1072 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (4), 1072—1075 (1979) [Vol. 52, No. 4

Synthesis and Electrical Resistivity of Bis(dialkyldithiocarbamato)-gold(III) Cation-TCNQ Radical Anion Salts

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(Received November 13, 1978)

Seven simple salts and one complex salt of TCNQ$^{\overline{\cdot}}$ radical anion with bis(dialkyldithiocarbamato)gold(III) cations, $[\mathrm{Au}(\mathrm{S_2CNR_2})_2]^+\mathrm{TCNQ}^{\overline{\cdot}}$ (R=Me, Et, *n*-Pr, *n*-Bu, *n*-C_6H_{13}, *n*-C_8H_{17}, and $CH_2C_6H_5$) and $[\mathrm{Au}(\mathrm{S_2CN}(\mathrm{CH_2C_6H_5})_2)_2]^+(\mathrm{TCNQ})_2^{\overline{\cdot}}$, were prepared. The complex salt was also obtained as an acetonitrile solvate, $[\mathrm{Au}(\mathrm{S_2CN}(\mathrm{CH_2C_6H_5})_2)_2]^+(\mathrm{TCNQ})_2^{\overline{\cdot}}\cdot\mathrm{MeCN}$. The electrical resistivity of the simple salt with R=$CH_2C_6H_5$ (2.9×10^4 ohm cm in compacted sample) is much lower than those of the remaining simple salts (1.1×10^7—2.2×10^{10} ohm cm). The resistivities of two complex salts are in the order of 10^2 ohm cm. Electronic absorption spectra and magnetic susceptibility measurements in the solid state indicate that the simple salts with R=Me, Et, *n*-Pr, *n*-C_6H_{13}, and $CH_2C_6H_5$ involve the TCNQ$^{\overline{\cdot}}$ radical anion monomer, whereas those with R=*n*-Bu and *n*-C_8H_{17} involve dimeric $(\mathrm{TCNQ})_2^{2-}$. The interaction between TCNQ$^{\overline{\cdot}}$ radical anion and neutral TCNQ in the complex salts is extremely weak, as suggested from no appreciable absorption band in the near-infrared region.

Much attention has been paid to unusual electrical propeties exhibited by one-dimensional materials in both fields of organic and inorganic chemistry.[1] Up to the present time, the most successful organic materials in this area have been based on the radical anion salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ),[2] while a prominent example in the inorganic field is partially oxidized platinum cyanide complexes ($K_2Pt(CN)_4\cdot X_{0.3}\cdot 3H_2O$, X=Cl, Br).[3] However, only a few TCNQ$^{\overline{\cdot}}$ radical anion salts containing transition metal complexes have been reported so far.[4]

It is well known that some square-planar d^8 transition metal complexes with 1,1-dithiolato ligands not only assume a columnar structure in the crystalline state, but also undergo reversible oxidation and reduction electrochemically in solution.[5] These facts prompted us to prepare TCNQ$^{\overline{\cdot}}$ radical anion salts of bis(dialkyldithiocarbamato)gold(III) cations. This paper reports the synthesis and electrical resistivity of some simple and complex salts of TCNQ$^{\overline{\cdot}}$ with these cations, $[\mathrm{Au}(\mathrm{S_2CNR_2})_2]^+\mathrm{TCNQ}^{\overline{\cdot}}$ (R=Me, Et, *n*-Pr, *n*-Bu, *n*-C_6H_{13}, *n*-C_8H_{17}, and $CH_2C_6H_5$), $[\mathrm{Au}(\mathrm{S_2CN}(\mathrm{CH_2C_6H_5})_2)_2]^+(\mathrm{TCNQ})_2^{\overline{\cdot}}$ and $[\mathrm{Au}(\mathrm{S_2CN}(\mathrm{CH_2C_6H_5})_2)_2]^+(\mathrm{TCNQ})_2^{\overline{\cdot}}\cdot\mathrm{MeCN}$. Electronic spectra and magnetic properties of these salts in the solid state are also discussed in terms of the stacking of TCNQ$^{\overline{\cdot}}$.

