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Syntheses, Structures, and Physical Properties of Nickel Bis(dithiolene) Complexes Containing Tetrathiafulvalene (TTF) Units

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To contribute to the development of single-component molecular metals, several nickel complexes with cyclohexeno-condensed or ethylenedioxy-substituted TTF (tetrathiafulvalene) dithiolate ligands, $(R_4N)_n[Ni(chdt)_2]$ [R = Me, $n = 2$ (**1**); R = ^{n}Bu, $n = 1$ (**2**); $n = 0$ (**3**)] and $(R_4N)_n[Ni(eodt)_2]$ [R = Me, $n = 2$ (**4**); R = ^{n}Bu, $n = 1$ (**5**); $n = 0$ (**6**)], were prepared. X-ray structures were determined on the monoanionic species **2** and **5**. The tetra-*n*-butylammonium complex of the monoanionic $[Ni(chdt)_2]$ (**2**) with a 1:1 composition revealed that its magnetic susceptibility gave a good agreement with the Bonner–Fisher model ($J/k_B = –28$ K), which was derived from the one-dimensional chains of anions with a regular interval. On the other hand, the magnetic susceptibility of the tetra-*n*-butylammonium complex of the monoanionic $[Ni(eodt)_2]$ (**5**) showed the Curie–Weiss behavior ($C = 0.376$ K·emu·mol^{-1} and $\Theta = –4.6$ K). Both of the monoanionic species **2** and **5** indicate that they belong to the $S = 1/2$ magnetic system and have relatively large and anisotropic *g*-values, suggesting the contribution of the nickel 3d orbital. Electrical resistivity measurements were performed on the compressed pellets of the neutral species **3** and **6**. Fairly large conductivities were obtained ($\sigma_{rt} = 1–10$ S·cm^{-1}). In addition, despite the measurements on the compressed pellets of powder samples, the neutral species **6** showed metallic behavior down to ca. 120 K and retained high conductivity even at 0.6 K [$\sigma(0.6\ K)/\sigma_{rt} \approx 1/30$], suggesting the crystal to be essentially metallic down to very low temperature. The electrical behavior and Pauli paramagnetism of **6** indicate the system to be a new single-component metal.

Introduction

The first clear evidence for the existence of one-dimensional metal electrons in organic crystals was obtained in (TTF)(TCNQ) three decades ago,[1] and the first organic superconductor, $(TMTSF)_2PF_6$ (TMTSF = tetramethyltetraselenafulvalene) was reported in 1980.[2] Since then, a great deal of molecular conductors have been developed.[3] There are two essential requirements for the design of the organic metals: (1) the requirement for the formation of conduction band; (2) the requirement for the generation of charge carriers. To our knowledge, all the organic conductors developed until very recently utilize the charge-transfer phenomena to generate the carriers. Therefore, unlike the typical inorganic metals consisting of single elements such as Na and Cu, all the molecular conductors are composed of more than two chemical species, that is, at least the molecules constructing the conduction band and other chemical species generating carriers by the charge transfer between the molecules constructing the conduction band. On the other hand, studies on transition metal bis(dithiolene) complexes have a longer history than those of TTF- (tetrathiafulvalene-) based systems and have been an area of great interest because these complexes showed various crystal structures and conducting properties that depend on the nature of the central metal atoms and counter ions and oxidation states.[4,5] Although an

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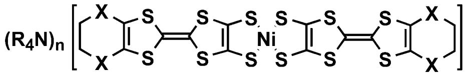
enormous amount of investigations have been carried out on the syntheses and characterization of transition metal bis(dithiolene) complexes with dmit (1,3-dithiole-2-thione-4,5-dithiolate) ligands and their analogues,[3,5] all these conducting materials have been also made up of the plural components. However, since the latter half of the 1990s, transition metal bis(dithiolene) complexes containing TTF-type dithiolate ligands have gone into the limelight because they displayed fairly high conductivities even in the neutral state.[6−9] We have recently succeeded in the preparation of a single-component molecular metal, [Ni(tmdt)$_2$] (tmdt = trimethylenetetrathiafulvalenedithiolate), with stable metallic state down to very low temperature (σ_{rt} = ca. 400 S$\cdot$cm^{-1}).[10,11] In addition, the first-principle density functional calculation of [Ni(tmdt)$_2$] by Rovira et al. has been reported.[12] More recently, a single-component molecular conductor incorporating magnetic moments, [Cu(dmdt)$_2$] (dmdt = dimethyltetrathiafulvalenedithiolate), and a highly conducting system with magnetic transition around 100 K, [Au(tmdt)$_2$], have been also reported.[13,14]

To contribute to the development of the new field of single-component molecular metals, we have tried to prepare TTF-type ligands fused with a six-membered ring such as cyclohexene and 1,4-dioxene rings because such six-membered rings have structural flexibility compared to that of structurally rigid five-membered ring as observed in the several kinds of polymorphism in the bis(ethylenedithio)-TTF salts,[3] which have played the most important role in the field of organic conductors and expanded the variety of the crystal structures and the resultant electronic structures. We report here the crystal structures and electrical and magnetic properties of nickel bis(dithiolene) complexes containing extended TTF ligands, $(R_4N)_n$[Ni(chdt)$_2$] [R = Me, n = 2 (**1**); R = ^{n}Bu, n = 1 (**2**); n = 0 (**3**); chdt = cyclohexenotetrathiafulvalenedithiolate] and $(R_4N)_n$[Ni(eodt)$_2$] [R = Me, n = 2 (**4**); R = ^{n}Bu, n = 1 (**5**); n = 0 (**6**); eodt = ethylenedioxytetrathiafulvalenedithiolate] (Chart 1)[15]

