



CpCo(dithiolene) complexes of highly flexible oxddt ligand with two different Z-shaped and U-shaped structures

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ABSTRACT

[CpCo(oxddt)] complex (**2**, oxddt = *o*-xylenediyldithioethylene-1,2-dithiolate, Cp = η^5 -cyclopentadienyl) was obtained from *o*-xylenediyldithioethylene-1,3-dithiol-2-one (O=C(oxddt)) (**1**). **2** further reacted with diazoalkanes (N₂CHR) to form some alkylidene-bridged adducts [CpCo(CHR)(oxddt)] (R = H (**3a**), SiMe₃ (**3b**)). Adduct **3a** further reacted with protic acids (HX) to give some *S*-methylated adducts [CpCo(X)(oxddt)(*S*-Me)] (X = Cl (**4a**), OCOF₃ (**4c**)), followed by the Co–C bond cleavage in the three-membered cobaltathiirane ring. Two different Z-shaped and U-shaped molecular structures were observed by X-ray diffraction studies. In the former structure (Z), the dithiolene and *o*-xylylene planes are located at almost parallel position each other, and in the latter structure (U), both planes are not parallel but the *o*-xylylene moiety is located closer to the dithiolene plane than the Z-shaped one. The Z-shaped structure involves **1** and **2**. The U-shaped structure involves **3a**, **3b**, **4a** and **4c**. Complex **1** showed a one-dimensional chain through intermolecular π – π interaction in the crystal. Complex **2** had a dimeric interaction between dithioethylenedithiolate moieties (S₂C₂S₂) in the oxddt. The SiMe₃ group in **3b** was placed at an *exo*-position with respect to the cobaltadithiolene ring due to a steric hindrance from the U-shaped oxddt ligand. In **4a**, the X and Me groups are located at the opposite side of the dithiolene plane (*anti*-form) but in **4c**, both groups are presented at the same side of the dithiolene plane (*syn*-form). The NMR analysis of **4a** in solution indicated existence of both *anti*- and *syn*-isomers (7:1).

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1. Introduction

General interests of dithiolene complexes are due to their specific π -electron systems which involve the π -electron delocalization for low energy HOMO–LUMO gap [1], photo-excited charge transfer due to the π -electron [2], the $(4n+2)\pi$ -conjugation for aromaticity (the Hückel's rule) [3], the π -electron-based magnetic interaction [4], the π -electron-induced electrical conductivity [5], thermally driven valence tautomerism due to M/L-CT [6], the dithiolene-based 'non-innocent behavior' [7], and so on. Those chemical and physical properties require an extremely planar π -extended dithiolene system. On the other hand, some distorted dithiolene rings have been observed as follows. There are organometallic dithiolene complexes such as [Cp₂M(dithiolene)] (M = Ti, Mo, W) [8,9], [CpMo(dithiolene)₂] [10], and dimeric [CpMo(dithiolene)₂] [11]. In addition, there are also homoleptic dithiolene complexes such as trisdithiolenes, [M(dithiolene)₃] (M = V, Cr, Mo, W,

Re, Nd, Ce) [12,13] having trigonal prismatic geometry, and recently some tetrakis(dithiolene) complexes (M = U, Ce) have been reported as well [14]. Their dithiolene planes noted above are folded along the S...S hinge (Chart 1).

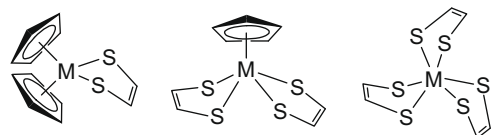
Some early papers described distorted metal dithiolene systems whose dithiolene rings are enough planar for π -conjugation, but the ring incorporates folded large heterocycles such as a seven-membered ring [15–19] for sake of increasing solubility [20]. Kobayashi et al. reported [M(ptdt)₂] complexes (Chart 1, M = Ni, Cu, Au; ptdt = propylenedithiotetrafulvalenedithiolate) whose terminal rings are seven-membered [20,21]. In typical, π -extended dithiolene complexes tend to be insoluble, however, the terminal propylene group in the [M(ptdt)₂] helps to solubilize the complexes in an organic solvent and finally good crystals are obtained for solid state magnetic and conductive studies. In fact, the planarity of the whole molecule is not always important to make S...S overlapping between the molecules.

However, dithiolene complexes bearing more folded ring than a seven-membered ring (e.g. eight-membered ring) are rarely reported [22–24]. In this work, we focused on [CpCo(dithiolene)] complex of *o*-xylenediyldithioethylene-1,2-dithiolate (oxddt) ligand (Scheme 1). Underhill et al. have previously reported (NR₄)[M(oxddt)₂] (M = Ni, Cu, Au; R = Et, Bu) and their oxidized

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Folded dithiolene along S...S hinge



Folded terminal large ring

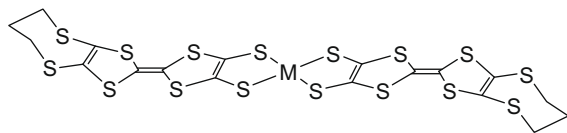


Chart 1.

species, but the products have been not structurally characterized [22], but no [CpCo(dithiolene)] and some other heteroleptic dithiolene complexes of oxddt have been not reported yet.

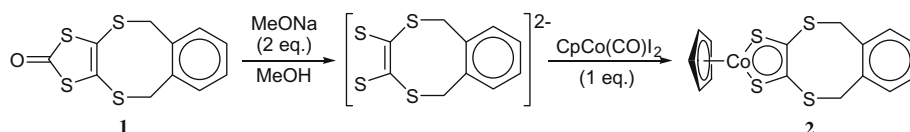
The oxddt and its analogue compounds are supposed to be some of structurally interesting dithiolene species because of their highly structural flexibility. The structure determinations of some organic oxddt derivatives ($S=C(\text{oxddt})$) have been reported [25,26]. Wang et al. have reported that the molecular structures of dibrominated *o*-xylenediylidithioethylene-1,3-dithiol-2-thione ($S=C(\text{oxddt-Br}_2)$, Chart 2) and dicyanated *o*-pyrazinediylidithioethylene-1,3-dithiol-2-thione whose molecular structures are Z-shaped [25]. In contrast, Wardell et al. have reported a U-shaped structure obtained from *o*-xylenediylidithioethylene-1,3-dithiol-2-thione ($S=C(\text{oxddt})$, Chart 2) [26], and also observed its order–disorder transition with different temperature and dimorphism obtained from recrystallization using various solvents. However, the structural study on metal complex of oxddt has been much less investigated. Fourmigué et al. have reported the paramagnetic [CpNi^{III}(oxddt)] complex having the Z-shaped structure and strong antiferromagnetic interaction at solid state between two molecules [24].

