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Square-planar metal dithiolene complexes (M = Ni, Au) exhibiting *cis* and *trans* forms based on structurally flexible *o*-xylylene backbone

Mitsushiro Nomura [*], Kazuto Harada, Toshinori Suzuki, Masatsugu Kajitani, Toru Sugiyama

Department of Materials and Life Sciences, Faculty of Science and Technology, Sophia University, 7-1, Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan

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ABSTRACT

The square-planar metal dithiolene complexes of *o*-xylenediyldithioethylene-1,2-dithiolate (oxddt) ligand, $(Et_4P)[Ni(oxddt)_2]$ (**1**), $(Ph_4P)[Ni(oxddt)_2]$ (**2**) and $(Ph_4P)[Au(oxddt)_2]$ (**3**), were prepared and characterized. Among them, the Ni complexes **1** and **2** showed *cis-anti*-form structures, whose two benzene rings of the $Ni(oxddt)_2$ molecule are closely located to the dithiolene rings but located on the opposite side with respect to the dithiolene ring. In contrast to these Ni complexes, the Au complex **3** has a *trans-anti* form, suggesting that a Ni/Au substitution in the $[M(oxddt)_2]$ modifies those molecular structures in the crystals. An intramolecular π orbital overlap at the α-LUMO + 5 level between benzene and dithiolene rings was observed in the $[Ni(oxddt)_2]$ complex with the *cis-anti*-form. Redox behavior of **1** and **3** were investigated by cyclic voltammetry measurements.

1. Introduction

Metal dithiolene complexes involve delocalized π-electron systems with planar five-membered metallacycles (metalladithiolene). In monodithiolene complexes [CpM(dithiolene)] (M = Co, Rh, Ir; Cp = η^5-cyclopentadienyl), the metallacycle has a delocalized 6π-electrons system suggesting that the metalladithiolene ring is pseudo-aromatic by the Hückel's rule [1]. In addition to the pseudo-aromaticity, unsaturation coexists in the metallacycle. In fact, we have observed diverse addition reactions on the M–S bond [2]. Bisdithiolene complexes $[M(dithiolene)_2]$ with group 10 and 11 metals (M = Ni, Pd, Pt, Au) have relatively larger π-delocalized systems compared with the monodithiolene complexes because of the square-planar geometry [3]. Trisdithiolene complexes (M = Mo, W) with a trigonal prismatic geometry show three-dimensional π-electron delocalization [4]. Among these metal complexes noted above, the square-planar $[M(dithiolene)_2]$ complexes have received many interests for various molecular materials based on the particular electronic structures.

We can reduce a HOMO–LUMO gap of the $[M(dithiolene)_2]$ complex, when the dithiolene ring is directly connected with other rigid π-conjugated systems to extend the effective π-conjugation length [5]. Many $[M(dithiolene)_2]$ complexes with π-extended structures show near-IR electronic absorption by the low energy HOMO–LUMO gap [6]. Magnetic and conducting properties based on the $[M(dithiolene)_2]$ complex has been intensively investigated [7,8], because of the π-delocalized radical anion $[M(dithiolene)_2]^{-\cdot}$ state. In contrast to the introduction of a rigid system to the dithiolene ring, introductions of flexible alkyl chains to the square-planar $[M(dithiolene)_2]$ complexes are efficient ways toward thermotropic metal complexes, allowing for the formations of smectic and nematic [9] as well as discotic mesophases [10,11]. Which mesophase we can obtain is due to the length and shape of the flexible alkyl chain.

In this work, we focused on an introduction of a dialkylene-aromatics group, which can be a mixture of rigid benzene and flexible dialkyl chains, to the dithiolene ring. The metal complex of the *o*-xylenediyldithioethylene-1,2-dithiolate (oxddt) ligand is just the case. In the oxddt ligand, there is an eight-membered ring between dithiolene and benzene rings (Chart 1). According to some previous works, one could observe *cis* and *trans* structural isomers based on the folding angle of the eight-membered ring such as 1,5-cyclooctadiene compounds [12]. Baik et al. first reported the molecular structure of a bis(cyclopentadienyl) metal complex of the oxddt ligand, which is formulated as $[Cp_2Mo(oxddt)]$ [13]. The oxddt ligand showed the *cis*-form (closed-form) as show in Chart 1. We previously reported that syntheses and molecular structures of the mono(cyclopentadienyl) [CpM(oxddt)] (M = Co, Ni) complexes and their derivatives [14,15]. It was different that [CpM(oxddt)] complexes showed the *trans*-form (opened-form). It was notable that the alkylidene adduct of the [CpCo(oxddt)] showed the *cis*-form. In addition to the [CpCo(oxddt)] derivatives, the oxone derivative of oxddt, [O=C(oxddt)], has the *trans*-form (Chart 1) [14], although the corresponding thione [S=C(oxddt)] has the *cis*-form [16].