Chart 1



1; R = Me, X = -CH$_2$-, n = 2 **4;** R = Me, X = -O-, n = 2
2; R = ^{n} Bu, X = -CH$_2$-, n = 1 **5;** R = ^{n} Bu, X = -O-, n = 1
3; X = -CH$_2$-, n = 0 **6;** X = -O-, n = 0

Experimental Section

General Methods. 4,5-Bis(2′-cyanoethylthio)-4,5-tetramethylenetetrathiafulvalene (**7**) and 4,5-bis(2′-cyanoethylthio)-4,5-ethylenedioxytetrathiafulvalene (**8**) were synthesized by the methods in ref 16. THF (tetrahydrofuran) was freshly distilled over sodium and benzophenone under argon atmosphere prior to use. MeOH (methanol) was distilled over magnesium methoxide under argon atmosphere and stored in refrigerator. Nickel(II) dichloride hexahydrate was recrystallized several times with distilled water and dried in vacuo. Supporting electrolytes of tetra-*n*-butylammonium perchlorate or tetra-*n*-butylammonium hexafluorophosphate were recrystallized several times from AcOEt (ethyl acetate) and dried in vacuo, respectively. MeCN (acetonitrile) was distilled in the presence of calcium hydride under argon atmosphere. PhCN (benzonitrile) was dried with calcium chloride and distilled over diphosphorus pentaoxide under reduced pressure. All other reagents were used without purification. Microanalyses were performed by the Research Center for Molecular-Scale Nanoscience, Institute for Molecular Science.

Synthesis of $(Me_4N)_2$[Ni(chdt)$_2$] (1). 4,5-Bis(2′-cyanoethylthio)-4,5-tetramethylenetetrathiafulvalene (**7**) (214 mg; 0.499 mmol) was hydrolyzed with a 25 wt % MeOH solution of tetramethylammonium hydroxide (732 mg; 2.01 mmol) in dry THF (15.0 mL) at room temperature and under argon atmosphere. The color of the solution changed from orange to red as the reaction proceeded. The solution was stirred for 30 min, and a reddish orange precipitate (**9**) was formed. A solution of nickel(II) dichloride hexahydrate (64.2 mg; 0.270 mmol) in MeOH (4.0 mL) was added dropwise to the reaction mixture at −78 °C, and the reaction mixture was stirred for 1 h at −78 °C and warmed to room temperature overnight. The resulting microcrystals was collected by filtration and washed several times with the mixed solvent of THF (10.0 mL) and MeOH (1.0 mL) under argon atmosphere to afford pink microcrystals (**1**). The measurement of microanalysis and the estimation of yield could not be performed due to its air-unstable nature.

Synthesis of $(Me_4N)_2$[Ni(eodt)$_2$] (4). The dianionic nickel complex **4** was obtained through the intermediate **10** by a procedure similar to that described above: it was obtained from 4,5-bis(2′-cyanoethylthio)-4,5-ethylenedioxytetrathiafulvalene (**8**)[16] (216 mg; 0.500 mmol), a 25 wt % MeOH solution of tetramethylammonium hydroxide (730 mg; 2.00 mmol), and a solution of nickel(II) dichloride hexahydrate (60.0 mg; 0.252 mmol) in MeOH (4.0 mL) as air-unstable reddish purple microcrystals. Thus, the measurement of microanalysis and the estimation of yield could not be also carried out in dianionic nickel species **4**.

Electrochemical Synthesis. All of the electrocrystallizations were carried out in a standard H-type cell without glass frit using two platinum electrodes (1 mm o.d. wires) under argon inert

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atmosphere. The dianionic species **1** (15.0−20.0 mg; 17.7 × 10^{-3}−23.6 × 10^{-3} mmol) and tetra-*n*-butylammonium perchlorate (80.0 mg; 234 mmol) were dissolved in PhCN (12.0 mL) under argon atmosphere. Electrochemical oxidation of this solution was carried out with a constant current of 0.5 μA at room temperature. Comparatively air-stable plate-shaped dark red single crystals of **2** grew on the anode within about 2−3 weeks. The obtained crystals were filtered, washed with EtOH (ethanol), and air-dried at room temperature. Anal. Calcd for $C_{36}H_{52}S_{12}NiN$: C, 45.89; H, 5.56; N, 1.49. Found: C, 45.94; H, 5.58; N, 1.49.

The other monoanionic and neutral species **3**, **5**, and **6** were prepared by a method similar to that described above for **2**:

The neutral species **3** was prepared from the dianionic species **1** (15.0−20.0 mg; 17.7 × 10^{-3}−23.6 × 10^{-3} mmol), tetra-*n*-butylammonium hexafluorophosphate (80.0 mg; 206 mmol), and PhCN (15.0 mL), by applying a regulated voltage of 1.0 V between the two electrodes by a constant voltage supply, at 40 °C, within about 3−4 weeks, as air-stable black microcrystals. Anal. Calcd for $C_{20}H_{16}S_{12}Ni$: C, 34.33; H, 2.31; N, 0.00. Found: C, 34.30; H, 2.36; N, 0.00.

The monoanionic species **5** was obtained from the dianionic species **4** (15.0−20.0 mg; 17.5 × 10^{-3}−23.4 × 10^{-3} mmol), tetra-*n*-butylammonium perchlorate (80.0 mg; 234 mmol), and MeCN (12.0 mL), with a constant current of 0.5 μA, at room temperature, within about 2−3 weeks, as relatively air-stable plate-shaped dark red crystals. Anal. Calcd for $C_{32}H_{44}S_{12}O_4NiN$: C, 40.45; H, 4.67; N, 1.47. Found: C, 40.29; H, 4.56; N, 1.46.

