



## Sulfur-rich CpCo(dithiolene) complexes: Isostructural or non-isostructural couples of CpCo(III) with CpNi(III) dithiolene complexes

Mitsushiro Nomura<sup>a,\*</sup>, Shigemi Kondo<sup>a</sup>, Souichi Yamashita<sup>a</sup>, Eriko Suzuki<sup>a</sup>, Yoshiko Toyota<sup>a</sup>, Glenn V. Alea<sup>b</sup>, Gerardo C. Janairo<sup>b</sup>, Chikako Fujita-Takayama<sup>a</sup>, Toru Sugiyama<sup>a</sup>, Masatsugu Kajitani<sup>a,\*\*</sup>

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

<sup>b</sup> Department of Chemistry, De La Salle University, 2401 Taft Avenue, 1104 Manila, Philippines

### ARTICLE INFO

#### Article history:

Received 12 April 2010

Received in revised form

24 May 2010

Accepted 28 May 2010

Available online 13 July 2010

#### Keywords:

Dithiolene

Isostructure

Crystal structure

Electronic absorption

Electrochemistry

### ABSTRACT

Eight new sulfur-rich [CpCo(dithiolene)] complexes were synthesized from [Zn(dmit)<sub>2</sub>]<sup>2-</sup> as a starting material. The structures, electrochemical behavior and electronic absorption spectra of the sulfur-rich [CpCo(S<sub>2</sub>C<sub>2</sub>S<sub>2</sub>Y)] complexes could be compared with the early data of analogous Ni complexes. [CpCo(pdtt)] (Y = -(CH<sub>2</sub>)<sub>3</sub>-), [CpCo(dpdt)] (Y = -CH<sub>2</sub>C(CH<sub>2</sub>)CH<sub>2</sub>-), [CpCo(bddt)] (Y = -(CH<sub>2</sub>)<sub>4</sub>-), [CpCo(dttd)] (Y = -CH<sub>2</sub>SCH<sub>2</sub>-) and [CpCo(poddt)] (Y = -CH<sub>2</sub>C(O)CH<sub>2</sub>-) crystallized in all isostructural with the corresponding paramagnetic [CpNi(dithiolene)]<sup>+</sup> complexes, but [CpCo(dmid)] (Y = C=O), [CpCo(dddt)] (Y = -(CH<sub>2</sub>)<sub>2</sub>-) and [CpCo(F<sub>2</sub>pdtt)] (Y = -CH<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>-) crystallized in non-isostructural with them. These molecules are associated with intermolecular short S...S contacts in the crystals. [CpCo(F<sub>2</sub>pdtt)] did not show any remarkable S...S contacts but indicated interesting fluorine segregation and Cp...Cp face-to-face interactions. Redox potentials of [CpCo(dithiolene)] complexes were obtained with the cyclic voltammetry measurements and dimerized by electrochemical oxidations. Electronic absorption spectra of [CpCo(dithiolene)] complexes showed visible absorption in the range of 585–701 nm as lowest energy wavelengths ( $\epsilon = 9800\text{--}11,800\text{ M}^{-1}\text{ cm}^{-1}$ ) in solutions, and they were higher energy than those of [CpNi(dithiolene)]<sup>+</sup> complexes (near-IR).

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

Metal dithiolene complexes are extensively investigated for their application as optical materials [1], magnetic materials [2], and electrical conducting materials [3]. Most of these complexes such as the square planar bisdithiolene [M(dithiolene)<sub>2</sub>] complex (M = Ni, Pd, Pt, Au) [4] involve homoleptic dithiolene complexes that have only dithiolene ligand. There are also several mono-dithiolene complexes formulated as [M(dithiolene)L<sub>2</sub>] (M = Ni, Pd, Pt) where L is an imine or a phosphine [5]. The so-called heteroleptic dithiolene complexes (M = Pt) are studied on photophysics and photochemistry. Another series of the heteroleptic complexes, organometallic dithiolene complex, involving dithiolene and  $\eta^5$ -cyclopentadienyl (Cp) ligands is also known with various Cp/dithiolene ratios and different metal centers [6]. Among them,

we have well developed the Cp/dithiolene 1:1 complexes with the group 9 and 10 metals [7,8].

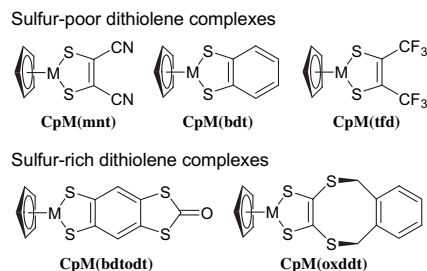
Mainly they are the diamagnetic [CpCo<sup>III</sup>(dithiolene)] and paramagnetic [CpNi<sup>III</sup>(dithiolene)]<sup>+</sup> complexes. In the former case, the five-membered cobaltadithiolene ring is aromatic due to 6 $\pi$ -electron delocalization in the metallacycle, but the ring shows interesting coexistence of aromaticity and unsaturation [9]. Accordingly, substitution reactions [10] and addition reactions [11] occur on the cobaltadithiolene ring based on both coexisted chemical properties. In the latter Ni complexes, there is a formal Ni<sup>III</sup> oxidation state but a spin delocalization has been observed in the whole molecule with 30–60% Ni<sup>III</sup> contributions [12]. Efficient synthetic methods have been established, and more than 20 [CpNi(dithiolene)]<sup>+</sup> complexes have been reported so far [8], in which most of them have been structurally and magnetically characterized [12].

On the basis of studies on both Co and Ni complexes, one typical observation is the isostructural behavior between [CpCo(dithiolene)] and [CpNi(dithiolene)]<sup>+</sup> complexes upon the same dithiolene ligand involved. There are several isostructures in the sulfur-poor [CpM(dithiolene)] complexes (Chart 1) such as [CpCo(mnt)] [13] vs [CpNi(mnt)]<sup>+</sup> [14] (mnt = maleonitrile-1,2-dithiolate), [CpCo(bdt)]

\* Corresponding author. Present address: Condensed Molecular Materials Laboratory, RIKEN, 2-1, Hirosawa, Wako-shi, Saitama 351-0198, Japan. Tel.: +81 48 467 9412; fax: +81 48 462 4661.

\*\* Corresponding author.

E-mail addresses: [mitsushiro@riken.jp](mailto:mitsushiro@riken.jp) (M. Nomura), [kajita-m@sophia.ac.jp](mailto:kajita-m@sophia.ac.jp) (M. Kajitani).



**Chart 1.** Early examples of isostructural [CpCo(dithiolene)] and [CpNi(dithiolene)] complexes.

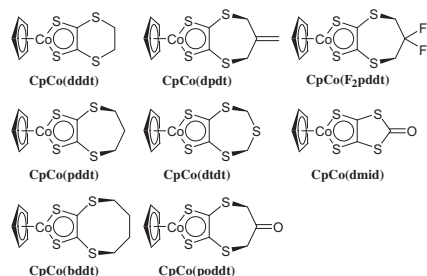
[15] vs [CpNi(bdt)]• [16] (bdt = benzene-1,2-dithiolate) and [CpCo(tfd)] [17] vs [CpNi(tfd)]• [18] (tfd = 1,2-bis(trifluoromethyl) ethylene-1,2-dithiolate). Furthermore, several isostructures of the sulfur-rich [CpM(dithiolene)] complexes (Chart 1) have been reported in [CpCo(oxddt)] [19] vs [CpNi(oxddt)]• [20] (oxddt = *o*-xylenediylthioethylene-1,2-dithiolate) and [CpCo(bdtodt)] [21] vs [CoNi(bdtodt)] [21] (bdtodt = benzo[1,3]dithiol-2-one-5,6-dithiolate) as well. We define here that the sulfur-poor dithiolene complex has sulfur atoms in dithiolene ring only, and the sulfur-rich dithiolene complex has sulfur atoms in dithiolene ring and also more sulfur atoms in the outer ring.