Experimental

Bis(dialkyldithiocarbamato)gold(III) chlorides, $[\mathrm{Au}(\mathrm{S_2CNR_2})_2]^+\mathrm{Cl}^-$ (R=Me, Et, *n*-Pr, *n*-C_6H_{13}, *n*-C_8H_{17}, and $CH_2C_6H_5$), were prepared by the reaction of $NaAuCl_4\cdot 2H_2O$ with the appropriate thiuram disulfide, $(R_2NC(S)S\text{-})_2$, in a mannar similar to the method[6] for $[\mathrm{Au}(\mathrm{S_2CN}(n\text{-Bu})_2)_2]^+\mathrm{Br}^-$; an oily product obtained was dissolved in dichloromethane, followed by the addition of diethyl ether to give a yellowish orange precipitate in 78—89% yields.

Bis(dialkyldithiocarbamato)gold(III)-TCNQ Simple Salts, $[\mathrm{Au}(\mathrm{S_2CNR_2})_2]^+\mathrm{TCNQ}^{\overline{\cdot}}$ (R=Me (1), Et (2), n*-Pr (3),* n*-Bu (4),* n*-C_6H_{13} (5),* n*-C_8H_{11} (6), and $CH_2C_6H_5$ (7)).* To a solution of $\mathrm{Li}^+\mathrm{TCNQ}^{\overline{\cdot}}$ (0.52 g, 25 mmol) in boiling ethanol (40 ml) was added a hot ethanol (30 ml) solution of $[\mathrm{Au}(\mathrm{S_2CNMe_2})_2]^+\mathrm{Cl}^-$ (1.1 g, 25 mmol). The mixture was allowed to stand at room temperature. The resulting precipitate was recrystallized from acetonitrile to give **1** in a 56% yield.

TABLE 1. PROPERTIES AND ANALYTICAL DATA OF THE TCNQ$^{\overline{\cdot}}$ SALTS

No.	Salt	Color	Mp(dec) °C	Found (Calcd) % C	H	N
1	$[\mathrm{Au}(\mathrm{S_2CNMe_2})_2]^+\mathrm{TCNQ}^{\overline{\cdot}}$	Dark-green needles	212—213	33.76 (33.70)	2.57 (2.51)	13.27 (13.10)
2	$[\mathrm{Au}(\mathrm{S_2CNEt_2})_2]^+\mathrm{TCNQ}^{\overline{\cdot}}$	Dark-green needles	201—202	37.90 (37.87)	3.46 (3.47)	12.05 (12.05)
3	$[\mathrm{Au}(\mathrm{S_2CN}(n\text{-Pr})_2)_2]^+\mathrm{TCNQ}^{\overline{\cdot}}$	Dark-green needles	174—177	41.22 (41.43)	4.17 (4.28)	11.05 (11.15)
4	$[\mathrm{Au}(\mathrm{S_2CN}(n\text{-Bu})_2)_2]^+\mathrm{TCNQ}^{\overline{\cdot}}$	Violet needles	148—150	44.18 (44.49)	4.90 (4.99)	10.40 (10.38)
5	$[\mathrm{Au}(\mathrm{S_2CN}(n\text{-}C_6H_{13})_2)_2]^+\mathrm{TCNQ}^{\overline{\cdot}}$	Dark-green needles	86—87	49.40 (49.50)	6.12 (6.25)	9.11 (9.11)
6	$[\mathrm{Au}(\mathrm{S_2CN}(n\text{-}C_8H_{17})_2)_2]^+\mathrm{TCNQ}^{\overline{\cdot}}$	Black microcrystals	55—57	53.01 (53.42)	7.05 (7.02)	8.20 (8.13)
7	$[\mathrm{Au}(\mathrm{S_2CN}(\mathrm{CH_2C_6H_5})_2)_2]^+\mathrm{TCNQ}^{\overline{\cdot}}$	Black microcrystals	186—188	53.22 (53.33)	3.40 (3.41)	9.18 (8.88)
8	$[\mathrm{Au}(\mathrm{S_2CN}(\mathrm{CH_2C_6H_5})_2)_2]^+(\mathrm{TCNQ})_2^{\overline{\cdot}}$	Dark-blue needles	211—213	56.48 (56.38)	3.15 (3.16)	12.12 (12.18)
9	$[\mathrm{Au}(\mathrm{S_2CN}(\mathrm{CH_2C_6H_5})_2)_2]^+(\mathrm{TCNQ})_2^{\overline{\cdot}}\cdot(\mathrm{MeCN})$	Black needles	212—214	56.18 (56.42)	3.22 (3.38)	12.93 (12.93)