The neutral species **6** was produced from the dianionic species **4** (15.0−20.0 mg; 17.5 × 10^{-3}−23.4 × 10^{-3} mmol), tetra-*n*-butylammonium perchlorate (80.0 mg; 234 mmol), and PhCN (15.0 mL), with a constant current of 0.5 μA, at room temperature, within about 3−4 weeks, as air-stable black microcrystals. Anal. Calcd for $C_{16}H_8S_{12}O_4Ni$: C, 27.16; H, 1.14; N, 0.00. Found: C, 27.06; H, 1.37; N, 0.00.

Crystal Structure Determination. Single-crystal X-ray structure determinations were made on the crystals of the tetra-*n*-butylammonium salts **2** and **5**. Data collection for the plate-shaped single crystals of the monoanionic species **2** and **5** was performed on a Rigaku/MSC Mercury CCD system with graphite-monochromated Mo Kα radiation (λ = 0.710 70 Å) at 293 K. The sizes of the crystals used for data collection were 0.7 × 0.3 × 0.05 mm^3 for **2** and 0.50 × 0.30 × 0.02 mm^3 for **5**. Experimental details and crystal data are listed in Table 1. The structure was solved by direct methods (SIR92)[17] and expanded using Fourier techniques (DIRDIF94).[18] The atomic scattering factors were taken from ref 19.[19] Anisotropic temperature factors were applied for the non-hydrogen atoms. The calculated positions of hydrogen atoms were not refined but included in the final calculation. All calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corp.[20]

Electron Spin Resonance (ESR). ESR spectra were measured on the monoanionic (**2** and **5**) and neutral (**6**) species using a Bruker ESP300E ESR spectrometer. Single crystals of the monoanionic species **2** and **5** mounted on a cut flat face of Teflon rod using a small amount of Apiezon grease M were placed in evacuated quartz tubes. Angular dependences of the ESR spectra were measured with rotating the crystal around the almost crystallographic *b*-axis in the cavity by use of goniometer at 300 K. Temperature dependence of the ESR spectra was also examined on the plate crystals of the monoanionic species **2** and **5** in the temperature range of 3.0−300 K. The magnetic field was applied along the directions approximately parallel to the crystal plane. Furthermore, the ESR measurements were carried out on the polycrystalline samples of the monoanionic species **2** (1.47 mg; 1.56 × 10^{-3} mmol) and **5** (2.03 mg; 2.14 × 10^{-3} mmol) at 300 K to estimate the spin susceptibilities (χ_{spin}). On the other hand, the ESR spectra of the polycrystalline sample of the neutral species **6** (3.50 mg; 4.95 × 10^{-3} mmol) in the evacuated quartz tube were also measured in the temperature range of 3.4−220 K. The ESR data for 3-carboxy-2,2,5,5-tetramethylpyrrolidine-1-oxyl (2.68 mg; 14.4 × 10^{-3} mmol) measured at 300 K under identical conditions were used as reference for the calculation of the χ_{spin} values.

Table 1. X-ray Crystallographic Data of the Monoanionic Species

	(^{n}Bu$_4$N)[Ni(chdt)$_2$] (**2**)	(^{n}Bu$_4$N)[Ni(eodt)$_2$] (**5**)
formula	$C_{36}H_{52}S_{12}NiN$	$C_{32}H_{44}S_{12}O_4NiN$
fw	942.24	950.12
cryst color, habit	black, plate	black, plate
cryst system	monoclinic	monoclinic
lattice params (Å, deg)	$a = 29.018(4)$	$a = 18.406(1)$
	$b = 8.5822(8)$	$b = 9.8418(5)$
	$c = 19.133(2)$	$c = 23.444(2)$
	$\beta = 113.628(5)$	$\beta = 101.280(4)$
V (Å^3)	4365.5(9)	4164.8(5)
space group	$C2/c$ (No. 15)	$P2/c$ (No. 13)
Z value	4	4
D_{calc} (g·cm^{-3})	1.434	1.52
μ(Mo Kα) (cm^{-1})	10.46	11.05
diffractometer	Rigaku/MSC Mercury CCD	Rigaku/MSC Mercury CCD
radiatn (λ, Å)	Mo Kα (0.710 70)	Mo Kα (0.710 70)
temp (K)	293	293
no. of reflcns measd	tot.: 4911	tot.: 39 107
		unique:12 224
struct soln	direct methods (SIR92)	direct methods (SIR92)
refinement	full-matrix least squares	full-matrix least squares
no. of observns	3904 [$I > 3.00\sigma$(I)]	4804 [$I > 4.00\sigma$(I)]
no. of variables	228	465
residuals: R_1;[a] R_w[b]	0.057; 0.057	0.057; 0.061
Goodness of fit indicator	1.41	1.78

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

Applied microwave power and modulation field were as follows: 1.0 mW and 1.0 G for monoanionic species **2**; 1.0 mW and 1.0 G for the monoanionic species **5**; 1.0 mW and 9.5 G for the neutral species **6**.