On the other hand, there has been one exceptional example between the sulfur-rich [CpCo(dmit)] (monoclinic,  $P2_1/n$ ) [22] and [CpNi(dmit)]• (monoclinic,  $P2_1$ ) [23] (dmit = 1,3-dithiol-2-thione-4,5-dithiolate), wherein they are closely related but differ by a disorder affecting the Cp ring in [CpNi(dmit)]•. On the basis of this background, we have been more looking for isostructural or *non-isostructural* couples of [CpCo(dithiolene)] with [CpNi(dithiolene)]• complexes in dmit-analogous complexes. Here we report herein eight new sulfur-rich [CpCo(dithiolene)] complexes (Chart 2) whose dithiolene ligands are all dmit derivatives derived from [Zn(dmit)<sub>2</sub>]<sup>2-</sup> complex, and the comparable CpNi complexes of them have been already reported [16,20,24]. We can expect diverse molecular and crystal structures since these complexes include various ring planarities or ring distortions by the outer 5, 6, 7 or 8-membered ring (Chart 2). Another interest in this work is the non-isoelectronic behavior existing between the Co<sup>III</sup> and Ni<sup>III</sup> complexes. Their electrochemical and spectroscopic properties are discussed from those CV data and electronic absorption spectra.

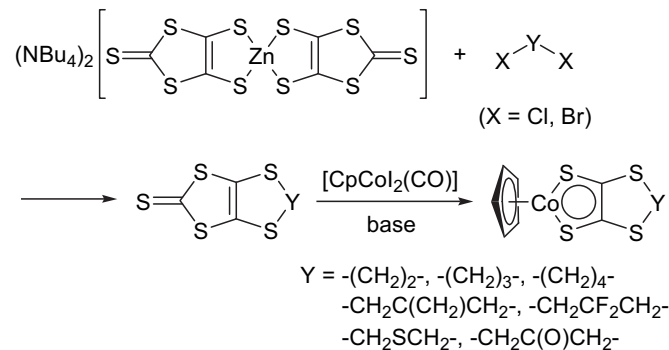
## 2. Results and discussion

### 2.1. Syntheses of sulfur-rich [CpCo(dithiolene)] complexes

The reactions of (NBu<sub>4</sub>)<sub>2</sub>[Zn(dmit)<sub>2</sub>] with alkyl dihalides generally give 1,3-dithiol-2-thione derivatives (S=C(S<sub>2</sub>C<sub>2</sub>S<sub>2</sub>Y))



**Chart 2.** Sulfur-rich [CpCo(dithiolene)] complexes studied in this work.

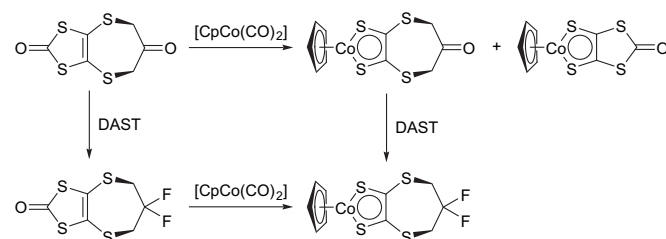


**Scheme 1.** Syntheses of sulfur-rich [CpCo(dithiolene)] complexes.

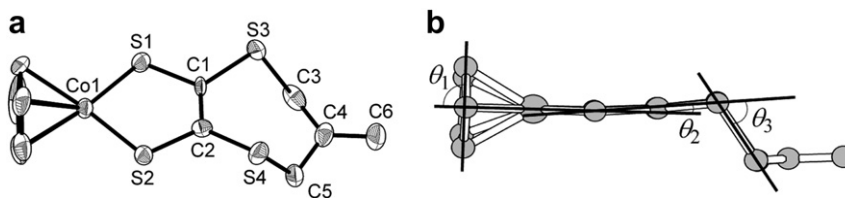
[25]. As shown in Scheme 1, 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, 3-chloro-2-chloromethyl-1-propene, bis(chloromethyl) sulfide or 1,3-dichloro-2-propanone were reacted with (NBu<sub>4</sub>)<sub>2</sub>[Zn(dmit)<sub>2</sub>] to form S=C(dddt) (Y = -(CH<sub>2</sub>)<sub>2</sub>-), S=C(pdpt) (Y = -(CH<sub>2</sub>)<sub>3</sub>-), S=C(bddt) (Y = -(CH<sub>2</sub>)<sub>4</sub>-), S=C(dpdt) (Y = -CH<sub>2</sub>C(CH<sub>2</sub>)CH<sub>2</sub>-), S=C(dttdt) (Y = -CH<sub>2</sub>SCH<sub>2</sub>-) or S=C(poddt) (Y = -CH<sub>2</sub>C(O)CH<sub>2</sub>-), respectively. All S=C(S<sub>2</sub>C<sub>2</sub>S<sub>2</sub>Y) compounds were further reacted with [CpCo<sub>2</sub>(CO)] under refluxing MeOH in the presence of sodium methoxide to yield the corresponding [CpCo(S<sub>2</sub>C<sub>2</sub>S<sub>2</sub>Y)] complexes (Scheme 1).

The S=C(poddt) (Y = -CH<sub>2</sub>C(O)CH<sub>2</sub>-) was reacted with Hg(OAc)<sub>2</sub> to give O=C(poddt), and it was further converted to the difluorinated product O=C(F<sub>2</sub>pdpt) (Y = -CH<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>-) by (diethylamino)sulfur trifluoride (DAST) [26] as reported in the literature (Scheme 2). O=C(poddt) was then reacted with [CpCo(CO)<sub>2</sub>] under heating (153 °C) to afford [CpCo(poddt)] in 42% yield however the reaction also gave [CpCo(dmtd)] (Y = C=O) [27] in 20% yield as a by-product (Scheme 2). The former complex could be formed after the C=O group elimination from the 1,3-dithiol-2-one moiety, and the latter complex might be formed after the elimination of the -CH<sub>2</sub>C(O)CH<sub>2</sub>- group in the seven-membered ring.

[CpCo(F<sub>2</sub>pdpt)] was obtained in 35% yield from O=C(F<sub>2</sub>pdpt) and [CpCo(CO)<sub>2</sub>] under heating condition (153 °C) but [CpCo(dmtd)] did not form. In addition, [CpCo(F<sub>2</sub>pdpt)] was directly formed by the fluorination of [CpCo(poddt)] with DAST in 38% yield (Scheme 2). The eight [CpCo(dithiolene)] complexes in Schemes 1 and 2 were characterized by spectroscopic data, elemental analyses and X-ray diffraction. All of them showed the corresponding molecular ion peak, [CpCoS<sub>2</sub>]<sup>+</sup> ( $m/z = 188$ ) and [CpCo]<sup>+</sup> fragments ( $m/z = 124$ ). In those <sup>13</sup>C NMR spectra, the dithiolene carbons of [CpCo(dddt)] appeared at 153.39 ppm; [CpCo(pdpt)], [CpCo(dpdt)], [CpCo(dttdt)], [CpCo(poddt)], [CpCo(F<sub>2</sub>pdpt)] and [CpCo(bddt)] showed those dithiolene carbons in the range of 163–167 ppm; [CpCo(dmtd)] showed it at 197.79 ppm. Their <sup>13</sup>C chemical shifts are probably due to the electron densities of those dithiolene ligand



**Scheme 2.** Syntheses of [CpCo(poddt)] and [CpCo(F<sub>2</sub>pdpt)].



**Fig. 1.** (a) ORTEP drawing of [CpCo(dpdt)]. Thermal ellipsoids are drawn at 30% probability level. All hydrogen atoms are omitted for simplicity. (b) A side view showing the definitions of the three folding angles (dihedral angles) reported in Table 2.  $\theta_1$  is the dihedral angle between Cp and CoS<sub>2</sub>,  $\theta_2$  represents the small folding angle along the S...S hinge in the metallacycle,  $\theta_3$  is the folding angle of the S...S hinge in the outer ring.

(see Table 3, redox potentials). Most sulfur-rich [CpCo(dithiolene)] complexes prepared in this work were air-stable in solution and solid state and only [CpCo(dddt)] was partially decomposed after two days in solution.

## 2.2. Structures of sulfur-rich [CpCo(dithiolene)] complexes

### 2.2.1. Molecular structures

The ORTEP drawings of [CpCo(dpdt)] and [CpCo(bddt)] are displayed in Figs. 1 and 2. The selected bond lengths and bond angles of the all [CpCo(dithiolene)] complexes are collected in Tables 1 and 2. The Co–S bond lengths are in the range of 2.10–2.13 Å and are slightly shorter than the Ni–S bond lengths of the corresponding [CpNi(dithiolene)]<sup>+</sup> complexes. The difference in bond length can be explained by the different electron numbers of the central metal. Formally, the Co<sup>III</sup> complexes (16-electron, d<sup>6</sup>) are coordinatively unsaturated and therefore more electron-poor than the Ni<sup>III</sup> complexes (17-electron, d<sup>7</sup>). Namely, the sulfur atoms in the dithiolene ligand can provide a strong  $\pi$ -donation to the central Co<sup>III</sup> atom, and eventually can shorten the Co–S bond lengths. The C1–C2 bond lengths in the metallacycles are 1.33–1.37 Å (Table 1) for both Co and Ni complexes, whose bond lengths are almost intermediary between typical single C–C and double C=C bonds. This fact indicates that the  $\pi$ -electrons in the metallacycle are delocalized [9]. The S–Co–S bond angles (90.9–93.0°) are always smaller than those of the S–Ni–S (91.6–94.9°). In contrast, the Co–S–C bond angles are larger than the Ni–S–C in most cases (Table 2).

