BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (11), 3457—3458 (1979)

Semiconducting Bis(dialkyldithiocarbamato)copper(III) Cation–TCNQ Radical Anion and –Bis(1,2-dicyano-1,2-ethylenedithiolato)nickel(III) Anion Salts: $[Cu(S_2CNR_2)_2]^+TCNQ^{\overline{\cdot}}$ and $[Cu(S_2CNR_2)_2]^+$-$[Ni(S_2C_2(CN)_2)_2]^-$ (R=Et, *n*-Pr, and *n*-Bu)

Yoshiji YUMOTO and Toshio TANAKA*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565

(Received May 25, 1979)

Synopsis. The title salts were synthesized. Segregated columnar structures of the salts are suggested from their electronic spectra and electrical resistivities; 10^4—10^5 Ω cm range at 25 °C with activation energies of 0.24—0.33 eV as compact samples.

In a previous paper, a report was given on the preparation and electrical resistivity of simple and complex salts formed by the reaction between bis(dialkyldithiocarbamato)gold(III) cations and $TCNQ^{\overline{\cdot}}$ radical anion; $[Au(S_2CNR_2)_2]^+TCNQ^{\overline{\cdot}}$ (R=Me, Et, *n*-Pr, *n*-Bu, *n*-C_6H_{13}, *n*-C_8H_{17}, and $CH_2C_6H_5$), $[Au(S_2CN(CH_2C_6H_5)_2)_2]^+(TCNQ)_2^{\overline{\cdot}}$, and $[Au(S_2CN(CH_2C_6H_5)_2)_2]^+(TCNQ)_2^{\overline{\cdot}}\cdot MeCN$, all of which showed semiconducting behavior.[1] This paper describes the preparation, electronic spectra, and electrical resistivity of some bis(dialkyldithiocarbamato)copper(III) cation–TCNQ radical anion and –bis(1,2-dicyano-1,2-ethylenedithiolato)nickel(III) anion simple salts; $[Cu(S_2CNR_2)_2]^+TCNQ^{\overline{\cdot}}$ and $[Cu(S_2CNR_2)_2]^+[Ni(S_2C_2(CN)_2)_2]^-$ (R=Et, *n*-Pr, and *n*-Bu).

Experimental

Bis(dialkyldithiocarbamato)copper(III) perchlorates, $[Cu(S_2CNR_2)_2]^+ClO_4^-$ (R=Et, *n*-Pr, and *n*-Bu),[2] and tetraethylammonium bis(1,2-dicyano-1,2-ethylenedithiolato)nickelate(III), $[Et_4N]^+[Ni(S_2C_2(CN)_2)_2]^-$,[3] were prepared by the methods reported.

Bis(dialkyldithiocarbamato)copper(III)–TCNQ, $[Cu(S_2CNR_2)_2]^+TCNQ^{\overline{\cdot}}$ (R=Et (1), n*-Pr (2), and* n*-Bu (3)).* To a boiling ethanol (30 ml) solution of $Li^+TCNQ^{\overline{\cdot}}$ (0.39 g, 1.8 mmol) was added a hot acetonitrile (40 ml) solution of $[Cu(S_2CNEt_2)_2]^+ClO_4^-$ (0.82 g, 1.8 mmol). The mixture was allowed to stand in a refrigerator overnight to afford dark green needles of **1** in a 60% yield. **2** and **3** were similarly obtained both as dark green needles in 58 and 55% yields, respectively, by the equimolar reaction of $TCNQ^{\overline{\cdot}}$ in ethanol with the appropriate bis(dialkyldithiocarbamato)copper(III) cations in acetonitrile.

No complex salt was obtained by the reaction of **1**—**3** with neutral TCNQ in acetonitrile, only the starting materials being recovered.

Bis(dialkyldithiocarbamato)copper(III) Bis(1,2-dicayno-1,2-ethylenedithiolato)nickelate(III), $[Cu(S_2CNR_2)_2]^+[Ni(S_2C_2(CN)_2)_2]^-$ (R=Et (4), n*-Pr (5), and* n*-Bu (6)).* To an acetone (50 ml) solution of $[Cu(S_2CNEt_2)_2]^+ClO_4^-$ (0.67 g, 1.5 mmol) was added $[Et_4N]^+[Ni(S_2C_2(CN)_2)_2]^-$ (0.68 g, 1.5 mmol) in acetone (30 ml). After being stirred for 1 h, the mixture was concentrated to about half the volume under reduced pressure, followed by cooling to *ca.* 5 °C to give dark brown microcrystals of **4** in a 80% yield. Two analogues with R=*n*-Pr and *n*-Bu were similarly prepared as black and dark brown microcrystals in 71 and 85% yields, respectively.