Static Magnetic Susceptibility. Static magnetic susceptibility (χ) measurements of the monoanionic species **2** (0.95 mg; 1.0 × 10^{-3} mmol) and **5** (2.36 mg; 2.48 × 10^{-3} mmol) and neutral one **6** (8.85 mg; 12.5 mmol) were performed by a Quantum Design MPMS-7XL SQUID (superconducting quantum interference device) magnetometer in the temperature range from 1.9 to 300 K. The applied magnetic fields were 5 kOe for the monoanionic species and 30 kOe for the neutral species, respectively. The samples were wrapped with a clean aluminum foil whose magnetic susceptibility was separately measured and subtracted. The diamagnetic contribution was calculated from Pascal's constants ($\chi^{dia} = -5.35 \times 10^{-4}$ emu·mol^{-1} for the monoanionic species **2**, $\chi^{dia} = -5.05 \times 10^{-4}$

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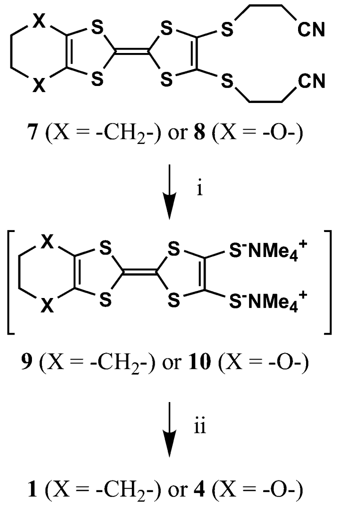
Scheme 1 [a]



7 (X = -CH$_2$-) or **8** (X = -O-)

9 (X = -CH$_2$-) or **10** (X = -O-)

1 (X = -CH$_2$-) or **4** (X = -O-)

[a] Reagents and conditions: i, 25 wt % Me$_4$NOH (4.0 equiv), dry THF, rt, 30 min; ii, Ni^{II}Cl$_2$·6H$_2$O/dry MeOH (0.5 equiv), −78 °C to rt, overnight.

emu·mol^{-1} for the monoanionic species **5**, and $\chi^{dia} = -2.98 \times 10^{-4}$ emu·mol^{-1} for the neutral species **6**).

Electrical Resistivity. The electrical resistivity was measured on a compressed pellet sample of the neutral species **6** down to 0.6 K with four-probe technique by use of a Huso Electro Chemical System HECS 994C-1 multichannel four-terminal conductometer. Electrical contacts were achieved with gold paste and gold wire (15 μm o.d.). Cooling of samples down to 1.5 K were performed by means of pumping liquid ^{4}He, and the experiments below 1.5 K were carried out by means of pumping liquid ^{3}He. A calibrated Cerenox thermometer was used over all the temperature range. On the other hand, the resistivity of a compressed pellet sample of **3** was also measured down to ca. 20 K by use of similar methods.

Results and Discussion

Synthesis of the Dianionic Species. Synthesis of the bis(tetramethylammonium) complexes of [Ni(chdt)2]$^{2-}$ (**1**) and [Ni(eodt)2]$^{2-}$ (**4**) were performed under argon atmosphere as shown in Scheme 1. Thus, the bis(tetramethylammonium) dithiolate ligands, (Me$_4$N)$_2$(chdt) (**9**) and (Me$_4$N)$_2$(eodt) (**10**), were prepared as reddish orange and purple powders by the hydrolytic cleavage of the corresponding bis(2′-cyanoethylthio)-substituted TTF derivatives **7** and **8**[16] with a 25 wt % MeOH solution of tetramethylammonium hydroxide in dry THF at room temperature, respectively. The dianionic nickel bis(dithiolene) complexes **1** and **4** were obtained by a successive treatment with a dry MeOH solution of nickel(II) dichloride hexahydrate from −78 °C to room temperature. The resulting precipitates were collected and washed with dry THF−MeOH [10/1 (v/v)] solution several times under argon to afford pink and reddish purple microcrystals, respectively.

Electrochemical Synthesis. The obtained dianionic nickel bis(dithiolene) complexes **1** and **4** are easily air-oxidized and are considerably less soluble in usual organic solvents. The monoanionic and neutral species **2**, **3**, **5**, and **6** were prepared by electrochemical oxidations of the dianionic nickel bis(dithiolate) complexes **1** and **4** in the presence of tetra-*n*-butylammonium perchlorate or tetra-*n*-butylammonium hexafluorophosphate as supporting electrolytes in dry MeCN or PhCN under a constant current of 0.5 μA or with applying a regulated voltage of 1.0 V between the two electrodes by a constant voltage supply at room temperature or 40 °C. Relatively air-stable plate-shaped dark red single crystals of **2** and **5** grew on the anode within about 2−3 weeks. These plate-shaped crystals were revealed by X-ray crystal structure analyses to have a 1:1 (tetra-*n*-butylammonium cation:anion) stoichiometry. On the other hand, the neutral species **3** and **6** were obtained as air-stable black microcrystals within about 3−4 weeks. In the preparations of the monoanionic species **2** and neutral species **3**, the conditions of the electrocrystallization are not the same for both. Namely, the monoanionic species **2** was prepared by the electrochemical oxidation of complex **1** in the presence of tetra-*n*-butylammonium perchlorate using the galvanostatic mode (0.5 μA) at room temperature, while neutral species **3** was obtained by the potentiostatic mode (1.0 V) in the presence of tetra-*n*-butylammonium hexafluorophosphate at 40 °C. On the other hand, in complexes **5** and **6**, the conditions of the electrocrystallization are almost the same for both except for the solvents (MeCN for **5** and PhCN for **6**). We consider that the selections of temperatures and/or solvents are very important factors for the growth of the crystals with the monoanionic or neutral states because the solubility of the monoanionic species could be varied by changing the temperatures and the solvents. If the solubilities of the intermediate monoanionic species were relatively high in the solvents during the electrocrystallization (namely, higher temperatures or changing used solvents), we could obtain the neutral species because further oxidation to the neutral species is considered to be conducted by the electrocrystallization. Therefore, we think the solubility of the monoanionic state will determine the oxidation state of the obtained crystals.