Several dihedral angles are defined as  $\theta_1$ ,  $\theta_2$  and  $\theta_3$  (Fig. 1, Table 2). All CpCo complexes adopt typical two-legged piano-stool geometries as similar as the monomeric CpNi [8,12], CpRh [28] and CpIr complexes [29], because the dihedral angle  $\theta_1$  between Cp and CoS<sub>2</sub> complete plane is almost 90°. The cobaltadithiolene ring is almost planar but slightly folded along the S...S hinge with the small  $\theta_2$  angles (0.6–8.8°). In addition, the outer seven-membered or eight-membered rings are well folded along the outer S...S hinge with the  $\theta_3$  angles. In those seven-membered rings, the  $\theta_3$  angles are in the range of 61–64°. On the other hand, the  $\theta_3$  of [CpCo(bddt)] is 77.01° in the eight-membered ring to suggest a large ring distortion (Fig. 2(b)). [CpCo(dddt)] has a six-membered ring and its  $\theta_3$  angle is relatively small (13.69° for Co1A, 25.91° for Co1B).

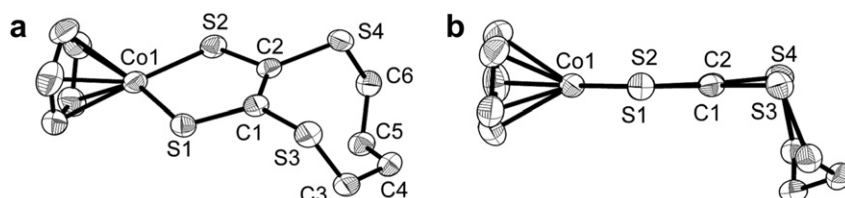
### 2.2.2. Crystal structures of sulfur-rich [CpCo(dithiolene)] complexes having isostructures with [CpNi(dithiolene)]<sup>+</sup> complexes

[CpCo(pdtt)] (Triclinic, *P*-1), [CpCo(dpdt)] (Monoclinic, *P*2<sub>1</sub>), [CpCo(dttd)] (Monoclinic, *P*2<sub>1</sub>/*c*), [CpCo(poddt)] (Monoclinic, *P*2<sub>1</sub>/*n*) and [CpCo(bddt)] (Monoclinic, *P*2<sub>1</sub>/*n*) crystallized in all isostructural with the corresponding [CpNi(dithiolene)]<sup>+</sup> complexes (Table 5). Some early papers [14–21] have also reported isostructures in [CpCo(dithiolene)] vs [CpNi(dithiolene)]<sup>+</sup> as shown in Chart 1. In addition, [CpCo(mnt)] [13] has been isostructural with the monomeric [CpRh(mnt)] [28a]. These facts noted above, suggest that the M substitution in the monomeric [CpM(dithiolene)] complexes does not modify their crystal structures. Moreover, the S/Se substitution in the metallacycle of the monomeric [CpM(dithiolene)] complexes does not change their crystals as well; e.g. [CpNi(bdt)]<sup>+</sup> vs [CpNi(bds)]<sup>+</sup> [16].

[CpCo(pdtt)] exhibited 1D interactions along the *c* axis with short S...S contacts (3.870, 3.876 Å) (Fig. 3(a)). [CpCo(dpdt)] also showed 1D intermolecular interactions between identical S...S contacts (3.802 Å) in the dithiolene ligand along the *b* axis (Fig. 3(b)). In [CpCo(bddt)], the molecular arrangement running along the *c* axis is almost similar to that of [CpCo(dpdt)], but the sulfur atom in the dithiolene ring interacts with the sulfur atom in the eight-membered ring with distances of 3.994 and 3.904 Å (Fig. 3(c)). [CpCo(dttd)] had totally 2D S...S interactions. One direction is running along the *b* axis with intermolecular interactions by several S...S contacts (3.67–4.06 Å) in the S<sub>2</sub>C<sub>2</sub>S<sub>2</sub> moiety. All molecules are associating in the same way along this direction. The other S...S interaction (3.659 Å) is between the terminal sulfur atoms in the seven-membered ring. Two columns running along the *b* axis are separated by the latter S...S interaction (Fig. 3(d)). [CpCo(poddt)] also showed 1D uniform stacks with short S...S contacts (3.802, 4.025 Å) along the *b* axis, and the all molecules are toward the same direction (Fig. 3(e)).

### 2.2.3. Crystal structures of sulfur-rich [CpCo(dithiolene)] complexes having non-isostructures with [CpNi(dithiolene)]<sup>+</sup> complexes

[CpCo(dddt)] crystallized in the triclinic system with space group *P*-1, wherein there are two crystallographically independent molecules (named as Co1A and Co1B) in the unit cell (Fig. 4(a)). [CpCo(F<sub>2</sub>pdtt)] crystallized in the monoclinic system with space group *C*2/*c*. [CpCo(dmid)] crystallized in the orthorhombic system with space group *Pbcn*. These three crystals were *non-isostructural*



**Fig. 2.** (a,b) ORTEP drawings of [CpCo(bddt)] from two different views. Thermal ellipsoids are drawn at 30% probability level. All hydrogen atoms are not shown.

**Table 1**  
Selected bond lengths (Å) in [CpM(dithiolene)] complexes (M = Co, Ni).

	M1–S1	M1–S2	S1–C1	S2–C2	C1–C2	Ref.
[CpCo(ddd)] A <sup>a</sup>	2.1053(7)	2.1155(7)	1.719(2)	1.722(2)	1.366(4)	This work
[CpCo(ddd)] B <sup>a</sup>	2.1065(7)	2.1110(7)	1.716(2)	1.715(2)	1.370(4)	This work
[CpNi(ddd)] <sup>b</sup>	2.125(2)	2.127(2)	1.711(10)	1.744(9)	1.336(13)	[16]
[CpCo(pd)]	2.106(3)	2.107(3)	1.720(9)	1.727(9)	1.362(12)	This work
[CpNi(pd)] <sup>*</sup>	2.1242(10)	2.1242(10)	1.725(3)	1.726(3)	1.358(5)	[24]
[CpCo(F <sub>2</sub> pd)]	2.1069(7)	2.1072(7)	1.717(2)	1.718(2)	1.368(3)	This work
[CpNi(F <sub>2</sub> pd)] <sup>*</sup>	2.1195(9)	2.1314(9)	1.724(3)	1.725(3)	1.349(4)	[24]
[CpCo(dp)]	2.102(3)	2.113(3)	1.736(8)	1.706(9)	1.358(4)	This work
[CpNi(dp)] <sup>*</sup>	2.128(4)	2.129(4)	1.807(11)	1.636(10)	1.387(6)	[24]
[CpCo(dt)]	2.1128(8)	2.0991(8)	1.721(2)	1.718(2)	1.368(3)	This work
[CpNi(dt)] <sup>*</sup>	2.1209(7)	2.1337(8)	1.729(3)	1.733(3)	1.356(4)	[24]
[CpCo(po)]	2.1080(5)	2.1087(5)	1.7171(16)	1.7209(15)	1.371(2)	This work
[CpNi(po)] <sup>*</sup>	2.1244(9)	2.1258(9)	1.729(3)	1.732(3)	1.357(4)	[24]
[CpCo(bd)]	2.1036(9)	2.1008(9)	1.713(3)	1.706(3)	1.365(4)	This work
[CpNi(bd)] <sup>*</sup>	2.1320(18)	2.1255(16)	1.738(5)	1.739(6)	1.337(7)	[20]
[CpCo(ox)]	2.118(3)	2.111(3)	1.751(10)	1.711(12)	1.361(13)	[19]
[CpNi(ox)] <sup>*</sup>	2.133(3)	2.121(3)	1.734(9)	1.720(8)	1.353(13)	[20]
[CpCo(dm)]	2.1220(6)	2.1312(6)	1.707(2)	1.703(2)	1.368(3)	This work
[CpNi(dm)] <sup>*</sup>	2.138(1)	2.145(1)	1.718(3)	1.712(3)	1.352(4)	[23b]

<sup>a</sup> Two crystallographically independent molecules were found.