Thus, these oxddt compounds can be structurally flexible based on the eight-membered ring moiety and the folding angle in the

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[*] Corresponding author. Current address: Condensed Molecular Materials Laboratory, RIKEN, 2-1, Hirosawa, Wako-shi, Saitama 351-0198, Japan.
E-mail address: mitsushiro@riken.jp (M. Nomura).

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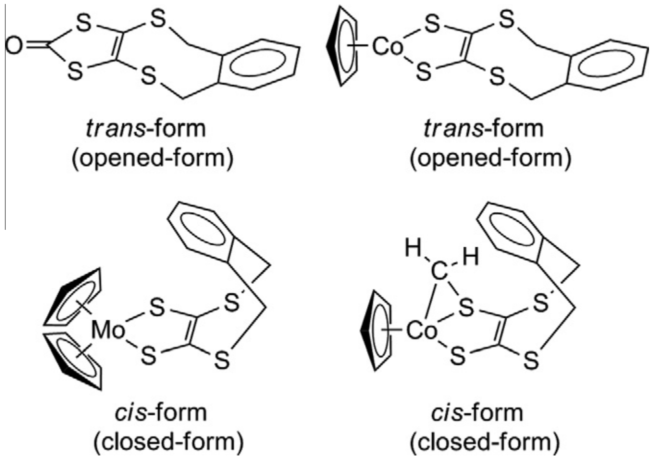


Chart 1. *trans*-Form (opened-form) and *cis*-form (closed-form) structures of oxddt derivatives.

solid state is controllable by chemical modifications. However, we have found that there are a few examples of square-planar dithiolene complexes of the oxddt ligand. Underhill et al. previously reported preparations of the four-coordinate $[M(oxddt)_2]^-$ (M = Ni, Cu, Au) anion salts with an ammonium cation and their oxidized species, but these products were not structurally characterized [17]. No structure of a bisdithiolene complex with the oxddt ligand has been known so far. Here we report three structurally characterized $[M(oxddt)_2]^-$ (M = Ni, Au) anion salts with a phosphonium cation. Electrochemical measurements and DFT calculations on the $[M(oxddt)_2]^-$ anion salts were also carried out to discuss their electronic structures.

2. Results and discussion

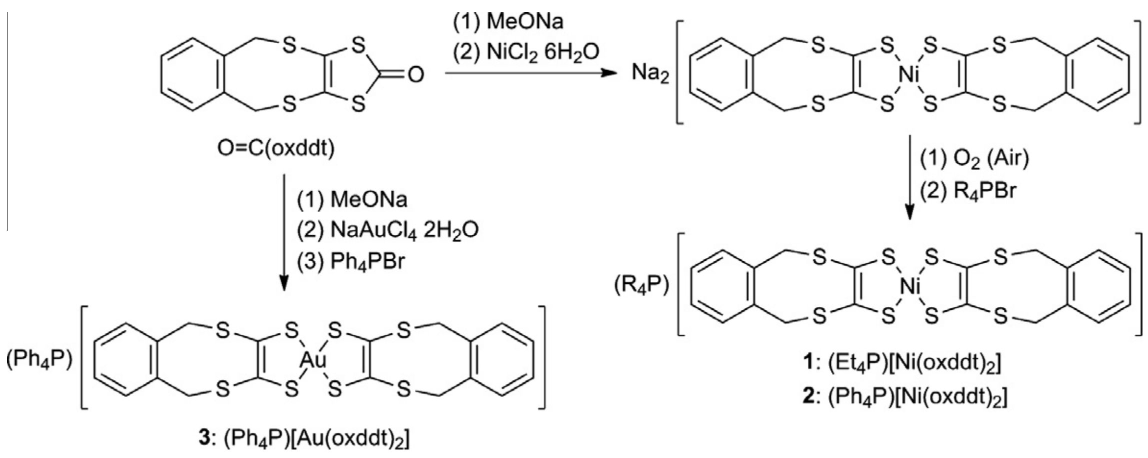
2.1. Preparations of $[M(oxddt)_2]$ complexes (M = Ni, Au)

The oxo derivative of oxddt, [O=C(oxddt)], was reacted with **2** equiv of sodium methoxide in methanol solution to generate air-sensitive $oxddt^{2-}$. A successive addition of $Ni^{II}Cl_2 \cdot 6H_2O$ into the resulted solution under Ar atmosphere gave the nickel complex with bis-oxddt ligand, $[Ni(oxddt)_2]^{2-}$ (Scheme 1). An aerial oxidation of the $[Ni(oxddt)_2]^{2-}$ and then an addition of phosphonium cation (Et_4P^+ or Ph_4P^+) gave the corresponding radical anion salt $(Et_4P)[Ni(oxddt)_2]$ (**1**) or $(Ph_4P)[Ni(oxddt)_2]$ (**2**), respectively. The reaction of the *in situ* generated $oxddt^{2-}$ with $NaAu^{III}Cl_4 \cdot 2H_2O$ directly afforded the air-stable monoanion $[Au(oxddt)_2]^-$ without aerial oxidation, and then the addition of Ph_4PBr gave the target $(Ph_4P)[Au(oxddt)_2]$ (**3**) salt (Scheme 1). The single crystals of **1**–**3** were obtained by recrystallizations using vapor diffusion of Et_2O into these acetone solutions. **1**–**3** crystallized in the monoclinic system with space group *C*2/*c*, respectively (Table 2). The three complexes are perfectly symmetric and each central metal atom as well as phosphorus atom lie on a crystallographic inversion center. Therefore, one half of each anion (or cation) is crystallographically unique (Fig. 1). The Et_4P^+ cation in **1** is disordered with two possible orientations (Fig. 2).