Crystal Structure of the Monoanionic Species 2. Figure 1 shows the molecular and crystal structures of the monoanionic nickel bis(dithiolene) complex **2**. The nickel atom of [Ni(chdt)$_2$]$^-$ anion and the nitrogen atom of the tetra-*n*-butylammonium cation exist on the special position. The molecular structure of the anion is almost planar except for the terminal two cyclohexene rings (see Figure 1a). As shown in Figure 1b,c, each [Ni(chdt)$_2$]$^-$ anion is arranged along the diagonal direction in the *ab*- and *ac*-planes with an overlap of only the terminal cyclohexene rings to each other. Moreover, the [Ni(chdt)$_2$]$^-$ anions form a one-dimensional array with a constant interval along the *c*-axis and there is one intermolecular S···S contact [3.646(1) Å] between the adjacent anions, indicating side-by-side interaction along the *c*-axis (see also Figure 1b). On the other hand, each anion chain is completely separated by a chain of the bulky tetra-*n*-butylammonium cations along the *b*-axis and there is no interaction between the anion chains (see Figure 1c). However, the shortest Ni···Ni distance [8.5822(8) Å] was found along the *b*-direction involving the bulky tetra-*n*-butylammonium cation. With respect to the anion chain along the *c*-axis, the shortest Ni···Ni distance corresponds to a half value of the unit cell parameter *c* [19.133(2) Å].

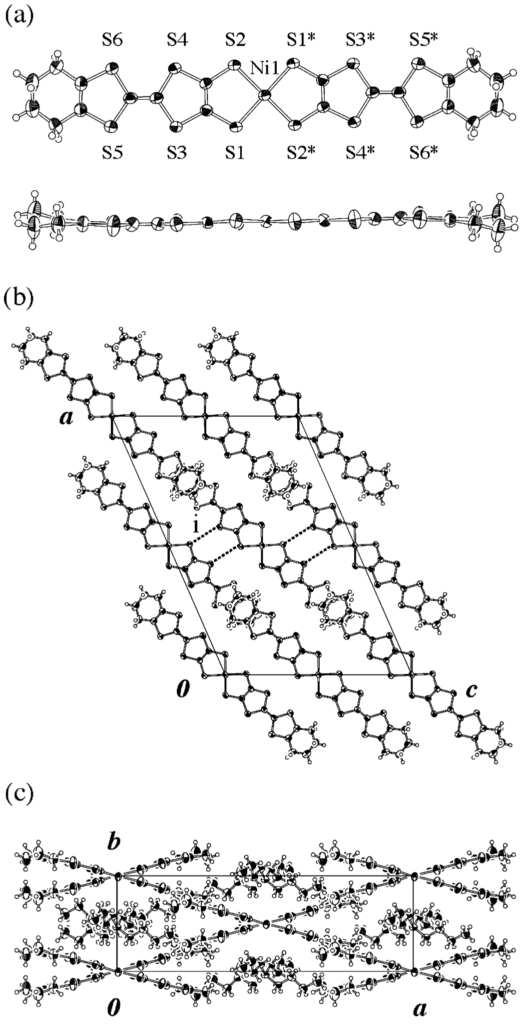


Figure 1. (a) Molecular structures and atomic numbering schemes of the anion molecule in (^{n}Bu$_4$N)[Ni(chdt)$_2$] (**2**). (b) Crystal structure of (^{n}Bu$_4$N)[Ni(chdt)$_2$] (**2**) projected onto the *ac*-plane. The bulky tetra-*n*-butylammonium cations are omitted for clarity. The intermolecular contact is (i) S2···S4* = 3.646(1) Å. (c) One-dimensional chain structure of (^{n}Bu$_4$N)[Ni(chdt)$_2$] (**2**) viewed along the *c*-axis.