Physical Measurements. Electrical resistivities, electronic spectra, and magnetic susceptibilities were measured as described previously.[1]

Results and Discussion

Linearity holds between log ρ (ρ: electrical resistivity) and $1/T$ for all the salts in the range 293—373 K (Table 1), indicating semiconducting behavior. Figure 1 shows the electronic absorption spectra of **1** and **4** in the solid state and **4** in acetonitrile; solid **1** exhibits three absorption maxima at 8800, 14800, and 24500 cm^{-1}. Similar spectra were observed in **2** and **3**. The spectral patterns of **1**—**3** closely resemble those of gold analogues, $[Au(S_2CN(n\text{-}Bu)_2)_2]^+TCNQ^{\overline{\cdot}}$ (λ_{max}: 8900, 13900, and 22400 cm^{-1}) and $[Au(S_2CN(n\text{-}C_8H_{17})_2)_2]^+TCNQ^{\overline{\cdot}}$ (λ_{max}: 10800, 14500, and 25100 cm^{-1}), both of which have been reported to involve dimeric $(TCNQ)_2^{2-}$.[1] The existence of the $(TCNQ)_2^{2-}$ dimer in **1**—**3** is supported by their diamagnetic properties at room temperature. Thus, **1**—**3** seem to have a segregated columnar stacking of $TCNQ^{\overline{\cdot}}$ radical anion in the crystalline state. This is in line with the ρ values of these salts in the order of 10^4 Ω cm. The columnar structure of **1** and **2** is in contrast to the corresponding gold salts, $[Au(S_2CNR_2)_2]^+TCNQ^{\overline{\cdot}}$ (R=Et and *n*-Pr), in which the cation and the anion are stacked alternatively: $D^+A^{\overline{\cdot}}D^+A^{\overline{\cdot}}\cdots$.[1]

The electronic spectrum of solid **4** shows absorption maxima at 8000, 13500, 16800, 22600, and 30200 cm^{-1}, of which the 22600 cm^{-1} band is due to the $[Cu(S_2CNEt_2)_2]^+$ cation and the remaining four bands to the $[Ni(S_2C_2(CN)_2)_2]^-$ anion. Thus, the solid state spectrum of **4** coincides with a superimposition of the spectra of the cation and anion moieties, indicating

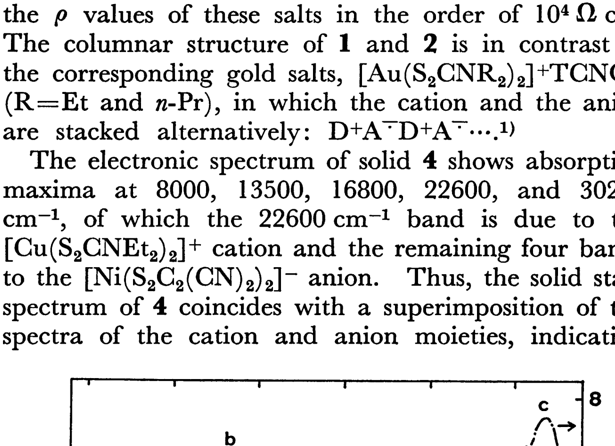


Fig. 1. Electronic absorption spectra of **1** (a) and **4** (b) in Nujol mulls, and **4** in acetonitrile (c).