2.2. Structural determinations of $[M(oxddt)_2]$ complexes

The ORTEP drawings of the $[M(oxddt)_2]^-$ anion moieties in **1** and **3** as well as definition of dihedral angles (θ_1–θ_4) of them are displayed in Fig. 1. The selected bond lengths, bond angles and dihedral angles are summarized in Table 1. All the bond lengths and angles of **1**–**3** in these metallacycles are in the range of normal $[Ni(dithiolene)_2]^-$ and $[Au(dithiolene)_2]^-$ complexes [3]. Two benzene rings of the $Ni(oxddt)_2$ molecule in **1** are closely located toward the dithiolene rings by folding of the eight-membered ring (closed-form) but each benzene ring is located on the opposite side with respect to the dithiolene ring, forming the *cis-anti*-form structure (Fig. 1(a)). In addition to **1**, the corresponding Ph_4P^+ salt **2** also showed the *cis-anti*-form based on the $[Ni(oxddt)_2]^-$ radical anion molecule. However, the structure of $[Ni(oxddt)_2]^-$ radical anion moiety was slightly modified by the cation effect. The dihedral angle θ_1 (dithiolene folding angle) of **1** or **2** was 7.23° or 2.73°, respectively. The other dihedral angles θ_2, θ_3 and θ_4 were also modified by the cation effect (Table 1). There are short intramolecular non-chemical bondings of C1···C5 and C2···C6 between dithiolene and benzene rings (Fig. 1(a)). The bonding distances in **2** (2.932 and 2.952 Å) are obviously shorter than those in **1** (3.038 and 3.083 Å). This result is reflected by degree of the dihedral angle θ_4 (61.98° for **1** and 50.06° for **2**).

In contrast to the Ni complexes with *cis-anti*-forms, each oxddt ligand of the Au complex **3** has a *trans*-form (opened-form). Since two benzene rings in **3** are located on the opposite side toward the dithiolene ring, this is a *trans-anti* form (Fig. 1(c)). The θ_2 and θ_3 dihedral angles in **3** (107.40° and 118.97°) are remarkably different from those of [CpCo(oxddt)] with the *trans*-form (116.683° and 108.892°) [14]. The packing diagrams of **1** and **3** show intermolecular interactions between benzene rings with the plane-to-plane distances of 3.627 and 3.786 Å, respectively (Figs. 2 and 3). However, no interaction was realized between dithiolene rings in **1** and **3** as well as **2**, whereas in the neutral [CpM(oxddt)] complexes, there were the intermolecular face-to-face interactions between



Scheme 1. Preparations of $[M(oxddt)_2]$ salts (M = Ni, Au).

Table 1
Selected bond lengths (Å), bond angles (°) and dihedral angles (°) in metalladithiolene ring.

	1	2	3	[CpCo(oxddt)]	[CpCo(CH_2)(oxddt)]
Structure type	*cis-anti*	*cis-anti*	*trans-anti*	*trans*	*cis*
Bond length					
M1–S1	2.1429(8)	2.1378(4)	2.3137(8)	2.118(3)	2.1858(7)
M1–S2	2.1496(9)	2.1486(4)	2.3195(9)	2.111(3)	2.2042(7)
S1–C1	1.737(3)	1.7300(17)	1.751(3)	1.751(10)	1.767(2)
S2–C2	1.726(3)	1.7259(17)	1.745(3)	1.711(12)	1.720(2)
C1–C2	1.353(5)	1.362(2)	1.340(4)	1.361(13)	1.352(3)
Bond angles					
S1–M1–S2	91.38(3)	91.313(15)	89.12(3)	91.14(12)	91.19(2)
M1–S1–C1	104.43(11)	104.79(6)	101.94(10)	104.5(3)	103.77(8)
M1–S2–C2	104.44(11)	104.72(6)	102.56(11)	106.6(3)	102.93(8)
S1–C1–C2	119.5(2)	119.58(13)	123.7(2)	119.2(8)	118.30(15)
S2–C2–C1	120.0(2)	119.46(12)	122.5(2)	118.0(8)	123.10(15)
Non-chemical bonding					
C1···C5	3.038	2.932	[b]	[b]	2.908
C2···C6	3.083	2.952	[b]	[b]	2.959
Dihedral angles[a]					
θ_1	7.23	2.73	3.08	8.026	7.896
θ_2	120.10	112.52	107.40	116.683	115.327
θ_3	121.82	117.51	118.97	108.892	114.484
θ_4	61.98	50.06	11.57	7.791	50.232
References	This work	This work	This work	[14]	[14]

[a] Dihedral angles (θ_1–θ_4) are defined in Fig. 1.
[b] Not relevant in the *trans* structure.

