bull. Chem. Soc. Jpn., 49,* 2358 (1976).

16 K. Mizoguchi, A. Tabata, A. Nakano, E. Tsuchida and I. Shinohara, *Nippon Kagaku Kaishi*, 1974 (1974).

17 L. D. Brown, D. W. Kalina, M. S. McClure, S. Schultz, S. L. Ruby, J. A. Ibers, C. R. Kannewurf and T. J. Marks, *J. Am. Chem. Soc.*, *101*, 2937 (1979).

18 S. Araki and T. Tanaka, *Bull. Chem. Soc. Jpn.*, *51*, 1311 (1978); Y. Yumoto, R. Nishioka and T. Tanaka, *ibid.*, *53*, 1247 (1980).

19 J. B. Torrance, J. J. Mayerle, V. Y. Lee and K. Bechgaard, *J. Am. Chem. Soc.*, *101*, 4747 (1979); S. Z. Goldberg, B. Spivack, G. Stanley, R. Eisenberg, D. M. Braitsch, J. S. Miller and M. Abkowitz, *ibid.*, *99*, 110 (1977); S. Z. Goldberg, R. Eisenberg, J. S. Miller and A. J. Epstein, *ibid.*, *98*, 5173 (1976).

20 M. Isci and W. R. Mason, *Inorg. Chem.*, *14*, 913 (1975).

21 Y. Iida, *Bull. Chem. Soc. Jpn.*, *42*, 71 (1969).

22 V. Dong, H. Enders, H. J. Keller, W. Moroni and D. Nöthe, *Acta Cryst.*, *B33*, 2428 (1977).

23 B. Morosin, H. J. Plastas, L. B. Coleman and J. M. Stewart, *Acta Cryst.*, *B34*, 540 (1978).

24 R. E. Long, R. A. Sparks and K. N. Trueblood, *Acta Cryst.*, *18*, 932 (1965).

25 Y. Iida, *Bull. Chem. Soc. Jpn.*, *42*, 637 (1969).