This paper reports on the synthesis and molecular structure of the diamagnetic [CpCo^{III}(oxddt)] complex which is possible to be isostructural to [CpNi^{III}(oxddt)]. Needless to say, [CpCo^{III}(oxddt)] is magnetically inert but the chemical reactivity is relatively interesting because of its coordinatively unsaturated metal center [27]. In fact, some addition reactions to the unsaturated moiety have been developed [28]. According to these background, we also study on the molecular structures of some alkylidene-bridged [CpCo(oxddt)] complexes (Scheme 2), which are derived from the reactions of [CpCo(oxddt)] with some diazoalkanes, and the structures of the *S*-alkylated [CpCo(oxddt)] complexes (Scheme 2) which are further derived from the alkylidene-bridged adduct. Characterizations of these products are performed by NMR and CV. Moreover, two different Z-shaped and U-shaped molecular geometries are determined by X-ray diffraction study.

2. Results and discussion

2.1. Preparations and characterizations of [CpCo(oxddt)], alkylidene-bridged [CpCo(CHR)(oxddt)] and *S*-methylated [CpCo(X)(oxddt)(*S*-Me)]

o-Xylenediylidithioethylene-1,3-dithiol-2-one (**1**) was prepared from *o*-xylenediylidithioethylene-1,3-dithiol-2-thione (Chart 2)



Scheme 1. Preparation of [CpCo(oxddt)] (2).

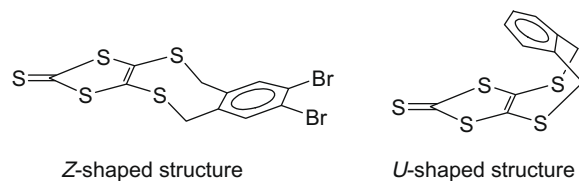


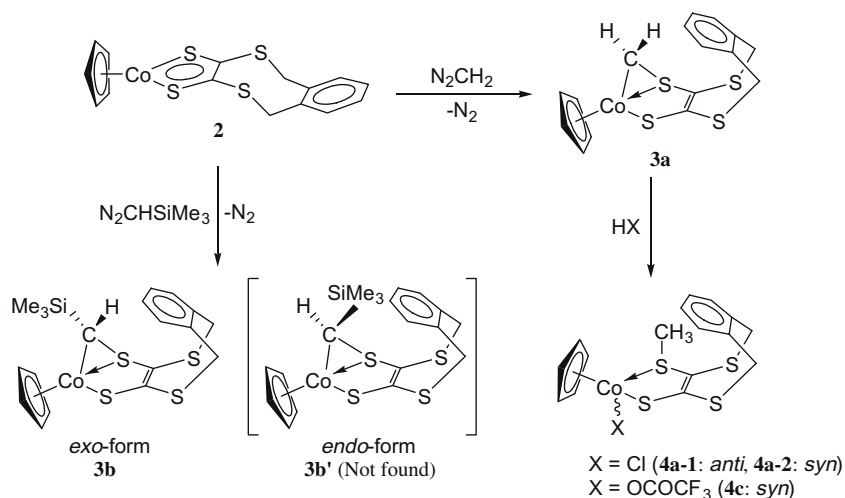
Chart 2.

and $\text{Hg}(\text{OAc})_2$ as previously described [29]. Complex **1** treated with 2 equiv of sodium methoxide in MeOH to form the oxddt dianion (not isolated), and then [CpCo(CO)₂] was successively added to the reaction mixture. After the reaction, a blue product was separated by column chromatography on silica gel. [CpCo(oxddt)] (**2**) was isolated as a blue solid in 60% yield (Scheme 1).

The reactions of [CpCo(dithiolene)] complexes with diazoalkanes have been developed. In typical, these reactions produce the alkylidene-bridged [CpCo(dithiolene)] adducts whose alkylidene group bridges at the Co–S bond [30]. Complex **2** rapidly reacted with diazomethane or (trimethylsilyl)diazomethane to afford the 1:1 alkylidene-bridged dithiolene complex which is formulated as [CpCo(CH₂)(oxddt)] (**3a**, 81% yield) or [CpCo(CHSiMe₃)(oxddt)] (**3b**, 65% yield), respectively (Scheme 2). As displayed in Scheme 2, the CH₂ adduct **3a** further reacted with hydrochloric acid or trifluoroacetic acid to form the *S*-methylated adducts [CpCo(X)(oxddt)(*S*-Me)] (X = Cl (**4a**, 75% yield), OCOF₃ (**4c**, 86% yield)), respectively. Complexes **2–4** were characterized by spectroscopic data, CV and elemental analyses.

The ¹H NMR spectra of the adducts **3a** and **3b** in CDCl₃ solution proved existence of single species only. This result suggested that the adduct **3b** has no isomers (**3b'**) based on the bridged CHSiMe₃ position but this result is slightly unusual for us. We have often found two geometrical isomers in the CHSiMe₃-bridged adducts of [CpCo(CHSiMe₃)(S₂NCPH)] (S₂NC = dithiazole) [31] and [Cp*Ir(CHSiMe₃)(S₂C₂(COOMe)₂)] [32]. In the former adduct, two isomers have been isolated [31]. The major isomer involves the CHSiMe₃-bridged adduct whose SiMe₃ group locates at the *exo*-position with respect to the cobaltadithiazole plane, and in the minor product, the SiMe₃ group locates at the *endo*-position. In contrast, the major isomer of [Cp*Ir(CHSiMe₃)(S₂C₂(COOMe)₂)] is an *endo*-form. Probably, one reason for single isomer of **3b** is due to a steric hindrance between the SiMe₃ group and the U-shaped oxddt ligand. Actually, the X-ray structure analysis of **3b** proved an *exo*-form with the U-shaped oxddt (see Fig. 5b).

The ¹H NMR spectrum of **4a** showed existence of two different species in CDCl₃ solution even if the isolated product was analytically pure. One species is supposed to be the major *anti*-isomer (**4a-1**) which can prior to crystallize (Fig. 6a), and most probably the other species is the corresponding *syn*-isomer (**4a-2**, see Scheme 2). The ratio of these isomers is 7:1 due to the ¹H NMR analysis. According to a previous paper [33], the *anti*-form of [CpCo(X)(dithiolene)(*S*-R)] complex determined by X-ray structure analysis, shows dual sets of ¹H NMR spectra, but in the complex of *syn*-form, the ¹H NMR spectrum is a single set. Complex **4c** was supposed to be the *syn*-form because the NMR showed a single set. In fact, the X-ray structure analyses of **4a** and **4c** revealed those *anti*- and *syn*-forms (see Fig. 6a and b), respectively.



Scheme 2. Preparations of the alkylidene-bridged adducts **3a** and **3b** from **2** and the S-methylated adducts from **3a**.