Table 2
Crystallographic data.

Compound	1	2	3
Formula	$C_{28}H_{36}NiPS_8$	$C_{44}H_{36}NiPS_8$	$C_{44}H_{36}AuPS_8$
Formula weight (g mol^{-1})	718.73	910.89	1049.19
Crystal color	Brown	Brown	Yellow
Crystal shape	Block	Block	Platelet
Crystal size (mm)	0.50 × 0.40 × 0.35	0.50 × 0.40 × 0.30	0.15 × 0.13 × 0.07
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$C2/c$ (No. 15)
Unit cell dimensions			
T (K)	293(2)	293(2)	293(2)
a (Å)	25.606(5)	25.8325(16)	23.674(7)
b (Å)	9.6765(17)	8.5894(2)	11.481(4)
c (Å)	16.812(3)	22.7112(11)	17.025(5)
β (°)	126.5960(10)	123.2290(10)	90.1674(15)
V ($Å^3$)	3344.4(11)	4215.3(3)	4627(2)
Z	4	4	4
D_{calc} (g cm^{-3})	1.427	1.435	1.506
μ (mm^{-1})	1.146	0.927	3.615
Total reflections	11920	15589	17425
Unique reflections (R_{int})	3756(0.0200)	4763(0.0172)	14069(0.030)
Unique reflections ($I > 2\sigma(I)$)	3355	4438	5269
R_1 ($I > 2\sigma(I)$)	0.0559	0.0324	0.0495
wR_2 ($I > 2\sigma(I)$)	0.1733	0.0873	0.1130
Goodness-of-fit (GOF)	1.117	1.046	1.038

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

dithioethylene-1,2-dithiolate moieties [14,15]. One reason why we did not observe such interaction in the $[M(oxddt)_2]^-$ anion salt may be due to Coulomb repulsion of the anionic molecule.

Fourmigué et al. reported that diverse molecular structures including *trans-syn* or *trans-anti* form derived from bis(2,2′-difluoropropylenedithio)tetrathiafulvalene or non-fluorinated bis(propylenedithio)tetrathiafulvalene radical cation salt with several different anions [18,19]. The molecular structure of the tetrathiafulvalene (TTF) derivative can be controlled by a halogen bonding (or hydrogen bonding) interaction between the terminal propylene group of TTF cation and halogen atom of the selected anion (Fig. 4). On the basis of the structural determinations of Ni/Au(oxddt)$_2$ complexes, we observed that the Ni/Au substitution causes the *cis/trans* structural change. The Ni/Au substitution in the normal $[M(dithiolene)_2]$ complexes often modifies those crystal structures (e.g. intermolecular arrangement) except some isostructural couples [20–22]. However, the molecular structure itself has not been changed by a substitution of the central metal. In the $[M(oxddt)_2]$ complexes, however, it is quite rare that the Ni/Au substitution modifies the molecular structure. One reason is probably due to a structural flexibility of the eight-membered ring moiety of the oxddt ligand. We think that our result is just similar case to *cis/trans* isomers of eight-membered 1,5-cyclooctadiene derivatives [12].

2.3. Molecular orbitals

Molecular orbital distributions of $[Ni(oxddt)_2]^-$ radical anion and $[Au(oxddt)_2]^-$ anion were obtained by density functional theory (DFT) methods. These frontier orbital distributions (HOMO,