<sup>b</sup> Data from one of four independent molecules.

with the corresponding [CpNi(ddd)]<sup>\*</sup> (monoclinic, *P*<sub>2</sub><sub>1</sub>) [16], [CpNi(F<sub>2</sub>pd)]<sup>\*</sup> (Orthorhombic, *Pbca*) [24] and [CpNi(dm)] (Orthorhombic, *Pnma*) [23] complexes. Therefore, these crystal structures are exceptional non-isostructural couples, since the only non-isostructural couple of [CpCo(dmit)] (Monoclinic, *P*<sub>2</sub><sub>1</sub>/*n*) [22] vs [CpNi(dmit)]<sup>\*</sup> (Monoclinic, *P*<sub>2</sub><sub>1</sub>) [23] has been reported so far.

[CpCo(ddd)] showed 2D intermolecular interactions through the S⋯S contacts. The two different molecules Co1A and Co1B are interacting but the same molecules are not associated with each other (Fig. 4(a)). On the other hand, [CpNi(ddd)]<sup>\*</sup> has shown four crystallographically independent molecules and the molecular arrangement has been 1D [16]. Fig. 4(b) exhibits the packing diagram of [CpCo(dm)]. There are lateral and vertical S⋯S contacts with distances of 3.746–3.995 Å (not shown). In addition, there are intermolecular face-to-face stacks between the dm ligands, and these intermolecular interactions lie on 1D column along the *c* axis in the crystal, with a pseudo-4-fold-symmetry

arrangement. The similar arrangement has been reported in the [Cp\*Co(dcdmp)] (dcdmp = 2,3-dicyano-5,6-dimercaptopyrazine) [30]. In the crystal of [CpNi(dm)]<sup>\*</sup>, the molecular stack is 1D, but different from [CpCo(dm)] because of the non-isostructure [23b].

[CpCo(F<sub>2</sub>pd)] did not show any remarkable S⋯S short contacts, but note that indicated interesting fluorine segregations and Cp⋯Cp face-to-face interactions (c.a. 3.5 Å) (Fig. 4(c)). Several fluorine segregations have been reported in the CF<sub>2</sub>-bound [M(dithiolene)<sub>2</sub>] complexes (M = Ni, Au) [31], CF<sub>2</sub>-bound TTF derivatives [32] and CF<sub>3</sub>-substituted TTF compounds [33]. No Cp⋯Cp interaction has been found in the [CpNi(F<sub>2</sub>pd)]<sup>\*</sup> because of the non-isostructure with the Co complex [24]. Several [CpM(dithiolene)] and [CpM(diselenolene)] complexes have shown the Cp⋯Cp interactions [16,18]. Among them, the paramagnetic [CpNi(bdt)]<sup>\*</sup> and [CpNi(bds)]<sup>\*</sup> (bds = benzene-1,2-diselenolate) complexes have caused exotic antiferromagnetic interactions through the Cp⋯Cp overlap [16].

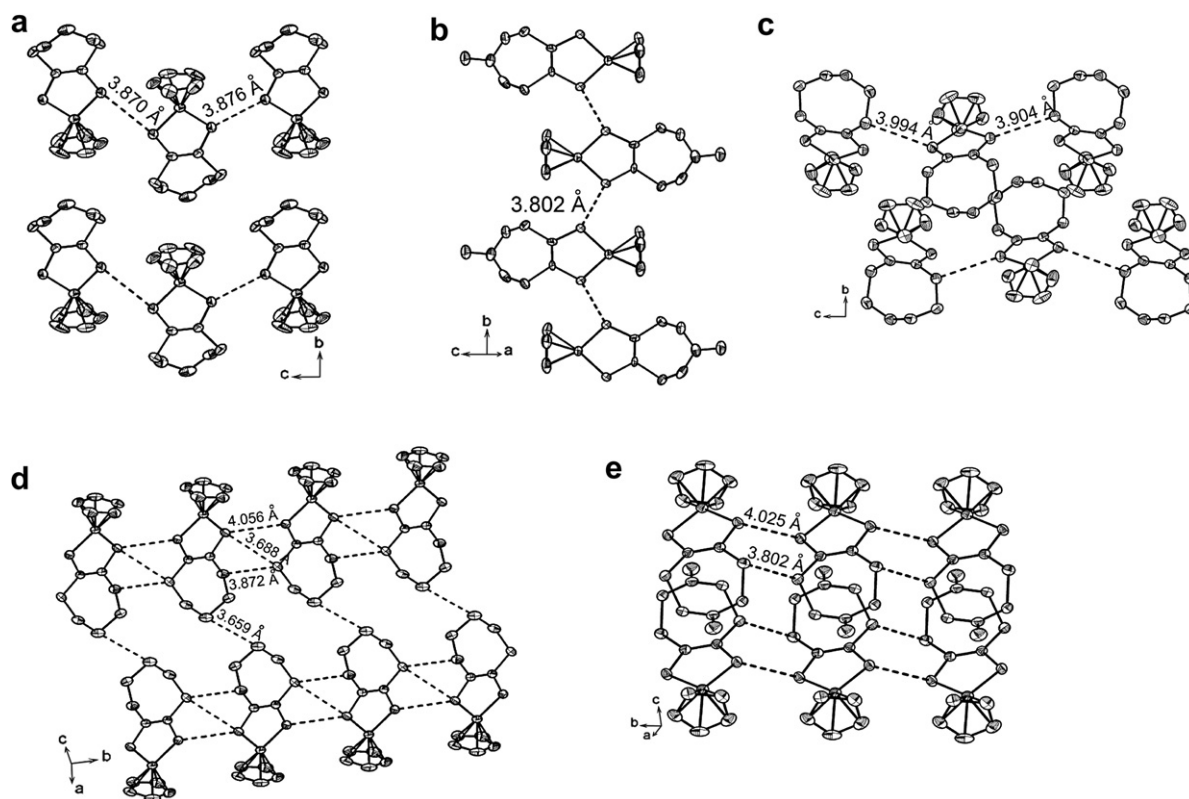
**Table 2**  
Selected bond angles (°) and dihedral angles (°) in [CpM(dithiolene)] complexes (M = Co, Ni).

	S1–M1–S2	M–S1–C1	M1–S2–C2	θ <sub>1</sub>	θ <sub>2</sub>	θ <sub>3</sub>	Ref.
[CpCo(ddd)] A <sup>a</sup>	91.12(3)	106.01(9)	105.67(9)	88.70	1.07	13.69	This work
[CpCo(ddd)] B <sup>a</sup>	90.91(3)	105.94(9)	106.14(9)	88.80	2.59	25.91	This work
[CpNi(ddd)] <sup>b</sup>	92.42(9)	103.4(3)	103.7(3)	86.9	1.0	– <sup>c</sup>	[16]
[CpCo(pd)]	91.22(13)	106.0(3)	105.5(3)	89.55	6.21	59.96	This work
[CpNi(pd)] <sup>*</sup>	92.42(4)	103.97(11)	103.85(11)	89.3	7.7	61.32	[24]
[CpCo(F <sub>2</sub> pd)]	91.15(2)	105.59(8)	105.91(8)	87.04	4.76	61.74	This work
[CpNi(F <sub>2</sub> pd)] <sup>*</sup>	92.58(3)	103.78(10)	103.45(10)	89.8	5.0	66.77	[24]
[CpCo(dp)]	91.31(5)	104.3(3)	106.6(4)	89.89	6.22	62.26	This work
[CpNi(dp)] <sup>*</sup>	92.51(4)	104.4(4)	103.4(3)	89.8	7.5	63.65	[24]
[CpCo(dt)]	91.43(3)	105.56(8)	105.69(9)	87.36	4.15	62.16	This work
[CpNi(dt)] <sup>*</sup>	92.74(3)	103.77(10)	103.67(10)	87.3	5.1	63.09	[24]
[CpCo(po)]	91.731(17)	105.26(6)	105.42(6)	86.08	2.22	63.76	This work
[CpNi(po)] <sup>*</sup>	93.03(3)	103.42(10)	103.64(11)	86.2	2.4	64.48	[24]
[CpCo(bd)]	91.11(3)	105.70(10)	105.85(10)	87.88	4.09	77.05	This work
[CpNi(bd)] <sup>*</sup>	92.34(6)	103.7(2)	103.90(19)	88.87	4.54	77.69	[20]
[CpCo(ox)]	91.14(12)	104.5(3)	106.6(3)	87.642	8.026	63.317	[19]
[CpNi(ox)] <sup>*</sup>	91.66(10)	103.9(3)	105.0(3)	87.37	8.78	64.42	[20]
[CpCo(dm)]	93.02(2)	103.56(7)	102.95(7)	88.611	0.65	1.01	This work
[CpNi(dm)] <sup>*</sup>	94.90(4)	100.84(11)	100.81(11)	– <sup>c</sup>	– <sup>c</sup>	– <sup>c</sup>	[23b]