An alkylation of the M–SR bond has been reported [34]. However, the reactions of [CpCo(dithiolene)] complex with MeX (X = I, $OCOCF_3$) did not occur. One reason may be low nucleophilicity of sulfur atoms on the dithiolene ligand, because the π -electrons of dithiolene ligand are well delocalized, but there is not π -electron delocalization enough in the [M(thiolate)₂] complex. On the other hand, the reduced [Ni(dithiolene)₂]²⁻ complex is easy to alkylate by RX on the sulfur atoms [35], although the oxidized complexes are not alkylated. This fact suggests that [CpCo(dithiolene)] complex may be not alkylated unless the complex is reduced. Tatsumi et al. have reported some coordinatively unsaturated [Cp*M(SDmp)] (M = Ru, Rh, Ir), [(η^6 -arene)Ru(SDmp)] and [(DmpS)Ru(PR₃)] complexes (SDmp = 2,6-dimesitylphenylthiolate), and their reactivities with CNtBu, CO, 2,2'-bipyridine, 1,10-phenanthroline, diazoalkane (N_2CHR), PhI=NTs, phenylacetylene and molecular hydrogen [36–38]. They found some interesting addition reactions on the M–S bond [36,37] and molecular hydrogen splitting [38].

The UV–Vis spectrum of **2** is shown in Fig. 1 together with that of the corresponding nickel complex [CpNi(oxddt)] [24] for a sake of comparison. Complex **2** exhibited electronic absorption at 602 nm as a lowest energy band, which was higher energy than that of [CpNi(oxddt)] ($\lambda_{max} = 825$ nm). [24] Typically, the λ_{max} of [CpNi(dithiolene)] complexes always show a larger red shift than the corresponding [CpCo(dithiolene)] complexes, and those λ_{max} differences are amounting to 120–290 nm [39]. In contrast, the [CpRh(dithiolene)] (c.a. $\lambda_{max} = 480$ –600 nm) and [CpIr(dithiolene)] (c.a. $\lambda_{max} = 410$ –480 nm) complexes show a larger blue shift than those of [CpCo(dithiolene)] complexes [40]. Namely, in the group 9 metals, electronic absorption wavelength results in the following order: CpCo > CpRh > CpIr. In the group 10 metals, [(η^4 -C₄R₄)-Pd(dithiolene)] ($\lambda_{max} = 560$ nm) [41] and [(η^4 -C₄R₄)-Pt(dithiolene)] (c.a. $\lambda_{max} = 430$ –535 nm) [42] complexes are also comparable (η^4 -C₄R₄ = cyclobutadiene ligand). The [(η^6 -C₆R₆)-Ru(dithiolene)] (c.a. $\lambda_{max} = 428$ –572 nm) [43,44] and [(η^6 -C₆R₆)-Ru(thiolate)₂] (c.a. $\lambda_{max} = 660$ –715 nm) [43] complexes have been reported (η^6 -C₆R₆ = arene ligand). The latter complexes show relatively lower energy electronic absorption. This lowest energy absorption (HOMO–LOMO) is almost assigned to LMCT [43]. The ligand-based HOMO level can be controlled by a modification of substituents on the dithiolene ligand [39].

The CV of **2** (Fig. 2a) showed a quasi-reversible reduction wave ($E_{1/2}(\text{red}) = -1.24$ V) and an irreversible oxidation wave ($E_p(\text{ox}) = +0.58$ V). This result suggests that the oxidized species of **2** is not stable enough on the CV time scale. After the oxidation of **2**, a

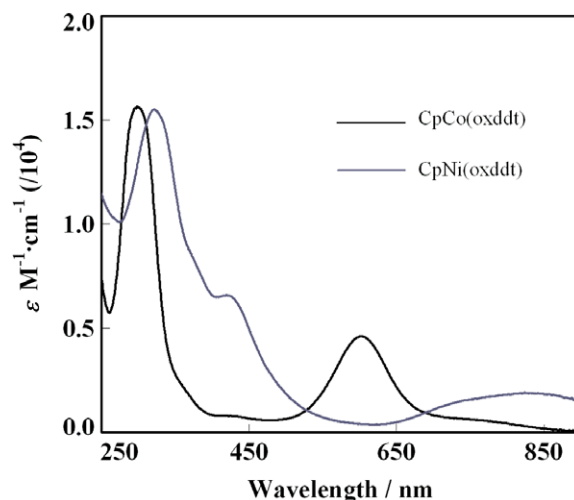


Fig. 1. UV–vis spectra of [CpCo(oxddt)] (**2**, black line) and [CpNi(oxddt)] (gray line) in dichloromethane solution.

rereduction wave around 0 V (Fig. 2a) indicates a formation of another species. This EC reaction can be explained by a monomer–dimer structural change of [CpCo(dithiolene)], as similar examples have been reported [39,45]. Indeed, the oxidation of **2** forms the dimeric cation [**2**]₂⁺ and it can be rereduced at a lower potential (around 0 V). On the other hand, the oxidation wave of [CpNi(oxddt)] have been reversible in the CV [24], because there is a difference of total electron number at the central metals between 16-electron Co^{III} complex and 17-electron Ni^{III} complex. As a similar example, the 16-electron [(η^6 -C₆R₆)-Ru(dithiolene)] complexes have shown a monomer–dimer structural change upon the monomer oxidized [44]. Usually, the rereduction of the dimer forms the original monomer again. Totally, the monomer–dimer structural change is reversible through the ECEC mechanism.

The alkylidene-bridged adducts **3a** and **3b** were reduced and oxidized in the CVs (Fig. 2a and b) at more negative potentials compared with those of the alkylidene-free complex **2** (Table 1). This result means that addition of alkylidene groups increases an electron density of the complex. In other word, the adduct became an 18-electron complex but the alkylidene-free complex **2** was 16-electron species. Although the reduction wave of **3a** was almost quasi-reversible, that of **3b** was completely irreversible (Fig. 2b and 2c). In the CV of **3b**, an existence of reoxidation wave at

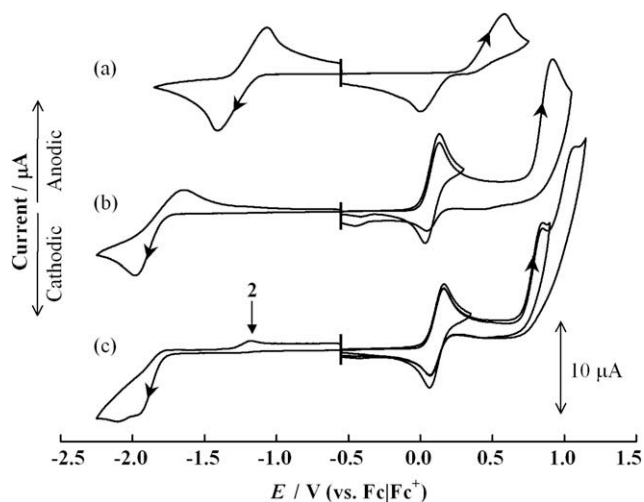


Fig. 2. Cyclic voltammograms of (a) complex **2**, (b) the CH₂ adduct **3a** and (c) CHSiMe₃ adduct **3b** in dichloromethane solution containing 0.1 M tetra-*n*-butylammonium perchlorate (Pt disk electrode, $v = 100 \text{ mV s}^{-1}$).