Other six simple salts, **2**—**7**, were similarly prepared by the equimolar reaction of TCNQ$^{\overline{\cdot}}$ in ethanol with the appropriate bis(dialkyldithiocarbamato)gold(III) cation in acetonitrile, 77—90% yields.

Bis(dibenzyldithiocarbamato)gold(III)–TCNQ Complex Salts, $[\mathrm{Au(S_2CN(CH_2C_6H_5)_2)_2}]^+(\mathrm{TCNQ})_2^{\overline{\cdot}}$ *(8) and* $[\mathrm{Au(S_2CN(CH_2C_6H_5)_2)_2}]^+(\mathrm{TCNQ})_2^{\overline{\cdot}}\cdot\mathrm{MeCN}$ *(9).* To a boiling acetonitrile (60 ml) solution of **7** (0.53 g, 0.56 mmol) was added two equivalent amounts of neutral TCNQ (0.23 g, 1.1 mmol) in boiling acetonitrile (40 ml). After filtration, the mixture was allowed to stand in a refrigerator overnight to afford microcrystals of **8** in a 87% yield. Acetonitrile solvate salt **9** was obtained on recrystallization of **8** from acetonitrile, 57% yield on the basis of **8**.

Physical Measurements. Electrical resistivities, electronic and infrared spectra, and magnetic susceptibilities were measured as described previously.[7)]

Results and Discussion

Preparation and Characterization. Simple salt **7** reacted with additional neutral TCNQ in acetonitrile to yield complex salt **8**, while in the reactions of the remaining simple salts (**1**—**6**) with neutral TCNQ in the same solvent the starting materials have only been recovered, respectively. Acetonitrile solvate complex salt **9** was characterized by elemental analysis, infrared spectrum, and differential scanning calorimetry (DSC); **9** in the solid state released acetonitrile on heating to 90 °C in a DSC cell, as confirmed by the fact that the infrared spectrum of **9** after heating coincides with that of **8**.

Electrical Properties. Temperature dependence of electrical resistivities for the simple and complex salts (compacted samples) are illustrated in Fig. 1; the results were satisfactorily reproducible. All the simple and complex salts show typical semiconducting behavior in the temperature range measured. Table 2 summarizes the specific resistivities (ρ) of these salts at 25 °C and the activation energies (E_a) obtained from the Arrhenius plots of the temperature dependence of resistivities, $\rho=\rho_0\exp(E_a/kT)$, together with the magnetic susceptibility (χ_M). The ρ values of **1**—**6** fall in the range of 10^7—10^{10} ohm cm, which are much larger than the resistivities of alkali metal salts of TCNQ$^{\overline{\cdot}}$ (10^2—10^5 ohm cm).[8)] Simple salt **7** behaves a smaller ρ value by three to six orders of magnitude than **1**—**6**. This is suggestive of the stacking of TCNQ$^{\overline{\cdot}}$ in **7** being different from those in **1**—**6**.

Table 2. Electrical resistivity (ρ), activation energy (E_a), and magnetic susceptibility (χ_M) of the TCNQ$^{\overline{\cdot}}$ salts

Salt	$\frac{\rho_{25^\circ\mathrm{C}}}{\text{ohm cm}}$	$\frac{E_a}{\text{eV}}$	$\frac{\chi_M}{\text{emu mol}^{-1}}$
Simple salt			
1	8.9×10^8	0.50	7.1×10^{-4}
2	2.2×10^{10}	0.58	9.8×10^{-4}
3	1.4×10^9	0.83	9.2×10^{-4}
4	3.0×10^7	0.43	-3.7×10^{-4}
5	5.4×10^7	0.55	8.2×10^{-4}
6	1.1×10^7	0.97	-5.2×10^{-4}
7	2.9×10^4	0.30	9.3×10^{-4}
Complex salt			
8	6.6×10^2	0.26	9.8×10^{-4}
9	1.6×10^2	0.13	4.0×10^{-4}