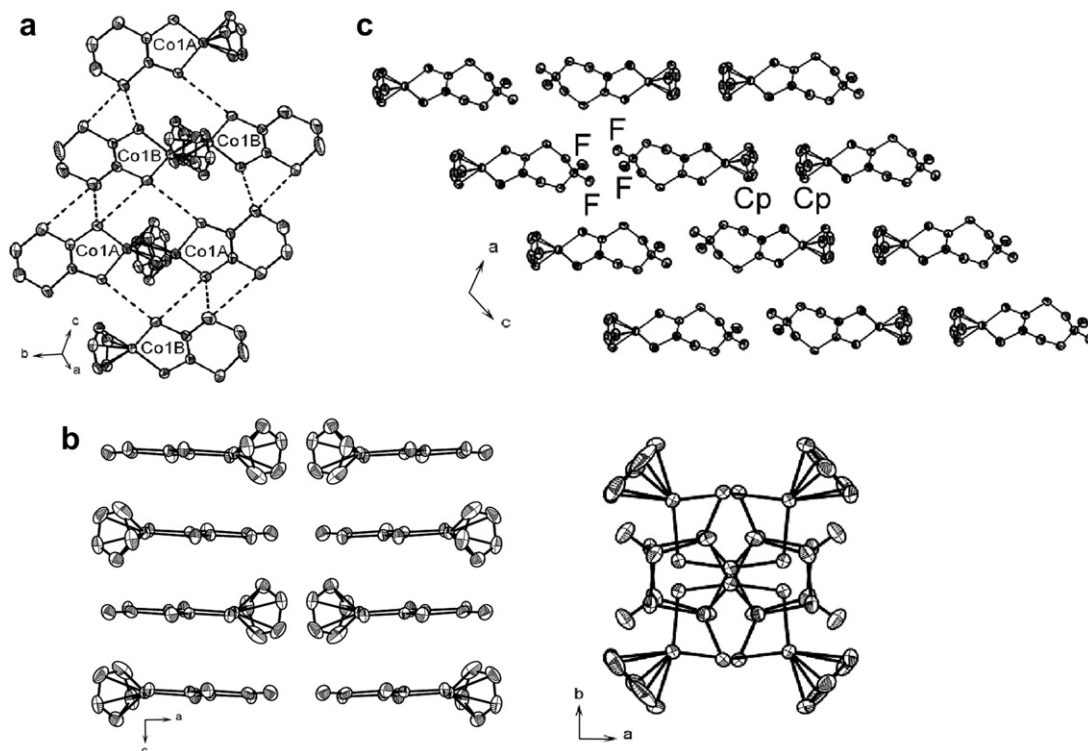
<sup>a</sup> Two crystallographically independent molecules were found.

<sup>b</sup> Data from one of four independent molecules.

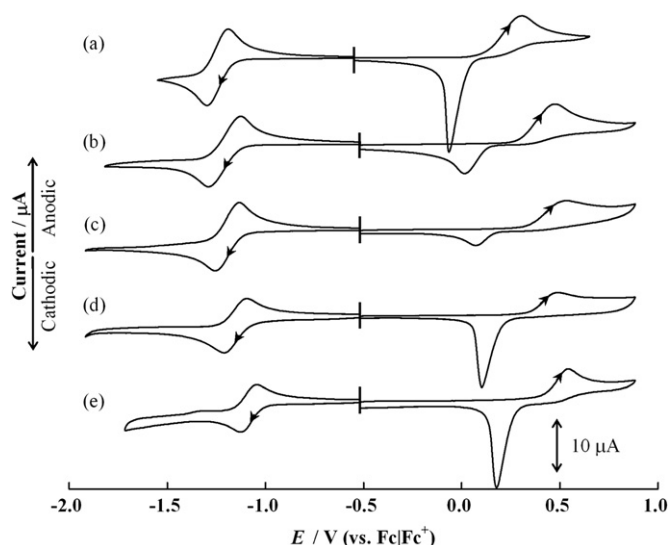
<sup>c</sup> Data are not available in the literature.



**Fig. 3.** Packing diagrams of (a) [CpCo(pdtt)], (b) [CpCo(dpdt)], (c) [CpCo(bdtt)], (d) [CpCo(dtdt)] and (e) [CpCo(poddt)]. Intermolecular short S...S contacts are shown as dotted lines.



**Fig. 4.** Packing diagrams of (a) [CpCo(ddd)], (b) [CpCo(dmid)] and (c) [CpCo(F<sub>2</sub>pdtt)]. Intermolecular short S...S contacts are shown as dotted lines. The short S...S contacts of (b) [CpCo(dmid)] are omitted for clarity reason.



**Fig. 5.** Cyclic voltammograms of (a) [CpCo(dddt)], (b) [CpCo(pdtt)], (c) [CpCo(dpdt)], (d) [CpCo(dttd)] and (e) [CpCo(poadd)] in dichloromethane solutions containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP). (Pt disk electrode with  $\Phi = 1.6$  mm,  $\nu = 100$  mV s<sup>-1</sup>).

### 2.3. Electrochemical and UV–vis spectral properties of sulfur-rich [CpCo(dithiolene)] complexes

The cyclic voltammograms (CVs) of some [CpCo<sup>III</sup>(dithiolene)] complexes are shown in Fig. 5(a–e) and those redox potentials are summarized in Table 3 together with the early data of [CpNi(dithiolene)]<sup>+</sup> complexes. All complexes indicated reversible reduction waves and irreversible oxidation waves. The reduction is due to the Co<sup>III</sup>/Co<sup>II</sup> redox couple and the oxidation of electron-rich dithiolene ligand moiety is conceivable. In the complexes with a seven-membered ring, the terminal electron-withdrawing group shifts their redox potentials to anodic potentials in the order of CF<sub>2</sub> > C=O > S > C=CH<sub>2</sub> > CH<sub>2</sub> (Table 3). A similar tendency has been also observed in the redox potentials of [CpNi(dithiolene)]<sup>+</sup> complexes with a seven-membered ring [24]. All reduction potentials of the CpCo complexes were more negative, the oxidation potentials were more positive, than those of the identical CpNi complexes. The redox potentials of [CpCo(pdtt)] ( $E_{1/2}(\text{red}) = -1.21$  V,  $E_p(\text{ox}) = +0.50$  V) were well comparable with those of [CpCo(bddt)] ( $E_{1/2}(\text{red}) = -1.22$  V,  $E_p(\text{ox}) = +0.53$  V). This fact suggests that the outer ring size did not modify the redox potential well. However, note that the

oxidation potential of [CpCo(dddt)] ( $E_p(\text{ox}) = +0.33$  V) is much more negative than those of [CpCo(pdtt)] and [CpCo(bddt)]. This may be one reason why the only [CpCo(dddt)] decomposed in the aerial solution.

Most [CpCo(dithiolene)] complexes could be dimerized by an electrochemical oxidation as usual. The irreversible oxidations of [CpCo(dithiolene)] complexes indicate that those oxidized species are unstable enough and thus can dimerize during the time scale of CV measurement. There have been three types of dimer: (1) M–M bond dimer [34], (2) M–S (inner S atom) bond dimer [35] and (3) M–S (outer S atom) bond dimer [36]. Among them, Guyon et al. reported that the dimeric [Cp<sup>\*</sup>Co(dddt)] and its structure were classified into the group (3) [36]. May be most dimers in this work are included into the group (3). The oxidized species of [CpCo(dddt)], [CpCo(dttd)], [CpCo(poadd)] and [CpCo(dmid)] clearly precipitated (or concentrated) on the electrode because quite intense rereduction waves appeared after the oxidation (Fig. 5). This result suggests that the electrochemically generated dimeric species are poorly soluble in the solution. In an early paper, [Cp<sup>\*</sup>Co(dddt)] has not given an intense rereduction wave. One reason is probably that the Cp<sup>\*</sup> complex is more soluble than the Cp complex.