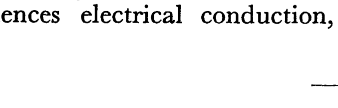
TABLE 1. ANALYTICAL DATA, ELECTRICAL RESISTIVITY (ρ), AND ACTIVATION ENERGY (E_a) OF THE SALTS[a]

No.	Salt	%C Found (Calcd)	%H Found (Calcd)	%N Found (Calcd)	$\rho_{25\,°C}$ / Ω cm	E_a[b] / eV
1	$[Cu(S_2CNEt_2)_2]^+TCNQ^{\cdot-}$	47.11 (46.83)	4.15 (4.29)	14.66 (14.89)	4.6×10^4	0.24
2	$[Cu(S_2CN(n\text{-}Pr)_2)_2]^+TCNQ^{\cdot-}$	50.05 (50.34)	5.17 (5.20)	13.70 (13.55)	7.1×10^4	0.28
3	$[Cu(S_2CN(n\text{-}Bu)_2)_2]^+TCNQ^{\cdot-}$	53.08 (53.26)	5.80 (5.96)	12.30 (12.42)	8.5×10^4	0.30
4	$[Cu(S_2CNEt_2)_2]^+[Ni(S_2C_2(CN)_2)_2]^-$	30.59 (30.92)	2.86 (2.88)	11.61 (12.02)	3.1×10^5	0.31
5	$[Cu(S_2CN(n\text{-}Pr)_2)_2]^+[Ni(S_2C_2(CN)_2)_2]^-$	34.88 (34.99)	3.69 (3.74)	11.09 (11.13)	4.0×10^5	0.31
6	$[Cu(S_2CN(n\text{-}Bu)_2)_2]^+[Ni(S_2C_2(CN)_2)_2]^-$	38.20 (38.49)	4.20 (4.47)	10.17 (10.36)	8.9×10^5	0.33

a) Mp (dec) >300 °C for all the salts. b) Calculated by the equation $\rho=\rho_0\exp(E_a/kT)$.

that in the solid state the anion and the cation are segregated from each other. This is supported by the fact that **4** in acetonitrile exhibits an additional band at 25000 cm^{-1} (Fig. 1), which may be due to an anion-cation interaction. The interaction of this type has been reported in some double complex salts, such as $[Pt(CNR)_4]^{2+}[Pt(CN)_4]^{2-}$ (R=Me, Et, and *t*-Bu), in solution.[4] Segregation between the anion and the cation is suggested also for solids **5** and **6** on the basis of their electronic spectra. Some bis(1,2-dithiolato)nickel(III) salts such as $[Et_4N]^+[Ni(S_2C_2(CN)_2)_2]^-$ ($\rho=3.5\times10^5$ and $4.9\times10^7\,\Omega$ cm for two crystalline forms) have been reported to adopt a segregated columnar structure.[5] Such a structure can be assumed in the crystals of **4**—**6**, since the ρ values (Table 1) are of the same orders as or smaller than those of $[Et_4N]^+$ salts.

In both series **1**—**3** and **4**—**6**, the ρ and E_a values trend to increase to some extent as the alkyl substituents on the carbamato nitrogen atom become bulky. A similar trend has been reported for a series of *N,N*-dialkyl-1,3-dithiolan-2-iminium–TCNQ$^{\cdot-}$ simple salts.[6]



$$(CH_2)_2\langle S,S\rangle \overset{+}{C=N}R_2\cdot TCNQ^{\cdot-}$$

(R=Me, *n*-Pr, *n*-C_6H_{13}, and *n*-C_8H_{17})

The interplanar distance between the cation moieties in segregated columnar structures significantly influences electrical conduction, where the cation behaves as a matrix for the arrangement or packing of the planar anion moieties.[7] It can be concluded that bulky substituents on the nitrogen atom of the cationic moieties increase the interplanar distances not only between the cation moieties but also between the anion moieties, raising electrical resistivity of the present salts.

The authors wish to express their thanks to the Central Research Institute, Matsushita Electric Industrial Co., Ltd. for supplying a sample of TCNQ. This work was carried out with a Grant-in-Aid for Scientific Research No. 347066 from the Ministry of Education, Science and Culture.

References

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

2) R. M. Golding, C. M. Harris, K. J. Jessop, and W. C. Tennant, *Aust. J. Chem.*, **25**, 2567 (1972).

3) A. Davison and R. H. Holm, *Inorg. Synth.*, **10**, 8 (1967).

4) H. Isci and W. R. Mason, *Inorg. Chem.*, **13**, 1175 (1974).

5) A. Kobayashi and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **50**, 2650 (1977).

6) S. Araki, H. Ishida, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **51**, 407 (1978); S. Araki and T. Tanaka, *ibid.*, **51**, 1311 (1978).

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