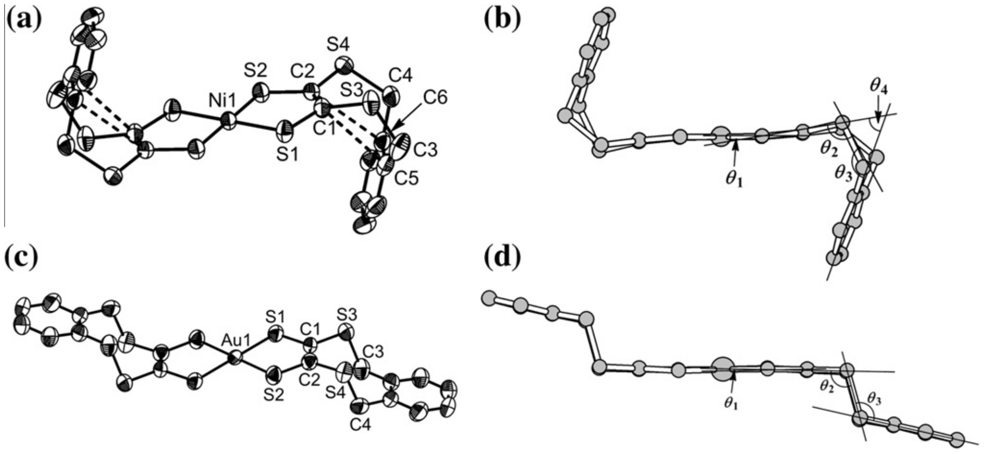


Fig. 1. ORTEP drawings of the anion moieties of (a) **1** and (c) **3**. Thermal ellipsoids are drawn at 40% probability level. Dotted lines in **1** show short intramolecular non-chemical bondings between dithiolene and benzene rings. Definition of dihedral angles for the anion moieties of (b) **1** and (d) **3**: θ_1 (dithiolene folding angle) = M1S1S2/S1S2C1C2S3S4, θ_2 = S1S2C1C2S3S4/S3S4C3C4, θ_3 = S3S4C3C4/benzene, θ_4 = S1S2C1C2S3S4/benzene.

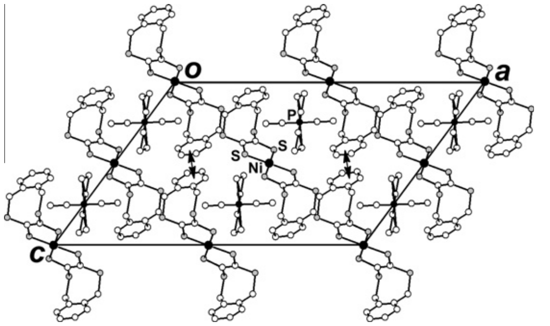


Fig. 2. Projection view along the *b*-axis of **1** demonstrating a π–π stacking through the benzene ring. The Et_4P^+ cation is disordered with two possible orientations.

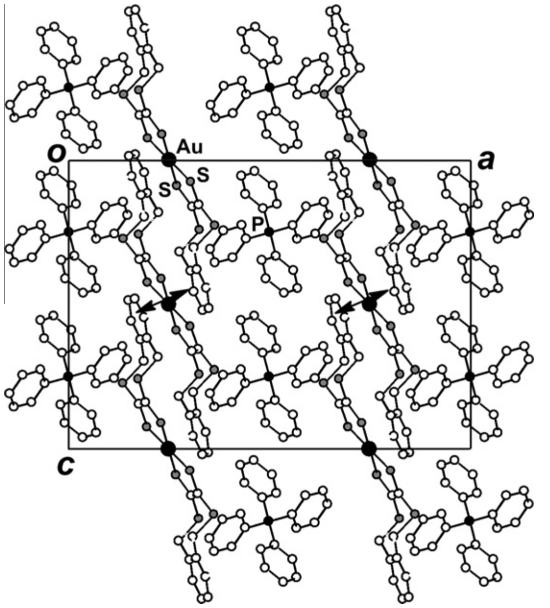


Fig. 3. Projection view along the *b*-axis of **3** demonstrating a π–π stacking through the benzene ring.

SOMO and LUMO) are similar to those of typical Ni/Au(dithiolene)$_2$ species [23,24]. As shown in Fig. 5, there are large contributions of dithiolene-π orbital for the α-SOMO in the $[Ni(oxddt)_2]^-$ radical anion (Fig. 5(b)) and for the HOMO in the $[Au(oxddt)_2]^-$ anion (Fig. 5(e)), but small contributions of d orbital for them. These SOMO and HOMO are mostly distributed to the five-membered metallacycle. In addition, the dithiolene-π orbital largely contributed for the α-LUMO of $[Ni(oxddt)_2]^-$ radical anion (Fig. 5(a)). It is different that the LUMO of $[Au(oxddt)_2]^-$ anion is due to the anti-bonding combination of the metal d_{xy} and the dithiolene ligand orbitals (Fig. 5(d)). The overlap between these two orbitals is favorable and provides an efficient pathway for ligand-to-metal σ electron donation, which is similar to the LUMO of $[Au(bdt)_2]$ (bdt = benzene-1,2-dithiolate) as previously obtained by Wieghardt et al. [23]. Furthermore, the α-LUMO + 5 of $[Ni(oxddt)_2]^-$ radical anion is distributed in the whole molecule including the terminal benzene rings. Among them, it is notable that there is an intramolecular overlap of π orbital between benzene and C=C