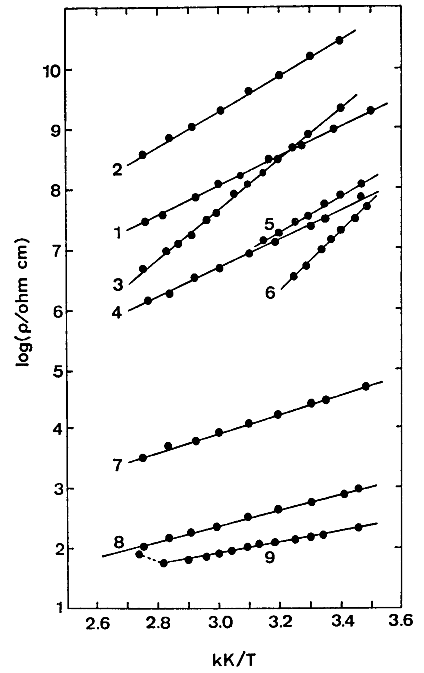
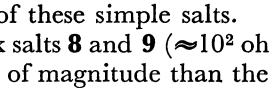


Fig. 1. Temperature dependence of the resistivity of the TCNQ$^{\overline{\cdot}}$ salts.

One of the authors has previously reported the preparation of *N*,*N*-dialkyl-1,3-dithiolan-2-iminium–TCNQ$^{\overline{\cdot}}$ simple salts,



$(\mathrm{CH_2})_2\langle\mathrm{S_2}\rangle\overset{+}{\mathrm{C}}{=}\mathrm{NR_2}\cdot\mathrm{TCNQ}^{\overline{\cdot}}$ (R=Me, *n*-Pr, *n*-$\mathrm{C_6H_{13}}$, and *n*-$\mathrm{C_8H_{17}}$), whose electrical resistivity (2.2×10^5—1.9×10^9 ohm cm) increases in the order of bulkiness of substituents on the iminium nitrogen atom.[7,9)] In contrast to this, the resistivity of the present simple salts seems to decrease as substituents on the carbamato nitrogen atom are bulky. Explanation for this unusual tendency has to await X-ray structure analysis of these simple salts.

The ρ values of complex salts **8** and **9** ($\approx10^2$ ohm cm) are smaller by two orders of magnitude than the corresponding simple salt **7**. Both the resistivity and activation energy of acetonitrile solvate complex salt **9** seem to be smaller than those of **8**, though these values fall in the same order.

Electronic and Magnetic Properties. All the simple salts in acetonitrile exhibited absorption maxima at *ca.* 12000 and 24000 cm^{-1} in the electronic spectra, regardless of the difference of substituents R in the $[\mathrm{Au(S_2CNR_2)_2}]^+$ cations. Appearance of the spectra closely resembles that of M$^+$TCNQ$^{\overline{\cdot}}$ (M=alkali metal or ammonium cation) in acetonitrile, where they are known to dissociate into the monomeric TCNQ$^{\overline{\cdot}}$ radical anion and the M$^+$ cation.[10)] The bands at *ca.* 12000 and 24000 cm^{-1} in acetonitrile have been assigned to locally-excited transitions of the TCNQ$^{\overline{\cdot}}$ moiety, LE$_1$ and LE$_2$, respectively.[11)]

Figure 2 illustrates the electronic absorption spectra

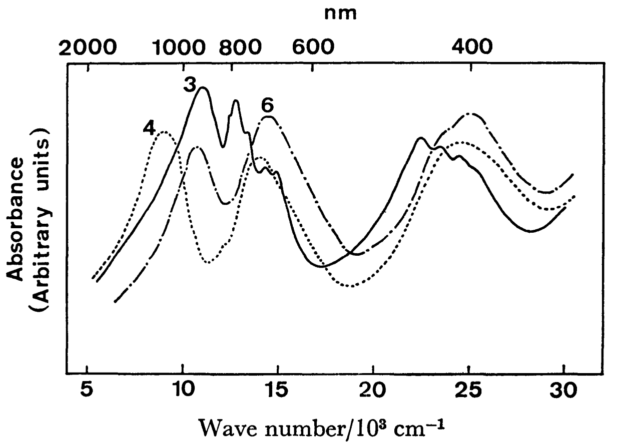
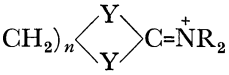