Table 1
Redox potentials (E vs. Fc/Fc⁺) of **2**, [CpNi(oxddt)], **3a** and **3b**.

	$E_{1/2}(\text{red})/\text{V}$	$E_p(\text{red})/\text{V}$	$E_{1/2}(\text{ox})/\text{V}$	$E_p(\text{ox})/\text{V}$
[CpCo(oxddt)] (2)	-1.24 (qr)	-1.41	-(ir)	+0.58
[CpNi(oxddt)]	-1.07 (r)	-1.14	+0.16 (r)	+0.24
3a	-1.83 (qr)	-1.98	+0.08 (r)	+0.13
3b	-(ir)	-1.98	+0.11 (r)	+0.16

(r) Reversible, (qr) quasi-reversible, (ir) irreversible.

-1.2 V suggests the formation of **2**, followed by the CHSiMe₃ elimination (Fig. 2c). A difference of reduction behavior between **3a** and **3b** can be explained by lifetime of reduced species. In conclusion, the bulky CHSiMe₃ group is easier to eliminate than the case of CH₂ group.

2.2. X-ray diffraction studies of [CpCo(oxddt)], [CpCo(CHR)(oxddt)] and [CpCo(X)(oxddt)](S-Me)

The molecular and crystal structures of the oxddt precursor **1** and complex **2** were determined by X-ray diffraction studies. The selected bond lengths, bond angles and dihedral angles are shown

Table 2
Selected bond lengths (Å), bond angles (°) and dihedral angles (°) in metalladithiolene ring.

	1-Z	2-Z	3a-U	3b-U	4a-U	4c-U
Bond length						
Co1-S1	-	2.118(3)	2.1858(7)	2.1674(18)	2.223(10)	2.221(3)
Co1-S2	-	2.111(3)	2.2042(7)	2.2160(16)	2.231(5)	2.222(3)
S1-C1	1.737(11)	1.751(10)	1.767(2)	1.767(5)	1.792(18)	1.774(9)
S2-C2	1.775(12)	1.711(12)	1.720(2)	1.711(6)	1.729(16)	1.742(9)
C1-C2	1.327(16)	1.361(13)	1.352(3)	1.357(8)	1.354(19)	1.324(12)
Bond angles						
S1-Co1-S2	-	91.14(12)	91.19(2)	90.49(6)	89.24(16)	89.81(10)
Co1-S1-C1	-	104.5(3)	103.77(8)	105.1(2)	103.94(13)	104.7(3)
Co1-S2-C2	-	106.6(3)	102.93(8)	102.9(2)	104.09(19)	102.7(3)
S1-C1-C2	116.6(8)	119.2(8)	118.30(15)	117.1(4)	118.47(10)	117.7(7)
S2-C2-C1	117.9(8)	118.0(8)	123.10(15)	123.6(4)	122.06(11)	124.4(7)
Dihedral angles^a						
θ_1	-	87.642	74.585	69.796	55.70	49.54
θ_2	-	8.026	7.896	9.895	12.53	7.13
θ_3	114.688	116.683	115.327	116.749	112.17	118.52
θ_4	110.531	108.892	114.484	120.010	121.78	121.49
θ_5	4.207	7.791	50.232	57.468	58.28	60.02
Co1S1S2/Co1S1C11	-	-	93.143	84.624	-	-

^a Dihedral angles (θ_1 - θ_5) are defined in Fig. 3.

in Table 2. Fig. 3 displays the molecular structure of **2** and some definitions of dihedral angles in the molecule (noted in the Fig. 3 caption). As shown in Table 2, the all bond lengths and angles in cobaltadithiolene ring in **2** are similar to those of typical [CpCo(dithiolene)] complexes such as [CpCo(dmit)] (dmit = 1,3-dithiol-2-thione-4,5-dithiolate) [46], [CpCo(mnt)] (mnt = maleonitrile-1,2-dithiolate), [CpCo(S₂C₂Ph₂)] and [CpCo(S₂C₂(COOMe)₂)] [30].

In **2**, the CoS₂ plane is located at a perpendicular position with respect to the Cp plane, because the θ_1 (Cp/CoS₂) is almost 90°. The cobaltadithiolene plane is slightly folded at the S...S hinge, because the dithiolene folding angle θ_2 (CoS₂/S₂C₂) is 8.026°. There is a Z-shaped structure (**2-Z**) between cobaltadithiolene plane and *o*-xylylene group in **2** (Fig. 3). In fact, the θ_5 (S₂C₂/benzene) is 7.791°. This result indicates that those planes are almost parallel located each other.

The 1,3-dithiol-2-one derivative **1** has also a Z-shaped structure (**1-Z**). The θ_5 angle is 4.207°. In contrast, the corresponding 1,3-dithiol-2-thione compound (S=C(oxddt)) has been previously observed as a U-shaped one (Chart 2) [26]. **1-Z** crystallized in the monoclinic system with the space group $P2_1/n$. Fig. 4a exhibits one-dimensional molecular π - π stacking along the *a* axis whose plane-to-plane distance is c.a. 3.5 Å. On the other hand, **2-Z** has a dimeric π - π stacking along the *b* axis by face-to-face between dithioethylenedithiolate (S₂C₂S₂) moieties at distances of c.a. 3.7 Å (Fig. 4b and 4c). **2-Z** crystallized in the triclinic crystal system with the space group $P\bar{1}$. Interestingly, **2-Z** is crystallographically isostructural to the corresponding nickel dithiolene complex, [CpNi(oxddt)] (**Z**-shaped) [24]. Temperature dependence of magnetic susceptibility measurement has evidenced a dimeric magnetic interaction due to the π - π stacking between dithiolene rings. In addition, the [CpNi(dithiolene)] complexes having large seven-membered rings, [CpNi(S₂C₂S₂(CH₂)₂X)] (X = CH₂, CF₂, C=CH₂, C=O, S), have been reported as well. Those terminal rings are folded as Z-shaped structures [19].