The UV–vis spectral data ( $\lambda_{\text{max}}$  and  $\epsilon$ ) of all [CpCo(dithiolene)] complexes and the early data of [CpNi(dithiolene)]<sup>+</sup> complexes are summarized in Table 4. The UV–vis spectra of [CpCo(dddt)], [CpCo(pdtt)] and [CpCo(bddt)] are displayed in Fig. 6. All complexes showed electronic absorption in the range of 585–701 nm as lowest energy (HOMO–LUMO) with  $\epsilon = 9800$ – $11,800$  M<sup>-1</sup> cm<sup>-1</sup>. These absorptions are attributed to LMCT [37]. The  $\lambda_{\text{max}}$  at 701 nm ( $\epsilon = 10,900$  M<sup>-1</sup> cm<sup>-1</sup>) for [CpCo(dddt)] is the lowest energy wavelength of all monometallic–monodithiolene Co complexes [7]. The sulfur-rich [CpCo(dithiolene)] complexes show relatively lower energy absorption than those of the sulfur-poor [CpCo(dithiolene)] complexes (550–600 nm) [7]. These results indicate that a sulfur-rich dithiolene ligand can help to increase the HOMO level. The [CpNi(dithiolene)]<sup>+</sup> complexes have shown near-IR absorption and always exhibit lower energy absorption compared with the [CpCo(dithiolene)] complexes. Interestingly, large differences of  $\lambda_{\text{max}}$  were observed between the [CpCo(dddt)] (701 nm) with a six-membered ring, [CpCo(pdtt)] (606 nm) with a seven-membered ring, and [CpCo(bddt)] (585 nm) with an eight-membered ring (Fig. 6). The low oxidation potential of [CpCo(dddt)] ( $E_p(\text{ox}) = +0.33$  V) supports that the HOMO level of dddt ligand is much higher than those of pdtt and bddt. It is obviously due to a distortion of the outer rings (see the  $\theta_3$  angles in Table 2), and has been observed in the corresponding [CpNi(dithiolene)]<sup>+</sup> complexes as well (Table 4) [16,20,24].

**Table 3**  
Redox potentials (vs Fc/Fc<sup>+</sup>) of sulfur-rich [CpM(dithiolene)] complexes (M = Co, Ni) Co complex.

Co complex	$E_{1/2}(\text{red})/\text{V}^a$	$E_p(\text{ox})/\text{V}^b$	$E_p(\text{rered})/\text{V}^b$	Ref.	Ni complex	$E_{1/2}(\text{red})/\text{V}$	$E_p(\text{ox})/\text{V}$	Ref.
CpCo(dddt)	-1.25	+0.33	-0.07 <sup>c</sup>	This work	CpNi(dddt)	-1.06	-0.02	[16]
CpCo(pdtt)	-1.21	+0.50	±0	This work	CpNi(pdtt)	-1.08	+0.07	[24]
CpCo(F <sub>2</sub> pdtt)	-1.11	+0.63	+0.22	This work	CpNi(F <sub>2</sub> pdtt)	-0.98	+0.25	[24]
CpCo(dpdt)	-1.19	+0.56	+0.05	This work	CpNi(dpdt)	-1.05	+0.12	[24]
CpCo(dttd)	-1.14	+0.51	+0.10 <sup>c</sup>	This work	CpNi(dttd)	-1.02	+0.19	[24]
CpCo(poadd)	-1.11	+0.56	+0.17 <sup>c</sup>	This work	CpNi(poadd)	-0.98	+0.22	[24]
CpCo(bddt)	-1.22	+0.53	±0	This work	CpNi(bddt)	-1.04	+0.14	[20]
CpCo(oxddt)	-1.24	+0.58	-0.02	[19]	CpNi(oxddt)	-1.07	+0.16	[20]
CpCo(dmid)	-1.03	+0.54	+0.36 <sup>c</sup>	This work	CpNi(dmid)	-0.80	+0.26	[23b]

<sup>a</sup> Half-wave potential.

<sup>b</sup> Peak potential.

<sup>c</sup> Intense rereduction wave appeared.

**Table 4**  
UV–vis–NIR spectral data.

Co complex	$\lambda_{\max}/\text{nm}$	$\epsilon/\text{M}^{-1} \text{cm}^{-1}$	Ref.	Ni complex	$\lambda_{\max}/\text{nm}$	$\epsilon/\text{M}^{-1} \text{cm}^{-1}$	Ref.
CpCo(dddt)	701	10,900	This work	CpNi(dddt)	1012	4700	[16]
CpCo(pddt)	606	11,600	This work	CpNi(pddt)	848	2100	[24]
CpCo(F <sub>2</sub> pddt)	587	11,800	This work	CpNi(F <sub>2</sub> pddt)	798	2000	[24]
CpCo(dpdt)	602	11,300	This work	CpNi(dpdt)	840	2400	[24]
CpCo(dttdt)	595	9800	This work	CpNi(dttdt)	823	1800	[24]
CpCo(poddt)	590	9900	This work	CpNi(poddt)	806	1700	[24]
CpCo(bddt)	585	10,300	This work	CpNi(bddt)	774	2100	[20]
CpCo(oxddt)	602	4600	[19]	CpNi(oxddt)	825	1900	[20]
CpCo(dmid)	642	10,700	This work				

### 3. Conclusion

In this work, we synthesized and fully characterized eight new sulfur-rich [CpCo(dithiolene)] complexes. Their molecular structures, crystal structures, electronic absorption spectra and electrochemical behavior could be compared with the corresponding [CpNi(dithiolene)]<sup>+</sup> complexes with the same dithiolene ligand. We found both isostructural and *non-isostructural* [CpM(dithiolene)] couples between the Co and Ni complexes. The latter case has been rare, but in conclusion, the sulfur-rich [CpM(dithiolene)] complexes including early [CpM(dmit)] case, can be relatively easier to form the non-isostructural couples. Probably, we can obtain a new Co<sup>III</sup>–Ni<sup>III</sup> mixed crystal by using the isostructural couple, but the crystal can involve non-isoelectronic properties. Namely, the paramagnetic [CpNi(dithiolene)]<sup>+</sup> can be dissolved in the diamagnetic [CpCo(dithiolene)] crystalline matrix. Dilution of paramagnetism and magnetic interaction can be expected. Previously, some early papers have already described the mixed crystals of isostructural [Ni(tmdt)<sub>2</sub>] with [Au(tmdt)<sub>2</sub>] [38] and isostructural [Ni(dmit)<sub>2</sub>] with [Pd(dmit)<sub>2</sub>] [39] to study on their conducting and magnetic behavior (alloy system).

### 4. Experimental section

#### 4.1. General remarks

All reactions were carried out under argon atmosphere by means of standard Schlenk techniques. MeOH and DMF for

synthetic reactions were purified by using CaH<sub>2</sub> before use. [CpCo<sub>2</sub>(CO)] [40], [CpCo(CO)<sub>2</sub>] [41], (NBu<sub>4</sub>)<sub>2</sub>[Zn(dmit)<sub>2</sub>] [42], S=C(dddt) [43], S=C(pddt) [44], S=C(F<sub>2</sub>pddt) [45], S=C(dpdt) [46], S=C(dttdt) [47], S=C(poddt) [48] and S=C(bddt) [49] were prepared by literature methods. 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, bis(chloromethyl) sulfide, 3-chloro-2-chloromethyl-1-propene, 1,3-dichloro-2-propanone, and (diethylamino) sulfur trifluoride (DAST) were purchased from Tokyo Chemical Industry Co., Ltd. Silica gel (Wakogel C-300) was obtained from Wako Pure Chemical Industries, Ltd. Sodium methoxide in MeOH solution was prepared from dry MeOH and fresh sodium metal. Mass spectrum was recorded on a JEOL JMS-D300. NMR spectra were measured with a JEOL LA500 spectrometer. The <sup>1</sup>H and <sup>13</sup>C chemical shifts ( $\delta$  in ppm) are referenced using chemical shifts of TMS at  $\delta$  0 ppm. Chloroform-d was purchased from Aldrich Chemicals. UV–Vis spectra were recorded on a Hitachi model UV-2500PC. Elemental analyses were determined by using a Shimadzu PE2400-II instrument.

#### 4.2. Abbreviations of dithiolene ligands in this work

dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate,  
 pddt = 6,7-dihydro-5*H*-1,4-dithiepin-2,3-dithiolate,  
 bddt = 5,6,7,8-tetrahydro-1,4-dithiocine-2,3-dithiolate,  
 F<sub>2</sub>pddt = 6,6-difluoro-6,7-dihydro-5*H*-1,4-dithiepine-2,3-dithiolate,  
 dpdt = 6,7-dihydro-6-methylene-5*H*-1,4-dithiepine-2,3-dithiolate,  
 dttdt = 5,7-dihydro-1,4,6-trithiin-2,3-dithiolate,  
 poddt = 5*H*-1,4-dithiepin-6(7*H*)-one-2,3-dithiolate,  
 dmid = 1,3-dithiol-2-one-4,5-dithiolate.