Fig. 2. Electronic absorption spectra of **3**, **4**, and **6** in Nujol mulls.

of **3**, **4**, and **6** in the solid state. The spectrum of **3** is similar in appearance to that of this salt in acetonitrile, indicating that the TCNQ$^{\overline{\cdot}}$ radical anion in solid **3** may exist as monomeric species. This is compatible with the paramagnetic property of **3** in the solid state at room temperature (Table 2). The presence of the discrete TCNQ$^{\overline{\cdot}}$ radical anion in the solid state is suggested also for **1**, **2**, and **5** on the basis of their solid state spectra similar to that of **3** and their paramagnetism at room temperature. These assumptions may be consistent with electrically high resistivities and large activation energies of **1**—**3** and **5**, which predict an alternate stacking of the $[Au(S_2CNR_2)_2]^+$ cation and the TCNQ$^{\overline{\cdot}}$ radical anion ($D^+A^{\overline{\cdot}}D^+A^{\overline{\cdot}}\cdots$). Both simple salts **4** and **6** exhibited three absorption maxima at *ca.* 9900, 14000, and 24000 cm^{-1} (Table 3). The spectral patterns closely resemble not only those of simple salts formed between *N*,*N*-dialkyl-1,3-dichalcogenacycloalkan-2-iminium and TCNQ$^{\overline{\cdot}}$,  $(CH_2)_n\langle{}^{Y}_{Y}\rangle C{=}\overset{+}{N}R_2\cdot \mathrm{TCNQ}^{\overline{\cdot}}$ ($n=2$, 3; Y=S, Se; R=Me, Et),⁷⁾ but also the reflectance spectra of some simple TCNQ$^{\overline{\cdot}}$ salts with Li^+, NH_4^+, and $MePh_3P^+$,¹⁰⁾ all of which have been reported to involve dimeric $(TCNQ)_2^{2-}$ on the basis of spectral assignments that the lowest energy band may be due to the CT transition between TCNQ$^{\overline{\cdot}}$ radical anions and that the remaining two to the $(TCNQ)_2^{2-}$ dimer.¹⁰,¹¹⁾ It is therefore suggested that the $(TCNQ)_2^{2-}$ dimer exists in solid **4** and **6**. This is supported also from their diamagnetic properties in the solid state at room temperature (Table 2). Such diamagnetism may confirm that two TCNQ$^{\overline{\cdot}}$ radical anions are coupled completely with each other. The fact that the CT band of **6** was fairly blue-shifted (*ca.* 2000 cm^{-1}) compared with that of **4** may be correlated with a larger activation energy in **6** than in **4** (Table 1).

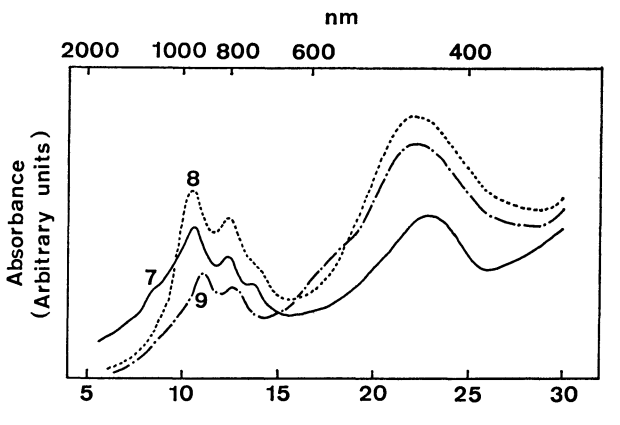


Fig. 3. Electronic absorption spectra of **7**, **8**, and **9** in Nujol mulls.