The molecular structures of **3a** and **3b** are shown in Fig. 5. They become three-legged piano-stool geometries by addition of the alkylidene group. The alkylidene groups in **3a** and **3b** are bridging between the cobalt and sulfur bonds to form three-membered cobaltathiirane ring (Co1-S1-C11) which is perpendicularly placed with respect to cobaltadithiolene plane. The dihedral angles of cobaltathiirane/CoS₂ are 93.143° (**3a**) and 84.624° (**3b**), respectively. The Co-S bonds in **3a** and **3b** (2.16–2.22 Å) become longer than those of the Co-S bonds in **2-Z** (2.11 Å). This result indicates that

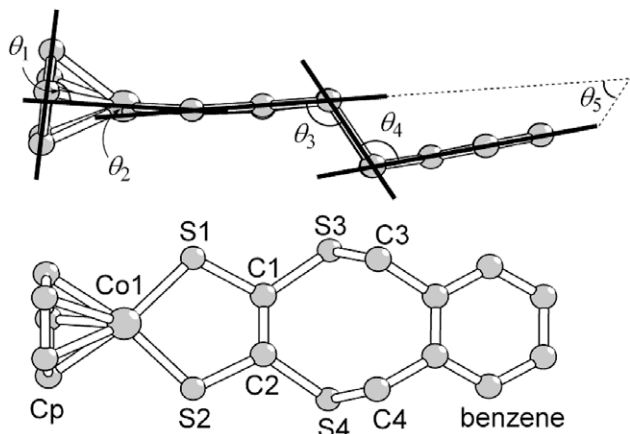


Fig. 3. Molecular structure of **2-Z** and definition of dihedral angles for all oxddt complexes: $\theta_1 = \text{Cp}/\text{Co1S1S2}$, θ_2 (dithiolene folding angle) = $\text{Co1S1S2}/\text{S1S2C1C2S3S4}$, $\theta_3 = \text{S1S2C1C2}/\text{S3S4C3C4}$, $\theta_4 = \text{S3S4C3C4}/\text{benzene}$, $\theta_5 = \text{S1S2C1C2}/\text{benzene}$.

π -electron donation from sulfur to metal more weakens than in case of **2-Z** because these alkylidene adducts become electron-rich (18-electron), although **2-Z** is coordinatively unsaturated. The bond

lengths of Co1–S1 (alkylidene-bridged moiety) are 2.1858(7) Å for **3a** and 2.1674(18) Å for **4a**. These bond lengths are shorter than those of the alkylidene-free Co1–S2 (2.2042(7) Å for **3a** and 2.2160(16) Å for **3b**). This fact suggests that the three-membered cobaltathirane ring (Co1–S1–C11) is distorted. We have reported some alkylidene- [30] and imido-bridged [CpCo(dithiolene)] [47] complexes obtained from the reactions of [CpCo(dithiolene)] with diazoalkanes or organic azides. The bond lengths and angles at cobaltadithiolene and cobaltathirane moieties in **3a** and **3b** are almost similar to those of the typical alkylidene-bridged adducts as previously reported [30].

Tatsumi et al. have also determined the molecular structures of some coordinatively unsaturated [Cp*M(SDmp)] (M = Ru, Rh, Ir), [(η^6 -arene)Ru(SDmp)], and [(DmpS)Ru(PR₃)] complexes. The Ru–S bond lengths are 2.211–2.294 Å and M–S bond lengths are 2.209–2.269 Å (M = Rh, Ir) [36–38], while the central metals are coordinatively unsaturated. When these complexes (M = Ru) become coordinatively saturated, the Ru–S bond are lengthened (2.305–2.431 Å) [36,37], because there is weak π -electron donation from sulfur to the coordinatively saturated metal center. Furthermore, the Rh–S or Ir–S bond lengths of [Cp*M(SDmp)] [38] are shorter than those of typical coordinatively saturated complexes (2.32–2.38 Å) [48].

Interestingly, both complexes **3a** and **3b** became *U-shaped structures (3a-U and 3b-U)* whose *o*-xylylene positions are quite

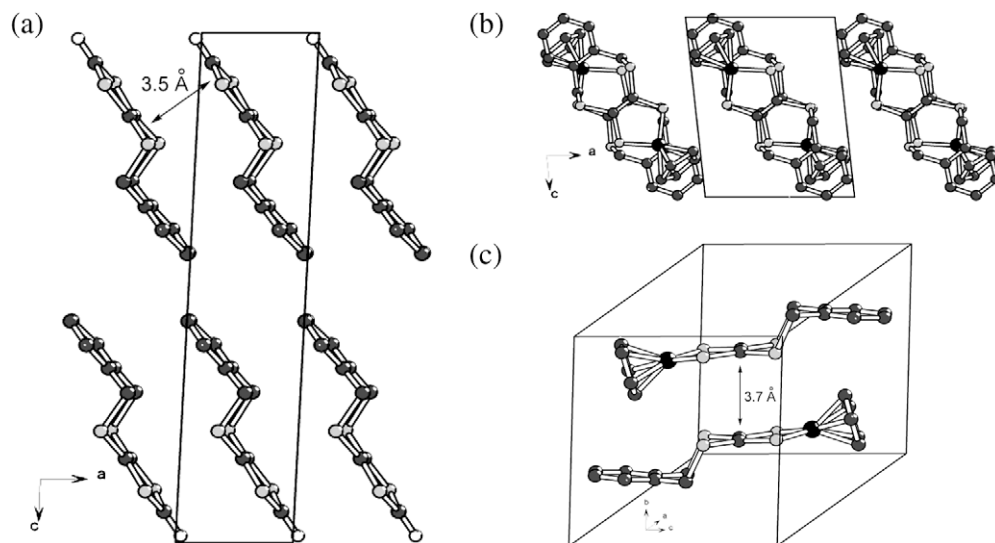


Fig. 4. (a) Projection view along the *b* axis of **1-Z** and (b) projection view along the *b* axis of **2-Z**, and (c) packing diagram of **2-Z** showing dithiolene...dithiolene interaction.

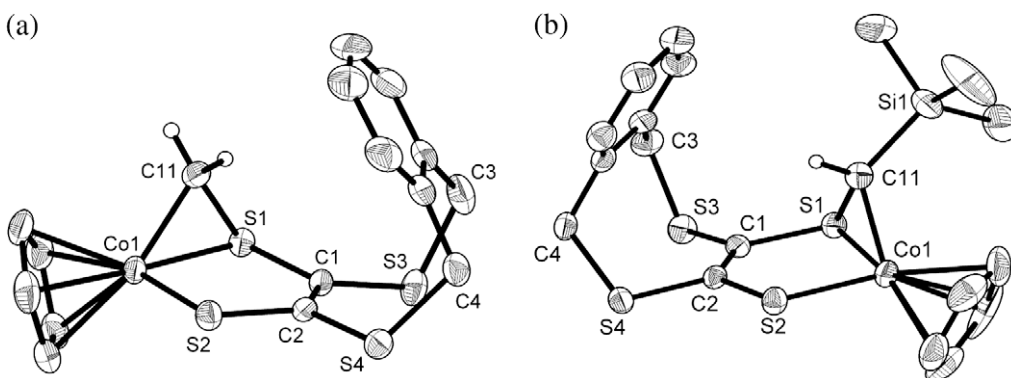


Fig. 5. (a) Molecular structures of CH₂-bridged adduct **3a-U** and of (b) CHSiMe₃-bridged adduct **3b-U**. The thermal ellipsoids are drawn at 30% probability level. Only hydrogen atom(s) at C11 (bridged carbon) are shown.