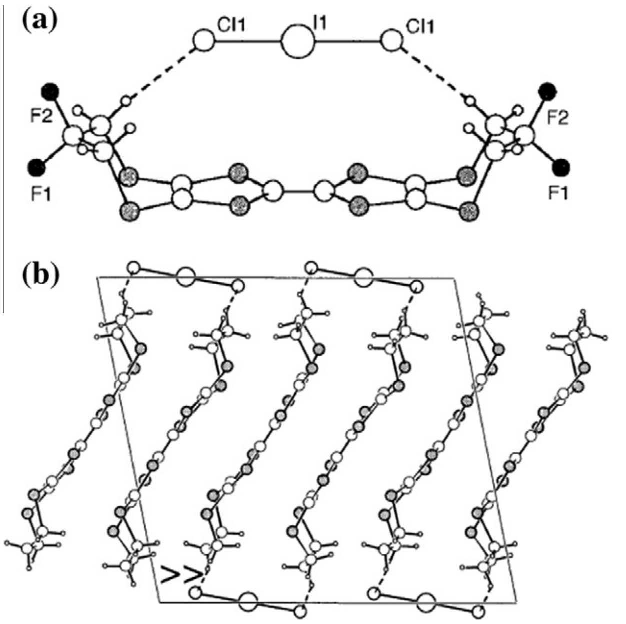


Fig. 4. (a) The *trans-syn* form of bis(2,2′-difluoropropylenedithio)tetrathiafulvalene radical cation salt with ICl_2 anion and (b) the *trans-anti* form of bis(propylenedithio)tetrathiafulvalene radical cation salt with ICl_2 anion (Adapted from Ref. [18]). Dotted lines show H···Cl halogen (or hydrogen) bonding interactions.

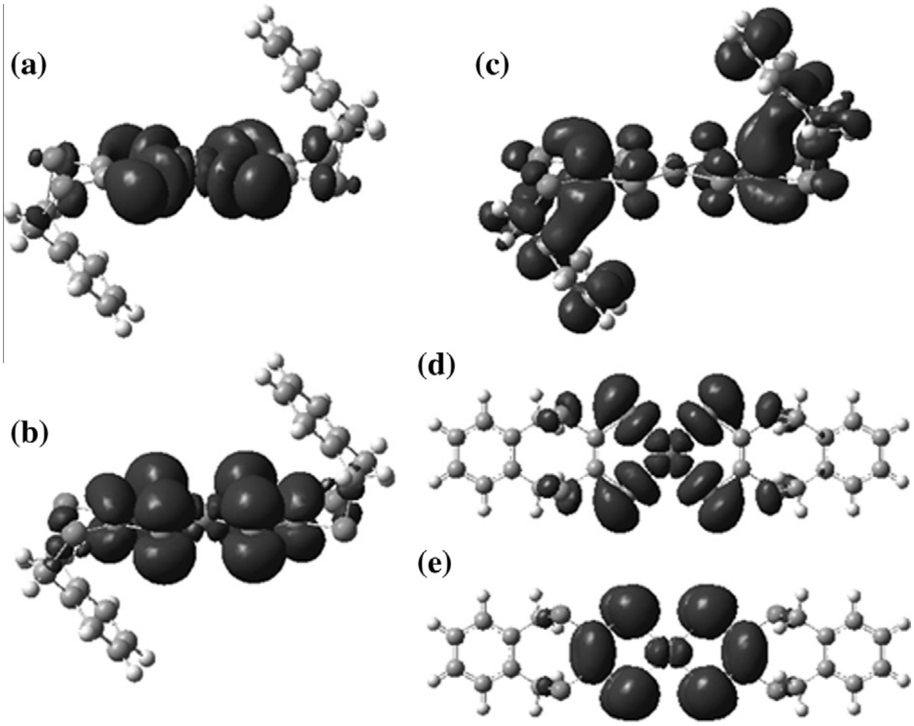


Fig. 5. (a) α-LUMO, (b) α-SOMO, (c) α-LUMO + 5 of $[Ni(oxddt)_2]^-$ radical anion moiety, (d) LUMO and (e) HOMO of $[Au(oxddt)_2]^-$ anion moiety obtained by DFT methods. The isovalue for the orbital plots is 0.02.

bond moiety in the metallacycle (Fig. 5(c)). The short intramolecular non-chemical bondings of C1···C5 and C2···C6 obtained by X-ray analyses (Fig. 1(a)) and obtained by the optimized structure (2.966 and 3.016 Å) support this π orbital overlap. Namely, one interesting thing of the *cis*-form is an intramolecular approach of these aromatic rings.