Figure 3 shows the electronic absorption spectra of simple salt **7** and complex salts **8** and **9** in the solid state. The spectrum of **7** is similar to that of **3**, while no fine structure has been observed in **7**. In fact, **7** exhibited paramagnetic susceptibility at room temperature. Its electrical resistivity, however, is much smaller than those of **1**—**6**, suggesting a segregated columnar stacking of the TCNQ$^{\overline{\cdot}}$ radical anion in **7**.

The electronic spectra of **8** and **9** show three absorption maxima at *ca.* 11000, 12500, and 22000 cm^{-1} (Table 3). The highest energy band is contributed from the electronic transitions in both the TCNQ$^{\overline{\cdot}}$ radical anion and neutral TCNQ.¹¹⁾ The remaining two bands may be due to the TCNQ$^{\overline{\cdot}}$ monomer, as previously described in the reflectance spectra of some TCNQ$^{\overline{\cdot}}$ complex salts.¹⁰⁾ The presence of monomeric TCNQ$^{\overline{\cdot}}$ is consistent with the fact that **8** and **9** exhibited paramagnetic susceptibilities in the solid state at room temperature. In addition, both **8** and **9** have not clearly shown a broad absorption band in the 5000 to 2500 cm^{-1} range; the band has been observed in many TCNQ$^{\overline{\cdot}}$ complex salts and assigned to the CT transition between

TABLE 3. ABSORPTION MAXIMA OF THE ELECTRONIC SPECTRA OF THE TCNQ$^{\overline{\cdot}}$ SALTS IN NUJOL MULLS

Salt	Wave number/10^3 cm^{-1}												
1		11.0	(12.7)	13.2		14.4		22.5	23.6		25.3		
2		11.3	(12.7)	13.1	(13.4)	14.3	14.7	22.5	23.5		25.1		
3		11.0	(12.7)	13.1	(13.3)	14.4	14.7	22.4	23.5	24.4	(25.2)		
4	8.9					13.9				22.4			
5		11.1	(12.7)	13.0	(13.3)	14.3	14.6	22.6	23.5	24.4	(25.3)		
6	10.8					14.5				25.1			
7	(8.8)	10.6	12.4	(13.9)						22.7			
8		10.6	12.4	(14.1)						22.0			
9		11.1	12.7			(17.1)				22.1			

a) Shoulders in parentheses.

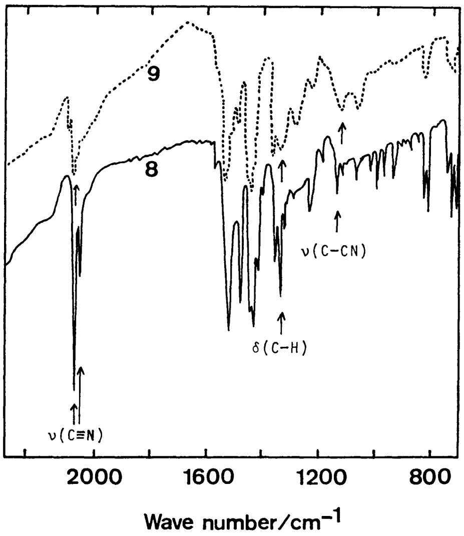


Fig. 4. Infrared spectra of **8** and **9** in Nujol mulls.

TCNQ$^{\cdot -}$ and neutral TCNQ.[10] It may therefore be concluded that the interaction between TCNQ$^{\cdot -}$ and neutral TCNQ in **8** and **9** is extremely weak. It should be mentioned, however, that the infrared spectrum of **9** shows considerably broad bands due to ν(C≡N), δ(C–H), and ν(C–CN) compared with that of **8**, as shown in Fig. 4. This sort of broadening observed in the spectra of many TCNQ$^{\cdot -}$ complex salts has been taken as an evidence for the resonance between TCNQ$^{\cdot -}$ and neutral TCNQ.[12] Thus, the interaction between TCNQ$^{\cdot -}$ and neutral TCNQ may be somewhat stronger in **9** than in **8**.

The authors are grateful to the Ministry of Education for support of this work through Grant-in-Aid for Scientific Research.

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