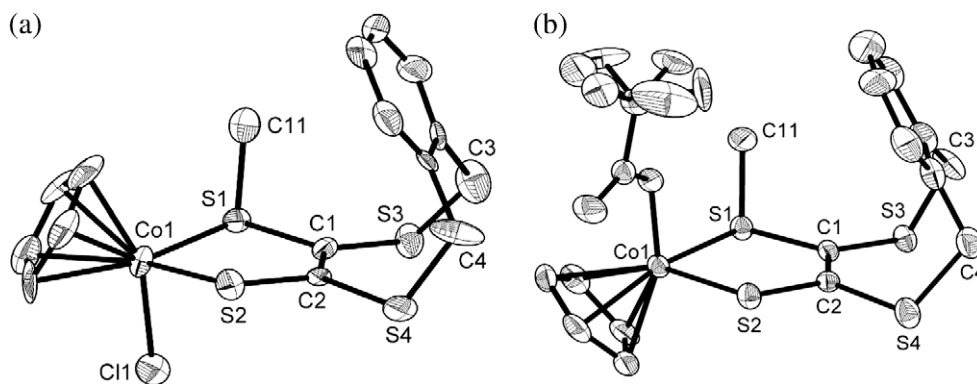


Fig. 6. (a) Molecular structures of the *S*-methylated adduct **4a-U** (*anti*-form) and of (b) the *S*-methylated adduct **4c-U** (*syn*-form). The thermal ellipsoids are drawn at 30% probability level. The fluorine atoms at the CF₃ group in **4c-U** are disordered.

Table 3
Crystallographic data.

Compound	1-Z	2-Z	3a-U	3b-U	4a-U	4c-U
Formula	C ₁₁ H ₈ OS ₄	C ₁₅ H ₁₃ CoS ₄	C ₁₆ H ₁₅ CoS ₄	C ₁₉ H ₂₃ CoS ₄ Si	C ₁₆ H ₁₆ CoS ₄ Cl	C ₁₈ H ₁₆ CoF ₃ O ₂ S ₄
Formula weight (g mol ⁻¹)	284.42	380.44	394.47	466.65	430.93	508.48
Crystal color	Colorless	Dark blue	Black	Black	Black	Brown
Crystal shape	Needle	Platelet	Block	Platelet	Cubic	Platelet
Crystal size (mm)	0.30 × 0.05 × 0.05	0.25 × 0.25 × 0.03	0.28 × 0.15 × 0.13	0.13 × 0.13 × 0.03	0.23 × 0.17 × 0.17	0.30 × 0.05 × 0.025
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	P2 ₁ /n (No. 14)	P $\bar{1}$ (No. 2)	C2/c (No. 15)	P2 ₁ /c (No. 14)	P2 ₁ /c (No. 14)	P $\bar{1}$ (No. 2)
T (K)	298	298	298	298	298	298
a (Å)	4.3920(18)	8.78390(10)	26.4997(18)	8.295(3)	14.712(3)	8.428(7)
b (Å)	12.878(5)	9.3195(2)	10.9004(5)	20.591(8)	8.080(3)	11.168(10)
c (Å)	20.956(9)	10.3523(5)	12.8466(9)	12.408(5)	15.371(2)	11.800(10)
α (°)	–	87.996(12)	–	–	–	97.625(8)
β (°)	92.7241(18)	84.010(11)	115.9702(8)	100.4775(17)	107.95(1)	100.595(9)
γ (°)	–	62.260(8)	–	–	–	107.583(10)
V (Å ³)	1183.9(8)	745.87(4)	3336.1(4)	2083.8(15)	1738.3(7)	1019.6(15)
Z	4	2	8	4	4	2
D _{calc} (g cm ⁻³)	1.596	1.694	1.571	1.487	1.646	1.656
μ (mm ⁻¹)	0.774	1.695	1.518	1.283	1.613	1.290
Total reflections	9050	5802	12 800	16 200	3741	7999
Unique reflections (R _{int})	2688(0.056)	3257(0.065)	3765(0.027)	4673(0.076)	3329(0.029)	4497(0.0504)
Unique reflections (I > 2σ(I))	1928	2847	2824	2242	960	2929
R ₁ (I > 2σ(I))	0.0627	0.0581	0.0287	0.0493	0.055	0.0623
wR ₂ (I > 2σ(I))	0.1283	0.1483	0.0841	0.1206	0.092	0.1485
Goodness-of-fit (GOF)	1.151	1.271	1.045	1.039	1.320	1.133

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

different from those of **1-Z** and **2-Z** (Figs. 3 and 4 vs. 5). The dihedral angles of θ_5 are 50.232° for **3a-U** and 57.468° for **3b-U**. In spite of large structural change from Z to U, the dihedral angles of θ_3 are consistent (115–116°) in the all complexes. As shown in Scheme 2 and Fig. 5b, the SiMe₃ group in **3b-U** is located at an *exo*-position because of a steric effect by the U-shaped geometry.

The molecular structures of **4a** and **4c** are shown in Fig. 4. There are Co–X bonds (X = Cl, OCOF₃) and one of two sulfur atoms in the dithiolene ring is methylated. Formally, the bridged CH₂ group is protonated by protic acid and the counter X anion coordinates to the cobalt atom. Eventually, an addition of HX acid cleaves the Co1–C11 bond in the three-membered cobaltathiirane. The Co1–S1 bond of **4a** (2.223(10) Å) and **4c** (2.221(3) Å) became longer than that of **3a** (2.1858(7) Å) by the Co1–C11 bond cleavage because the distortions of three-membered rings were alleviated. In **4a**, the Cl ligand and Me group attached to sulfur atom locate at the opposite side of cobaltadithiolene plane (*anti*-form). In contrast, both X and Me groups in **4c** are placed at the same side of the cobaltadithiolene plane (*syn*-form). A previous paper has reported some *S*-alkylated [CpCo(X)(dithiolene)(S–CH₂R)] complexes (X = Cl, Br, I, OCOF₃; R = H, SiMe₃, COEt) and those X-ray structure

analyses have indicated both *anti*- and *syn*-forms [33]. Both *S*-methylated adducts **4a** and **4c** maintains the U-shaped structures (**4a-U** and **4c-U**) while compared with the corresponding alkylidene adduct **3a-U**. This result is somewhat unexpected because the *anti*-form in **4c-U** looks sterically crowded.