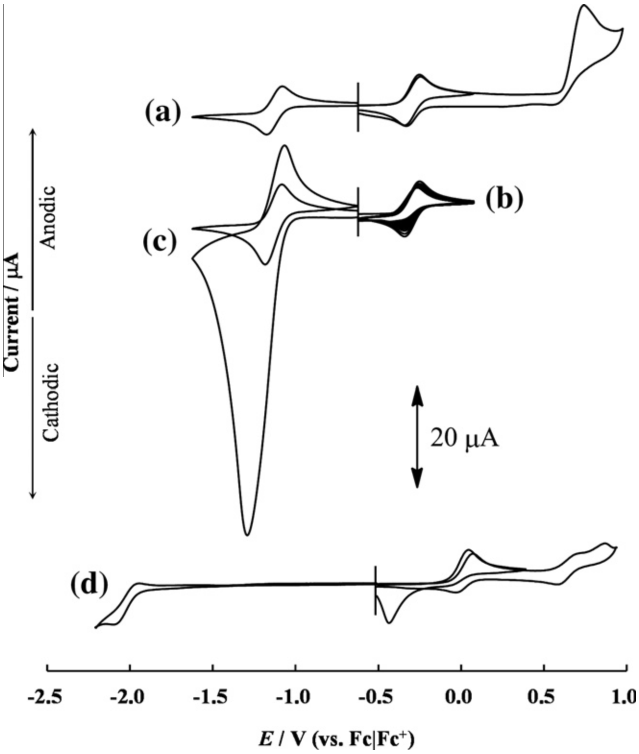


Fig. 6. (a) Cyclic voltammograms of **1**, (b) multiple scan of the first oxidation wave of **1**, (c) reduction wave after the multiple scan of **1** and (d) CV of **3**: all materials were measured in dichloromethane containing tetra-*n*-butylammonium perchlorate (TBAP).

2.4. Electrochemical behavior

In order to study electrochemical behavior, the cyclic voltammograms of **1** and **3** were obtained in dichloromethane solution containing tetra-*n*-butylammonium perchlorate (TBAP). **1** showed a reversible reduction wave at $E_{1/2}(\text{red}) = -1.13$ V (versus Fc/Fc^+), a reversible oxidation wave at $E_{1/2}(\text{ox}) = -0.29$ V and an irreversible oxidation wave at $E_p(\text{ox}) = +0.72$ V (Fig. 6(a)). This CV result suggests that there are stable dianionic $[Ni(oxddt)_2]^{2-}$ and neutral $[Ni(oxddt)_2]^0$ states on the time scale of this CV measurement but very unstable cationic $[Ni(oxddt)_2]^+$ state. However, the multiple potential scan of the first oxidation of **1** demonstrated decrease of the redox current with increasing the number of potential scan, and then irreversibility of the first oxidation wave (Fig. 6(b)). We assume that robust precipitation of the neutral $[Ni(oxddt)_2]^0$ species on the electrode occurred during the multiple potential scan. In fact, after the multiple scan, a potential scan to −1.6 V showed a large cathodic current (Fig. 6(c)), indicating the electrochemical reduction and following desorption of the precipitated $[Ni(oxddt)_2]$. On the other hand, **3** showed a reversible reduction wave at $E_{1/2}(\text{red}) = -2.02$ V and an irreversible oxidation wave at $E_p(\text{ox}) = +0.05$ V. Furthermore, there were several oxidation waves at more than +0.5 V (Fig. 6(d)). Thus, the CV of the Au complex **3** showed negative shift of a reduction potential and positive shift of an oxidation potential, compared with each of the Ni complex **1**. Namely, it seems that $[Ni(oxddt)_2]^-$ radical anion has a small HOMO–LUMO gap to explain its near-IR absorption at $\lambda_{max} = 934$ nm ($\varepsilon = 9400\ M^{-1}\ cm^{-1}$) in dichloromethane solution, although the absorption energy of $[Ni(oxddt)_2]^-$ is higher than those of $[Ni(dddt)_2]^-$ (1175 nm), $[Ni(pddt)_2]^-$ (938 nm) and $[Ni(dmit)_2]^-$ (1137 nm), where dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate, pddt = 6,7-dihydro-5*H*-1,4-dithiepin-2,3-dithiolate and dmit = 1,3-dithiol-2-thione-4,5-dithiolate [25]. Furthermore, the irreversible oxidation wave of **3** suggested that the neutral radical $[Au(oxddt)_2]^0$ is very unstable and then immediately undergoes a chemical reaction. This result is usual because a neutral $[Au(dithiolene)_2]^0$ complex is normally unstable unless there is a bulky group or a long alkyl chain on the dithiolene ligand [26].

3. Conclusion

In this work, we studied on the square-planar metal dithiolene complexes of the *o*-xylenediyldithioethylene-1,2-dithiolate (oxddt) ligand exhibiting *cis* and *trans* structures. Previously, it has been known that the molecular structure of the mono(dithiolene) complex, [CpCo(oxddt)], can be modified by addition of an alkylidene group on the Co–S bond (Chart 1). However, we observed that a metal substitution of bis(dithiolene) complex, $[M(oxddt)_2]$, also modifies the molecular structure. Such diverse structural change is probably due to the structurally flexible oxddt ligand with an eight-membered ring. It may be suggesting that we can observe diverse molecular structures by introducing a large-membered ring (e.g. more than eight-member) to the dithiolene ligand. In addition to such attractive structural changes, we also found intramolecular π orbital overlap between benzene and metallacycle, based on DFT calculations. It is just rare that the π orbital of organic aromatics overlapped with that of aromatic metallacycle.