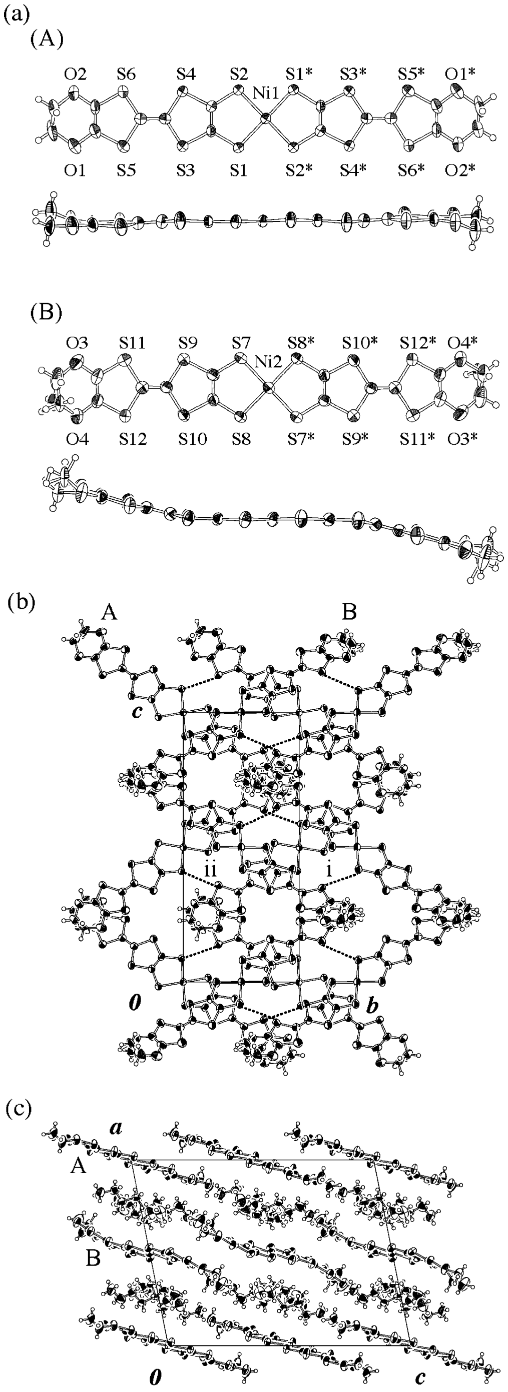


Figure 2. (a) Molecular structures and atomic numbering schemes of the anion molecules in (^{n}Bu$_4$N)[Ni(eodt)$_2$] (**5**). Two kinds of anions (A and B) exist in the crystal. (b) Anion arrangement projected onto the *bc*-plane in (^{n}Bu$_4$N)[Ni(eodt)$_2$] (**5**). The bulky tetra-*n*-butylammonium cations are omitted for clarity. The intermolecular contacts are (i) S7···S12* = 3.540(2) Å and (ii) S1···S6* = 3.643(2) Å. (c) Crystal structure of (^{n}Bu$_4$N)[Ni(eodt)$_2$] (**5**) projected onto the *ac*-plane.

Crystal Structure of the Monoanionic Species 5. The molecular and crystal structures of the nickel bis(dithiolene) complex **5** is shown in Figure 2. The unit cell contains the two crystallographically independent halves of the [Ni(eodt)$_2$]$^-$ anions (A and B), where the nickel atoms are on the inversion center, and one tetra-*n*-butylammonium cation. Among them, one [Ni(eodt)$_2$]$^-$ anion (A) is almost planar except for the terminal ethylene bridge (see Figure 2a). The other one (B) has a heavily bent structure at the positions of sulfur atoms of the TTF part with a dihedral angle of 11.37° and adopts a chair-formed conformation (see also Figure 2a). On account of the examination of the oxidation state between these two complexes (A and B), we checked the C═C bond lengths of two nickel complexes. However, there is no significant difference of the bond lengths between these two complexes. Figure 2b shows the projection onto the *bc*-plane. The anions (A and B) are arranged in a zigzag manner with overlapping the dioxene rings of the ligands to each other between the neighboring anions along the *c*-axis, and two kinds of layers composed of anions A and B individually are formed by the combination of each zigzag array in the *bc*-plane. As shown in Figure 2c, the layers of anions (A and B) and tetra-*n*-butylammonium cations (C) are arranged alternately along the *a* direction (−A−C−B−C′−...). There is no intermolecular S···S contact less than the sum of van der Waals radii (3.7 Å) between the anions along the *a*-axis due to such a sandwiched structure separated by the bulky tetra-*n*-butylammonium cations. The close S···S distances [3.540(2) and

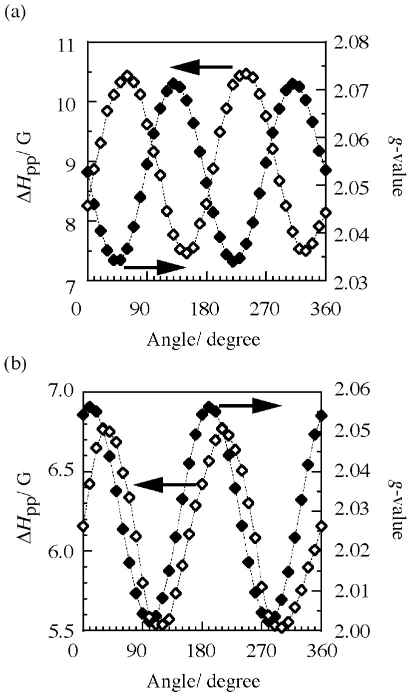


Figure 3. Angular dependence of peak-to-peak linewidths (ΔH_{pp}) and *g*-values estimated by the ESR measurements of the monoanionic species at 300 K: (a) (^{n}Bu$_4$N)[Ni(chdt)$_2$] (**2**); (b) (^{n}Bu$_4$N)[Ni(eodt)$_2$] (**5**).

3.643(2) Å] exist only in the transverse direction of the anions. On the other hand, the shortest Ni···Ni distance along the *b*-axis is 9.8418(5) Å.

Electron Spin Resonance Study of the Monoanionic Species. Since the monoanionic species **2** and **5** are almost isolated from the neighboring molecules except for the transverse S···S contacts, the unpaired electron of the monoanion will tend to be localized on each molecule. The angular dependence of ESR spectra of single crystals of the monoanionic species **2** and **5** was measured by rotating the crystal around almost the crystallographic *b*-axis in the cavity by use of the goniometer at 300 K. The monoanionic species **2** and **5** gave Lorentzian-type ESR signals. As shown in Figure 3a,b, the single-crystal ESR studies of the complexes **2** and **5** revealed angular-dependent narrow peak-to-peak linewidths ΔH_{pp} (7.4−10.5 G for **2** and 5.5−6.8 G for **5**) and relatively large *g*-values (2.03−2.07 for **2** and 2.00−2.06 for **5**), suggesting the contribution of the nickel 3d orbital.

Variable-temperature ESR measurements were carried out for the monoanionic species **2** and **5** in the temperature range of 3.0−300 K. The ΔH_{pp} values of **2** and **5** decrease monotonically, but below ca. 20 K, complex **2** showed a slight increase of the ΔH_{pp} values with decreasing temperature. As shown in Figure 4, the χ_{spin} values of the monoanionic species **2** and **5** increase from 300 K to the low-temperature region with decreasing temperature. Concerning complex **2**, the χ_{spin} values decrease below ca. 20 K, indicating the emergence of an antiferromagnetic interaction.