3. Conclusion

Early works have described that the molecular structures of organic oxddd derivatives such as S=C(oxddd) (U-shaped) [26] and S=C(oxddd-Br₂) (Z-shaped) [25]. This work reported the molecular structures of CpCo complexes and O=C analogues of the oxddd. Interestingly, a structural conversion from Z to U (or U to Z) could be possible by molecular modifications such as an oxygenation of sulfur atom (U to Z), complexation (Z retained), alkylidene group addition (Z to U) and so on. We can really conclude that these U–Z structural changes can be originated by a structural flexibility of oxddd ligand, depending on the large eight-membered ring. A remarkable difference between U and Z was observed in these crystal packing structures. The relatively linear Z-shaped structure

is easy to make an intermolecular interaction between the oxddt moieties (Fig. 4), but the U-shaped structure could be more difficult to make it, because the U-shaped *o*-xylylene group hides one side of the dithiolene plane. Therefore, the U–Z structural change may be a kind of molecular switch for intermolecular interactions such as the dithiolene π – π stacking, and magnetic interaction, while complex is paramagnetic, due to a high flexibility of the oxddt ligand. Needless to say, square-planar bisdithiolene complexes of the oxddt (M = Ni, Pd, Pt, Cu, Au) and TTF analogues of the oxddt will be interesting molecules for solid state studies, according to some reasons noted above.

4. Experimental

4.1. Materials and instrumentation

All reactions were carried out under argon atmosphere by means of standard Schlenk techniques. All solvents for reactions were purified by Na–benzophenone for diethyl ether or CaH₂ for MeOH and dichloromethane before use. *o*-Xylenediyldithioethylene-1,3-dithiol-2-thione [29], *o*-xylenediyldithioethylene-1,3-dithiol-2-one (**1**) [29], and [CpCo(CO)₂] [49] were prepared by literature method. Diazomethane was carefully prepared by a literature method [50], and instantly used it. Sodium methoxide in MeOH solution was prepared by dry MeOH and fresh sodium metal. Trimethylsilyldiazomethane in *n*-hexane solution was produced by Sigma–Aldrich Fine Chemicals. Hydrochloric acid, trifluoroacetic acid, MgSO₄ and silica gel (Wakogel C-300) were obtained from Wako Pure Chemical Industries, Ltd. Mass spectrum was recorded on a JEOL JMS-D300. NMR spectra were measured with a JEOL LA500 spectrometer. UV–Vis spectra were recorded on a Hitachi model UV-2500PC. Elemental analyses were determined by using a Shimadzu PE2400-II instrument.

4.2. Preparation of [CpCo(oxddt)] (**2**)

Sodium methoxide in MeOH (2.1 mL, *c* = 1.0 M, 2.1 mmol) was added to a solution of **1** (0.284 g, 1.0 mmol) in MeOH (50 mL) and stirred for 15 min. An initial colorless solution was changed to yellow. Then [CpCo(CO)₂] (0.406 g, 1.0 mmol) was added and the reaction mixture was stirred at room temperature for 6 h. Finally a dark blue solution was obtained. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel (eluent = dichloromethane). Recrystallization from dichloromethane/*n*-hexane afforded a dark blue crystalline solid in 60% yield (228 mg, 0.60 mmol).

Complex 2. Mass (EI⁺, 70 eV) *m/z* (rel. intensity) 380 (M⁺, 100), 188 (CpCoS₂⁺, 42), 168 (CpCoSC⁺, 81), 124 (CpCo⁺, 87). ¹H NMR (CDCl₃, vs. TMS, 500 MHz) δ 7.00 (s, 4H, C₆H₄), 5.23 (s, 5H, Cp), 4.26 (s, 4H, CH₂). UV–Vis (CH₂Cl₂) λ_{\max}/nm ($\epsilon/M^{-1} cm^{-1}$) 602 (4600), 296 (15 700). Elemental Anal. Calc. for C₁₅H₁₃CoS₄: C, 47.35; H, 3.44; S, 33.71. Found: C, 47.57; H, 3.44; S, 33.54%.

4.3. Preparation of the alkylidene adduct [CpCo(CH₂)(oxddt)] (**3a**)

Excess diazomethane gas was blown into the dichloromethane/diethyl ether solution of **2** (76 mg, 0.2 mmol) at 0 °C. Solution was changed from dark blue to brown. After the solvent was removed under reduced pressure, the brown residue was separated by column chromatography (silica–gel, eluent = dichloromethane). The brown residue was purified by recrystallization (*n*-hexane/dichloromethane). Adduct **3a** was obtained as a brown solid in 81% (64 mg, 0.16 mmol) yield.

Complex 3a. Mass (EI⁺, 70 eV) *m/z* (rel. intensity) 394 (M⁺, 42), 380 (M⁺–CH₂, 35), 188 (CpCoS₂⁺, 29), 168 (CpCoSC⁺, 100), 124

(CpCo⁺, 82). ¹H NMR (CDCl₃, vs. TMS, 500 MHz) δ 7.06–7.23 (m, 4H, C₆H₄), 5.09 (d, *J* = 12 Hz, 1H, CH₂), 4.90 (s, 5H, Cp), 4.24 (d, *J* = 12 Hz, 1H, CH₂), 4.13 (d, *J* = 12 Hz, 1H, CH₂), 3.55 (d, *J* = 12 Hz, 1H, CH₂), 2.89 (d, *J* = 12 Hz, 1H, CH₂), –0.01 (d, *J* = 12 Hz, 1H, CH₂). ¹³C NMR (CDCl₃, vs. TMS, 125 MHz) δ 173.25 (dithiolene carbon), 135.96, 135.29, 130.79, 130.06, 128.44, 127.54 (C₆H₄), 103.55 (dithiolene carbon), 83.09 (Cp), 39.18, 37.13, 24.27 (CH₂). Elemental Anal. Calc. for C₁₆H₁₅CoS₄: C, 48.71; H, 3.83; S, 32.51. Found: C, 48.55; H, 3.80; S, 32.41%.

4.4. Preparation of alkylidene adduct [CpCo(CHSiMe₃)(oxddt)] (**3b**)

The 1.2 mmol dm^{–3} *n*-hexane solution of trimethylsilyldiazomethane (0.75 mL, 0.9 mmol) was added into a dichloromethane solution (50 mL) of **2** (120 mg, 0.3 mmol). The reaction mixture was reacted under refluxing for 26 h. Finally a brown solution was formed. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (silica–gel, eluent = dichloromethane). The brown residue was purified by recrystallization (*n*-hexane/dichloromethane). Adduct **3b** was obtained as an orange solid in 65% (91 mg, 0.195 mmol) yield.