4. Experimental

4.1. Materials and instrumentation

All reactions were carried out under argon atmosphere by means of standard Schlenk techniques. MeOH was obtained from Wako Pure Chemical Industries, Ltd. and then distilled by CaH_2 before use. MeONa was prepared by dry MeOH with sodium metal. $NiCl_2\cdot6H_2O$, $NaAuCl_4\cdot2H_2O$, Ph_4PBr and Et_4PBr were obtained from Wako Pure Chemical Industries, Ltd. *o*-Xylenediyldithioethylene-1,3-dithiol-2-one, O=C(oxddt),[27] was prepared by the reaction of S=C(oxddt) with mercuric acetate. Elemental analyses were determined by using a Shimadzu PE2400-II instrument. NMR spectra were measured with a JEOL LA500 spectrometer. UV–Vis spectra were recorded on a Hitachi model UV-2500PC.

4.2. Preparation of $[M(oxddt)_2]$ salts

Sodium methoxide in MeOH (2.8 ml, 2.8 mmol) was added to a solution of O=C(oxddt) (0.378 g, 1.33 mmol) in MeOH (50 ml) and stirred for 1 h. The initial colorless solution was changed to yellow. $NiCl_2\cdot6H_2O$ (159 mg, 0.67 mmol) was added into the reaction mixture as solid. A brown solution was rapidly formed and the reaction mixture was further stirred for 1 h. The dianionic $[Ni(oxddt)_2]^{2-}$ was supposed to be generated at this time. This solution was left under air atmosphere to form the monoanionic $[Ni(oxddt)_2]^-$. When tetraphenylphosphonium bromide (281 mg, 0.67 mmol) was added, brown precipitates were generated. The brown solids were isolated by filtration and were washed with extra MeOH. The product was recrystallized by acetone/*i*PrOH. $(Ph_4P)[Ni(oxddt)_2]$ (**2**) was obtained in 72% (439 mg, 0.48 mmol) yield. Elemental *Anal.* Calc. for $C_{44}H_{36}NiPS_8$: C, 58.01; H, 3.98. Found: C, 58.22; H, 3.88.

The corresponding Et_4P^+ salt (**1**) was prepared in 65% yield by the similar procedure to that of **2**. $(Et_4P)[Ni(oxddt)_2]$ (**1**): UV–Vis–NIR (CH_2Cl_2) λ_{max}/nm (ε/$M^{-1}\,cm^{-1}$) 934 (9400), 392 (10900), 331 (21300). Elemental *Anal.* Calc. for $C_{28}H_{36}NiPS_8$: C, 46.79; H, 5.05. Found: C, 46.97; H, 5.24. The Au complex **3** was also prepared in 50% yield by using $NaAuCl_4\cdot2H_2O$ instead of $NiCl_2\cdot6H_2O$. After the addition of $NaAuCl_4\cdot2H_2O$, no aerial oxidation is necessary. Spectroscopic and analytical data of **3** are as follows: ^1H NMR ($CDCl_3$, versus TMS, 500 MHz) δ 7.08 (br-s, 4H, benzene), 4.14 (br-s, 4H, CH_2). UV–Vis (CH_2Cl_2) λ_{max}/nm (ε/$M^{-1}\,cm^{-1}$) 345 (16500). Elemental *Anal.* Calc. for $C_{44}H_{36}AuPS_8$: C, 50.37; H, 3.46. Found: C, 50.44; H, 3.51.

4.3. CV measurements

All electrochemical measurements were performed under an argon atmosphere. Solvents for electrochemical measurements were dried by molecular sieve 4A before use. A platinum wire served as a counter electrode, and the reference electrode Ag/AgCl was corrected for junction potentials by being referenced internally to the ferrocene/ferrocenium (Fc/Fc^+) couple. A stationary platinum disk (1.6 mm in diameter) was used as a working electrode. The Model CV-50W instrument from BAS Co. was used for cyclic voltammetry (CV) measurements. CVs were measured in 1 mmol dm^{-3} dichloromethane solutions of complexes containing 0.1 mol·dm^{-3} tetra-*n*-butylammonium perchlorate (TBAP) at 25 °C.

4.4. Density functional theory (DFT) calculation

Geometries of $[Ni(oxddt)_2]^-$ radical anion and $[Au(oxddt)_2]^-$ anion were optimized with no constraint using the GAUSSIAN 03 package [28] and the hybrid functional B3LYP for closed-shell molecules or UB3LYP for opened-shell molecules [29]. The standard 3-21G* basis set [30] was used for H, C and S together with the LanL2DZ for Co. Energy minima were confirmed by frequencies analysis.

4.5. X-ray diffraction study

Single crystals of **1**–**3** were obtained by recrystallization using vapor diffusion of Et_2O into the acetone solution. A single crystal was mounted on the top of a thin glass fiber. The measurement was made on a Rigaku Mercury diffractometer with graphite-monochromated MoKα radiation. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques [31]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All the calculations were carried out using the CRYSTAL STRUCTURE CRYSTALLOGRAPHIC software package [32] for **3** and WINGX software package for **1** and **2** [33]. Crystallographic data are summarized in Table 2.

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