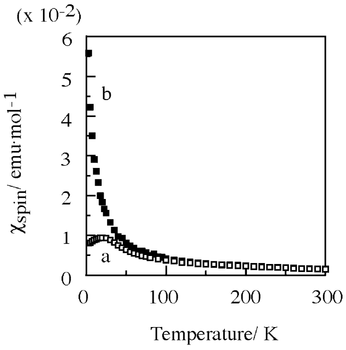


Figure 4. Temperature dependence of spin susceptibilities (χ_{spin}) estimated by the ESR measurements of the monoanionic species (a) (^{n}Bu$_4$N)[Ni(chdt)$_2$] (**2**) and (b) (^{n}Bu$_4$N)[Ni(eodt)$_2$] (**5**).

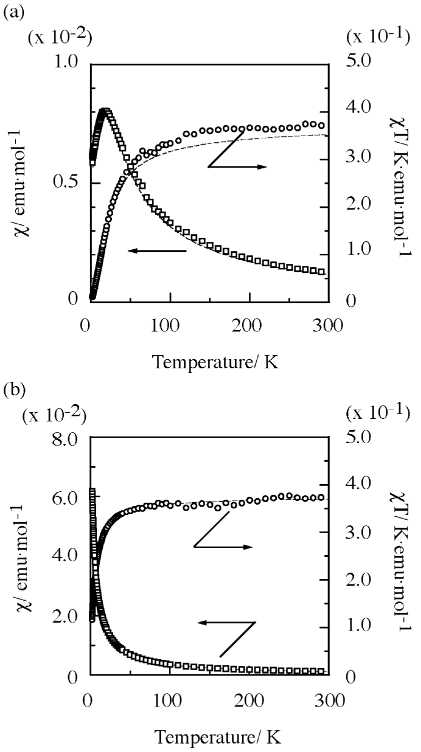


Figure 5. Temperature dependence of magnetic susceptibilities (χ) of polycrystals of the monoanionic species (a) (^{n}Bu$_4$N)[Ni(chdt)$_2$] (**2**) and (b) (^{n}Bu$_4$N)[Ni(eodt)$_2$] (**5**) at the field of 5 kOe. The dotted lines indicate fitting curves of the Bonner−Fisher model ($J/k_B = -28$ K) for (a) and the Curie−Weiss law ($C = 0.376$ K·emu·mol^{-1} and $\Theta = -4.6$ K) for (b), respectively.

Static Magnetic Susceptibility of the Monoanionic Species. The static magnetic susceptibilities of the monoanionic species **2** and **5** were measured using a SQUID magnetometer. The temperature dependences of the χ values are shown in Figure 5. The data were corrected for the diamagnetic contribution estimated from Pascal's constants. Complex **2** showed room-temperature susceptibility ($\chi_{rt} = 1.25 \times 10^{-3}$ emu·mol^{-1}) corresponding to one $s = 1/2$ localized spin per an anion with the maximum of the magnetic susceptibility at 18 K as shown in Figure 5a. The temperature dependence of magnetic susceptibility of the complex **2** is in good agreement with the Bonner−Fisher model with $J/k_B = -28$ K, exhibiting the existence of an antiferromagnetic one-dimensional Heisenberg chain.[21] This result is consistent with the above-mentioned structural feature, namely, the arrangement of anions with the regular distance along the one-dimensional chain (along the *c*-axis).

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(21) Estes, W. E.; Gavel, D. P.; Hatfield, W. E.; Hodgson, D. *Inorg. Chem.* **1978**, *17*, 1415−1421.

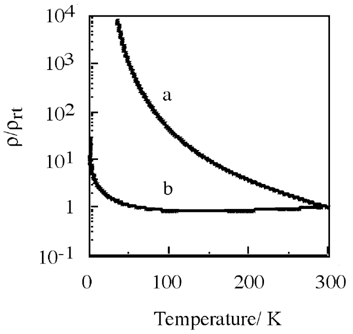

Figure 6. Temperature dependence of electrical resistivities of the neutral nickel complexes measured by use of compressed pellets: (a) [Ni(chdt)$_2$] (**3**); (b) [Ni(eodt)$_2$] (**6**).

On the other hand, the magnetic susceptibilities of complex **5** can be well fitted by the Curie−Weiss plot: $\chi = C/(T - \Theta)$, $C = 0.376$ K·emu·mol^{-1} and $\Theta = -4.6$ K (see Figure 5b). This negative Weiss temperature ($\Theta = -4.6$ K) indicates the dominant magnetic interaction to be antiferromagnetic. However, complex **5** did not show any transition down to 1.9 K. The Curie constant ($C = 0.376$ K·emu·mol^{-1}) is approximately equal to 0.375 K·emu·mol^{-1} [$=N_Ag^2\mu_Bs(s + 1)$] expected for the $s = 1/2$ localized spin system with $g = 2.0$.

Conductivity and Magnetic Properties of the Neutral Species. Conductivity of the Neutral Species. The recent most interesting feature concerning the transition metal complexes with extended TTF-type ligands will be the possibility of the development of metallic crystal consisting of single neutral molecules. Since sufficiently large single crystals were not prepared, the electrical resistivities of the neutral species **3** and **6** were measured on the compressed pellets by the four-probe method as shown in Figure 6. Their room-temperature conductivities were fairly high ($\sigma_{rt} = 1-10$ S·cm^{-1}) as for the compressed pellets of powder samples. As seen from Figure 6, the resistivity of the neutral complex **3** increases gradually with decreasing temperature. On the other hand, despite the compressed pellet sample, the resistivity of the neutral complex **6** decreased down to ca. 120 K. Below ca. 120 K the resistivity increased very slowly and the sample retained fairly high conductivity even at 0.6 K (see Figure 6). These results suggest neutral complex **6** is metallic down to at least 120 K and will essentially keep its metallic state to lower temperature region.