Complex 3b. Mass (EI⁺, 70 eV) *m/z* (rel. intensity) 466 (M⁺, 28), 380 (M⁺–CHSiMe₃, 26), 362 (M⁺–C₆H₄(CH₂)₂, 100), 289 (CpCoS₂C₂SCH⁺, 37), 188 (CpCoS₂⁺, 20), 168 (CpCoSC⁺, 60), 124 (CpCo⁺, 42), 104 (C₆H₄(CH₂)₂⁺, 25). ¹H NMR (CDCl₃, vs. TMS, 500 MHz) δ 7.00–7.25 (m, 4H, C₆H₄), 5.15 (d, *J* = 12 Hz, 1H, CH₂), 4.90 (s, 5H, Cp), 4.16 (d, *J* = 12 Hz, 1H, CH₂), 4.10 (d, *J* = 12 Hz, 1H, CH₂), 3.52 (d, *J* = 12 Hz, 1H, CH₂), 0.36 (s, 1H, CH), 0.11 (s, 9H, SiMe₃). Elemental Anal. Calc. for C₁₉H₂₃CoSiS₄: C, 48.90; H, 4.97. Found: C, 48.56; H, 5.05%.

4.5. Preparation of the *S*-methylated adduct [CpCo(Cl)(oxddt)(*S*-Me)] (**4a**)

Hydrochloric acid (0.1 mL, 16 mmol) was added into a dichloromethane solution (100 mL) of **3a** (160 mg, 0.44 mmol). The reaction mixture was stirred at room temperature for 30 min. The reaction mixture was washed with water in three times, and the organic layer was dried with MgSO₄. After the solvent of filtrate was removed under reduced pressure, the black residue was purified by recrystallization (*n*-hexane/dichloromethane). Complex **3a** was obtained as a black solid in 75% yield.

Complex 4a. Mass (EI⁺, 70 eV) *m/z* (rel. intensity) 395 (M⁺–Cl, 4), 380 (M⁺–Cl–Me, 55), 188 (CpCoS₂⁺, 23), 168 (CpCoSC⁺, 43), 124 (CpCo⁺, 82), 104 (C₆H₄(CH₂)₂⁺, 100). Mass (FAB⁺, NBA matrix) 430 (M⁺). ¹H NMR (CDCl₃, vs. TMS, 500 MHz). **Major isomer** (*anti*-form): δ 7.06–7.31 (m, 4H, C₆H₄), 5.18 (s, 5H, Cp), 4.44 (d, *J* = 11 Hz, 1H, CH₂), 4.34 (d, *J* = 11 Hz, 1H, CH₂), 4.21 (d, *J* = 12 Hz, 1H, CH₂), 4.16 (d, *J* = 12 Hz, 1H, CH₂), 2.03 (s, 3H, Me). **Minor isomer** (*syn*-form): δ 5.30 (s, 5H, Cp), 4.50 (d, *J* = 12 Hz, 1H, CH₂), 4.01 (d, *J* = 12 Hz, 1H, CH₂), 2.33 (s, 3H, Me). Other signals were not observed because of weak signals. ¹³C NMR (CDCl₃, vs. TMS, 125 MHz) δ 173.25 (dithiolene carbon), 135.96, 135.29, 130.79, 130.06, 128.44, 127.54 (C₆H₄), 103.55 (dithiolene carbon), 83.09 (Cp), 39.18, 37.13, 24.27 (CH₂). Elemental Anal. Calc. for C₁₆H₁₆ClCoS₄: C, 44.59; H, 3.74. Found: C, 44.74; H, 3.83%.

4.6. Preparation of the *S*-methylated adduct [CpCo(OCOFC₃)(oxddt)(*S*-Me)] (**4c**)

Trifluoroacetic acid (46 μ L, 0.6 mmol) was added into a dichloromethane solution (50 mL) of **3a** (170 mg, 0.44 mmol). The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was washed with water in three times, and the organic layer was dried with MgSO₄. After the solvent of filtrate

was removed under reduced pressure, the black residue was purified by recrystallization (*n*-hexane/dichloromethane). Complex **3c** was obtained as a black solid in 86% yield.

Complex 4c. Mass (EI^+ , 70 eV) m/z (rel. intensity) 508 (M^+ , 2), 395 ($M^+ - OCOF_3$, 39), 380 ($M^+ - OCOF_3 - Me$, 81), 188 ($CpCoS_2^+$, 51), 168 ($CpCoSC^+$, 75), 124 ($CpCo^+$, 76), 104 ($C_6H_4(CH_2)_2^+$, 100). Mass (FAB^+ , NBA matrix) 430 (M^+). 1H NMR ($CDCl_3$, vs. TMS, 500 MHz) δ 7.03–7.31 (m, 4H, C_6H_4), 5.34 (s, 5H, Cp), 4.54 (d, $J = 12$ Hz, 1H, CH_2), 4.31 (d, $J = 12$ Hz, 1H, CH_2), 4.27 (d, $J = 12$ Hz, 1H, CH_2), 4.13 (d, $J = 12$ Hz, 1H, CH_2), 1.74 (s, 3H, Me). Elemental Anal. Calc. for $C_{18}H_{16}CoF_3O_2S_4$: C, 42.51; H, 3.17. Found: C, 42.01; H, 3.26%.

4.7. 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.

4.8. X-ray diffraction study

Single crystals of **1-Z**, **2-Z**, **3a-U**, **3b-U**, **4a-U**, and **4c-U** were obtained from recrystallization by vapor diffusion of hexane into those dichloromethane solutions. Crystals were mounted on the top of a thin glass fiber. Measurement for **4a-U** was made on Rigaku AFC5S four-circle diffractometer, and for the others was made on Rigaku Mercury CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Each structure was solved by direct methods and expanded Fourier techniques [51]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations, and these were not refined. Absorption corrections were applied. For **4a-U**, idealized positions were used for the TEXSAN crystallographic software package of Molecular Structure Corp. [52]. All calculations for **1-Z**, **2-Z**, **3a-U**, and **3b-U** were performed using the crystal structure software package [53], and for **4c-U** was done using WINGX software package [54]. Crystallographic data are summarized in Table 3.

5. Supplementary material

CCDC 733633, 733634, 733635, 733636 and 733637 contain the supplementary crystallographic data for (**1-Z**), (**2-Z**), (**3a-U**), (**3b-U**), (**4c-U**) and (**4a-U**), respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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