#### 4.3. Typical synthetic procedure of sulfur-rich [CpCo(dithiolene)] complexes from [CpCo<sub>2</sub>(CO)]

Sodium methoxide in MeOH (0.49 mmol) was added by syringe to a solution of S=C(pddt) (109 mg, 0.46 mmol) in MeOH (200 ml) and stirred for 60 min at room temperature. Then [CpCo(CO)<sub>2</sub>] (198 mg, 0.49 mmol) was added and the reaction mixture was refluxed for 4 h. The solvent was removed *in vacuo* and the residue was placed into a separatory funnel. An organic layer was extracted from CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O (100 ml/100 ml) solutions, and was dried over MgSO<sub>4</sub>. The resulted mixture was chromatographed on silica gel with CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane eluent (1:1 (v/v)). A blue product was further purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane (1:1 (v/v)). The product [CpCo(pddt)] was obtained as a dark blue crystalline solid in 68% yield (106 mg, 0.33 mmol). The other sulfur-rich [CpCo(dithiolene)] complexes were also obtained by the similar procedure as noted above. Results are as follows: [CpCo(dddt)] dark blue solid (20% yield), [CpCo(F<sub>2</sub>pddt)] dark purple solid (60% yield), [CpCo(dpdt)] dark blue solid (14% yield), [CpCo(dttdt)] dark green solid (44% yield), [CpCo(poddt)] dark blue solid (55% yield), [CpCo(bddt)] dark blue solid (35% yield).

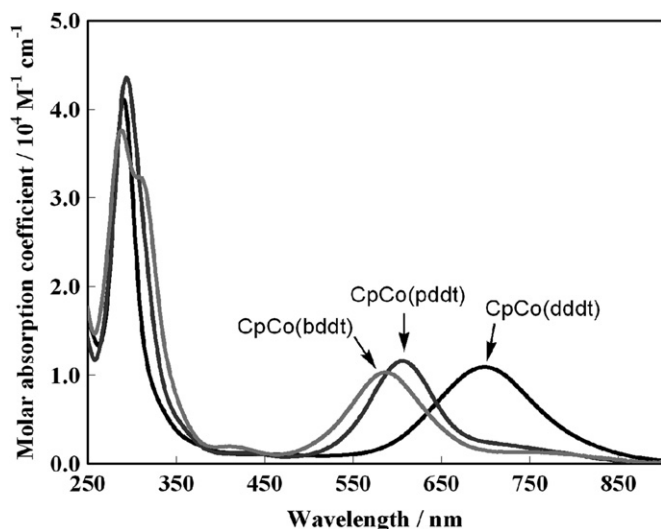


Fig. 6. UV–vis spectra of [CpCo(dddt)], [CpCo(pddt)] and [CpCo(bddt)] in dichloromethane solution.

## 4.3.1. [CpCo(dddt)]

Mass ( $\text{EI}^+$ , 70 eV)  $m/z$  (rel. intensity) 304 ( $[\text{M}^+]$ , 100), 188 ( $[\text{CpCoS}_2^+]$ , 36), 168 ( $[\text{CpCoSC}^+]$ , 13), 124 ( $[\text{CpCo}^+]$ , 76).  $^1\text{H}$  NMR ( $\text{CDCl}_3$  vs TMS, 500 MHz)  $\delta$  5.26 (s, 5H, Cp), 3.11 (s, 4H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  vs TMS, 125 MHz)  $\delta$  153.39 (dithiolene carbon), 78.78 (Cp), 28.26 ( $\text{CH}_2$ ). UV–vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ) 701 (10,900). Anal. Calcd. for  $\text{C}_9\text{H}_9\text{CoS}_4$ , C 35.52, H 2.98, S 42.14; Found C 35.89, H 3.00, S 42.20.

## 4.3.2. [CpCo(pddt)]

Mass ( $\text{EI}^+$ , 70 eV)  $m/z$  (rel. intensity) 318 ( $[\text{M}^+]$ , 70), 212 ( $[\text{CpCoS}_2\text{C}_2^+]$ , 25), 188 ( $[\text{CpCoS}_2^+]$ , 25), 168 ( $[\text{CpCoSC}^+]$ , 46), 124 ( $[\text{CpCo}^+]$ , 100).  $^1\text{H}$  NMR ( $\text{CDCl}_3$  vs TMS, 500 MHz)  $\delta$  5.30 (s, 5H, Cp), 2.70 (4H, t,  $\text{CH}_2$ ), 2.37 (2H, m,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  vs TMS, 125 MHz)  $\delta$  166.96 (dithiolene carbon), 79.48 (Cp), 34.93 ( $\text{CH}_2$ ), 33.96 ( $\text{CH}_2$ ). UV–vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ) 606 (11,600), 294 (45,000). Anal. Calcd. for  $\text{C}_{10}\text{H}_{11}\text{CoS}_4$ , C, 37.72; H 3.48; S 40.28; Found C, 37.69; H 3.38; S 40.05.

## 4.3.3. [CpCo(dpdt)]

Mass ( $\text{EI}^+$ , 70 eV)  $m/z$  (rel. intensity) 330 ( $[\text{M}^+]$ , 65), 188 ( $[\text{CpCoS}_2^+]$ , 52), 168 ( $[\text{CpCoSC}^+]$ , 24), 124 ( $[\text{CpCo}^+]$ , 100).  $^1\text{H}$  NMR ( $\text{CDCl}_3$  vs TMS, 500 MHz)  $\delta$  5.34 (s, 5H, Cp), 4.92 (2H, s,  $\text{C}=\text{CH}_2$ ), 3.25 (4H, s,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  vs TMS, 125 MHz)  $\delta$  167.0 (dithiolene carbon), 146.5 ( $\text{C}=\text{CH}_2$ ), 115.07 ( $\text{C}=\text{CH}_2$ ), 79.63 (Cp), 40.80 ( $\text{CH}_2$ ). UV–vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ) 602 (11,300), 297 (38,800). Anal. Calcd. for  $\text{C}_{11}\text{H}_{11}\text{CoS}_4$ , C, 39.99; H 3.36; S 38.82; Found C, 40.20; H 3.31; S 38.33.

## 4.3.4. [CpCo(dttd)]

Mass ( $\text{EI}^+$ , 70 eV)  $m/z$  (rel. intensity) 336 ( $[\text{M}^+]$ , 36), 188 ( $[\text{CpCoS}_2^+]$ , 90), 124 ( $[\text{CpCo}^+]$ , 100).  $^1\text{H}$  NMR ( $\text{CDCl}_3$  vs TMS, 500 MHz)  $\delta$  5.36 (s, 5H, Cp), 4.11 (4H, s,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  vs TMS, 125 MHz)  $\delta$  165.1 (dithiolene carbon), 79.8 (Cp), 38.1 ( $\text{CH}_2$ ). UV–vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ) 595 (9800), 293 (42,200). HR-Mass ( $\text{EI}^+$ , 70 eV) Calcd. for  $\text{C}_9\text{H}_9\text{CoS}_5$ : 335.8640; Found 335.8644.

## 4.3.5. [CpCo(bddt)]

Mass ( $\text{EI}^+$ , 70 eV)  $m/z$  (rel. intensity) 332 ( $[\text{M}^+]$ , 70), 212 ( $[\text{CpCoS}_2\text{C}_2^+]$ , 17), 188 ( $[\text{CpCoS}_2^+]$ , 25), 168 ( $[\text{CpCoSC}^+]$ , 95), 124 ( $[\text{CpCo}^+]$ , 100).  $^1\text{H}$  NMR ( $\text{CDCl}_3$  vs TMS, 500 MHz)  $\delta$  5.33 (s, 5H, Cp), 2.93 (4H, q,  $\text{CH}_2$ ), 1.58 (4H, m,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  vs TMS, 125 MHz)  $\delta$  165.96 (dithiolene carbon), 79.71 (Cp), 39.05 ( $\text{CH}_2$ ), 27.05 ( $\text{CH}_2$ ). UV–vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ) 585 (10,300), 288 (37,500). Anal. Calcd. for  $\text{C}_{11}\text{H}_{13}\text{CoS}_4$ , C, 39.74; H 3.94; S 38.59; Found C, 40.07; H 3.86; S 38.74.