Magnetic Properties of the Neutral Species 6. The static magnetic susceptibility of neutral complex **6** was measured by a Quantum Design MPMS7XL SQUID magnetometer down to 1.9 K at 30 kOe. The paramagnetic susceptibility was corrected by subtracting the diamagnetic contribution calculated from Pascal's constants. As shown in Figure 7, the χ values were almost constant (ca. 2.6×10^{-4} emu·mol^{-1}) at the temperature range of 120−300 K, indicating the Pauli paramagnetism characteristic of metallic electrons. The Pauli paramagnetism of 2.6×10^{-4} emu·mol^{-1} is approximately equal to that of the first single component molecular metal with the stable metallic state down to low temperature, [Ni(tmdt)$_2$] (3.0×10^{-4} emu·mol^{-1}).[10,11] Below 120 K, the magnetic susceptibility increases with the lowering temperature, probably due to the paramagnetic impurities.

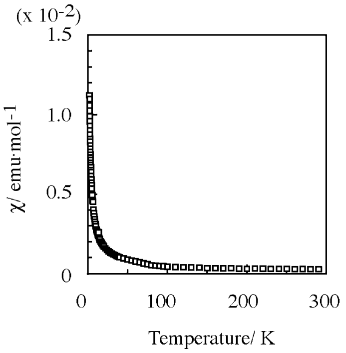

Figure 7. Temperature dependence of magnetic susceptibilities (χ) of polycrystals of the neutral species [Ni(eodt)$_2$] (**6**) at the field of 30 kOe.

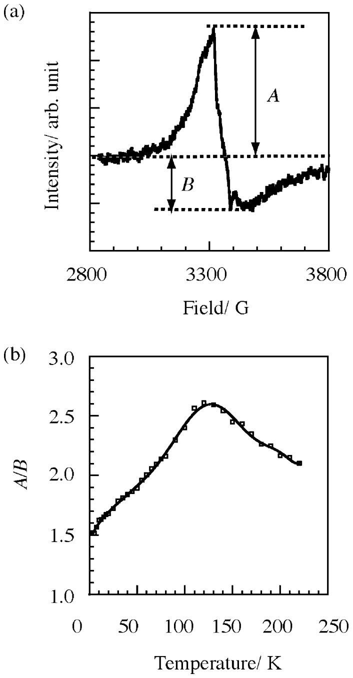

Figure 8. (a) Dysonian-like ESR signal at 120 K and (b) temperature dependence of the *A*/*B* values of the neutral species [Ni(eodt)$_2$] (**6**). *A* and *B* are the intensities of the top and bottom of the ESR signals, respectively.

The ESR measurement of the neutral complex **6** was carried out in the temperature range of 3.4−300 K. As Figure 8a indicates, complex **6** showed Dysonian-like ESR signals around room temperature as expected for its metallic conductivity. Defining the intensities of the maximum and minimum of the ESR signal as *A* and *B*, respectively, the ratio of *A*/*B* increases down to ca. 120 K, below which the ratio approaches $A/B = 1$ corresponding to a Lorentzian-like signal (for example, $A/B =$ ca. 2.1 at 220 K, $A/B =$ ca. 2.6 at 120 K, and $A/B =$ ca. 1.5 at 3.4 K) (see Figure 8a,b). This behavior of the *A*/*B* values is in agreement with the results of electrical resistivity measurement because the *A*/*B* values are considered to increase relative to the conductivity, which decreases below ca. 120 K.

Conclusions

In conclusion, we prepared new nickel bis(dithiolene) complexes with the ligands containing six-membered rings such as a cyclohexeno-fused or ethylenedioxy-substituted TTF skeleton, $(R_4N)_n[Ni(chdt)_2]$ [R = Me, $n = 2$ (**1**); R = ^{n}Bu, $n = 1$ (**2**); $n = 0$ (**3**)] and $(R_4N)_n[Ni(eodt)_2]$ [R = Me, $n = 2$ (**4**); R = ^{n}Bu, $n = 1$ (**5**); $n = 0$ (**6**)], and examined their crystal structures and physical properties. With regard to the monoanionic species **2** and **5**, both of them were obtained by electrocrystallization as single crystals good enough to perform crystal structure determinations. The monoanionic species **2** and **5** have sandwiched structures, in which the chains or layers of the nickel complexes and cations are arranged alternately. Thus, the monoanionic species indicated that there is no interchain or interlayer S···S contact less than the sum of van der Waals radii between the complex molecules along the sandwiched directions. On the other hand, the close S···S distances were observed only in the transverse direction. The magnetic properties of the monoanionic species **2** and **5** indicated the paramagnetism with the antiferromagnetic interaction between the anions of $s = 1/2$ states. The magnetic behavior of the monoanionic species **2** is in good agreement with the Bonner−Fisher model ($J/k_B = -28$ K). While **5** exhibits the Curie−Weiss behavior ($C = 0.376$ K·emu·mol^{-1} and $\Theta = -4.6$ K). The neutral species **3** and **6** showed fairly large room-temperature electrical conductivities (1−10 S·cm^{-1}) though the measurements were made on the compressed pellets of samples. Especially, complex **6** showed metallic temperature dependence down to 120 K and retained high conductivity even at 0.6 K [$\sigma(0.6\ K)/\sigma_{rt} \approx 1/30$], suggesting the system to be essentially metallic down to very low temperature. That is, complex **6** is considered to be a new single-component metal.

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Supporting Information Available: Two X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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