## 4.3.6. [CpCo(poddt)]

Mass ( $\text{EI}^+$ , 70 eV)  $m/z$  (rel. intensity) 332 ( $[\text{M}^+]$ , 100), 188 ( $[\text{CpCoS}_2^+]$ , 52), 124 ( $[\text{CpCo}^+]$ , 100).  $^1\text{H}$  NMR ( $\text{CDCl}_3$  vs TMS, 500 MHz)  $\delta$  5.38 (s, 5H, Cp), 3.36 (s, 4H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  vs TMS, 125 MHz)  $\delta$  203.3 ( $\text{C}=\text{O}$ ), 163.5 (dithiolene carbon), 79.9 (Cp), 43.2 ( $\text{CH}_2$ ). UV–vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ) 593 (9900), 294 (39,200). HR-Mass ( $\text{EI}^+$ , 70 eV) Calcd. for  $\text{C}_{10}\text{H}_9\text{CoOS}_4$ : 331.8868; Found 331.8869.

4.3.7. [CpCo( $\text{F}_2$ pddt)]

Mass ( $\text{EI}^+$ , 70 eV)  $m/z$  (rel. intensity) 354 ( $[\text{M}^+]$ , 100), 212 ( $[\text{CpCoS}_2\text{C}_2^+]$ , 25), 188 ( $[\text{CpCoS}_2^+]$ , 18), 168 ( $[\text{CpCoSC}^+]$ , 62), 124 ( $[\text{CpCo}^+]$ , 91).  $^1\text{H}$  NMR ( $\text{CDCl}_3$  vs TMS, 500 MHz)  $\delta$  5.39 (s, 5H, Cp), 2.93 (br-t,  $J_{\text{H-F}} = 12.8$  Hz, 4H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  vs TMS, 125 MHz)  $\delta$  164.20 (dithiolene carbon), 122.5 (t,  $J_{\text{C-F}} = 243$  Hz,  $\text{CF}_2$ ), 79.9 (Cp), 38.8 (t,  $J_{\text{C-F}} = 19$  Hz,  $\text{CH}_2$ ). UV–vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ) 587 (11,800), 293 (45,000). HR-Mass ( $\text{EI}^+$ , 70 eV) Calcd. for  $\text{C}_{10}\text{H}_9\text{CoF}_2\text{S}_4$ : 353.8887; Found 353.8895.

4.4. Syntheses of [CpCo(poddt)] and [CpCo( $\text{F}_2$ pddt)] from [CpCo( $\text{CO}$ ) $_2$ ]

[CpCo( $\text{CO}$ ) $_2$ ] (0.26 ml, 1.82 mmol) reacted with  $\text{O}=\text{C}(\text{poddt})$  (0.424 g, 1.79 mmol) in refluxing DMF (30 ml) for 2 h. After the reaction, solvent was removed under reduced pressure with heating. The residue was separated by column chromatography on silica gel. [CpCo(poddt)] was obtained as a dark blue solid in 42% yield (0.250 g, 0.75 mmol) and [CpCo(dmid)] was also formed as a dark green solid in 20% yield (0.108 g, 0.35 mmol). [CpCo( $\text{CO}$ ) $_2$ ] (0.26 ml, 1.82 mmol) and  $\text{O}=\text{C}(\text{F}_2\text{pddt})$  (0.424 g, 1.79 mmol) were reacted in refluxing DMF (30 ml) for 2 h. A dark blue component was separated by the similar procedure to [CpCo(poddt)]. [CpCo( $\text{F}_2$ pddt)] was isolated as a dark purple solid in 35% yield (0.222 g, 0.63 mmol).

DAST (9.6 mg, 0.06 mmol) in dichloromethane (1 ml) was added from dropping funnel into the dichloromethane solution of [CpCo(poddt)] (20 mg, 0.06 mmol) at 0 °C. The reaction mixture was further stirred for 2 h at 0 °C. Some cold water was added. The organic layer was extracted and dried over  $\text{MgSO}_4$ . The resulted mixture was chromatographed on silica gel. [CpCo( $\text{F}_2$ pddt)] (38%) and recovery of [CpCo(poddt)] (62%) were obtained.

## 4.4.1. [CpCo(dmid)]

Mass ( $\text{EI}^+$ , 70 eV)  $m/z$  (rel. intensity) 304 ( $[\text{M}^+]$ , 74), 276 ( $[\text{M}^+-\text{CO}]$ , 27), 188 ( $[\text{CpCoS}_2^+]$ , 32), 168 ( $[\text{CpCoSC}^+]$ , 40), 124 ( $[\text{CpCo}^+]$ , 100).  $^1\text{H}$  NMR ( $\text{CDCl}_3$  vs TMS, 500 MHz)  $\delta$  5.43 (s, 5H, Cp).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  vs TMS, 125 MHz)  $\delta$  206.88 ( $\text{C}=\text{O}$ ), 197.79 (dithiolene carbon), 79.19 (Cp). UV–vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ) 642 (10,700), 286 (24,400). Anal. Calcd. for  $\text{C}_8\text{H}_5\text{OCoS}_4$ , C 31.57, H 1.66; Found C 31.47, H 1.59.

## 4.5. CV measurements

All electrochemical measurements were performed under an argon atmosphere. Solvents for electrochemical measurements were dried by molecular sieve 4 Å before use. A platinum wire served as a counter electrode, and the reference electrode  $\text{Ag}/\text{AgCl}$  was corrected for junction potentials by being referenced internally to the ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) 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  $\text{dm}^{-3}$  dichloromethane solutions of complexes containing 0.1 mol  $\text{dm}^{-3}$  tetra-*n*-butylammonium perchlorate (TBAP) at 25 °C.

## 4.6. X-ray diffraction study

Single crystals of the all [CpCo(dithiolene)] complexes were obtained from recrystallization by vapor diffusion of *n*-hexane into those dichloromethane solutions. Single crystal of slightly air-sensitive [CpCo(dddt)] was made under Ar atmosphere. Crystals were mounted on the top of a thin glass fiber. Measurement was made on Rigaku Mercury CCD diffractometer with graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$  Å). Each structure was solved by direct methods and expanded Fourier techniques [50]. 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. All calculations for the products except [CpCo(dmid)] were performed using WinGX software package [51]. All calculations for [CpCo(dmid)] were carried out by the crystal structure software package [52]. The structure of [CpCo(dpdt)] was also solved with space group  $P2_1/m$  instead of  $P2_1$ . However, the five carbons on the Cp ligand were



**Table 5**  
Crystallographic data.

Compound	CpCo(pdtdt)	CpCo(dpdt)	CpCo(dttdt)	CpCo(podtdt)	CpCo(bddt)	CpCo(dddt)	CpCo(F <sub>2</sub> pdtdt)	CpCo(dmid)
Formula	C <sub>10</sub> H <sub>11</sub> CoS <sub>4</sub>	C <sub>11</sub> H <sub>11</sub> CoS <sub>4</sub>	C <sub>9</sub> H <sub>9</sub> CoS <sub>5</sub>	C <sub>10</sub> H <sub>9</sub> CoS <sub>5</sub>	C <sub>11</sub> H <sub>11</sub> CoS <sub>4</sub>	C <sub>9</sub> H <sub>9</sub> CoS <sub>4</sub>	C <sub>10</sub> H <sub>9</sub> CoF <sub>2</sub> S <sub>4</sub>	C <sub>9</sub> H <sub>9</sub> CoS <sub>4</sub>
FW (g mol <sup>-1</sup> )	318.36	330.37	336.39	332.34	332.38	304.33	354.34	304.30
Crystal color	Darkblue	Darkblue	Darkgreen	Darkblue	Darkblue	Darkblue	Purple	Darkgreen
Crystal shape	Needle	Platelet	Block	Platelet	Chunk	Platelet	Prismatic	Block
Crystal size (mm)	0.575 × 0.025 × 0.025	0.20 × 0.18 × 0.03	0.14 × 0.125 × 0.075	0.125 × 0.075 × 0.075	0.30 × 0.125 × 0.125	0.25 × 0.20 × 0.05	0.125 × 0.125 × 0.075	0.30 × 0.15 × 0.12
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	P-1 (No. 2)	P2 <sub>1</sub> (No. 4)	P2 <sub>1</sub> /c (No. 14)	P2 <sub>1</sub> /n (No. 14)	P2 <sub>1</sub> /n (No. 14)	P-1 (No. 2)	C2/c (No. 15)	Pbcn (No. 60)
Z	298	298	298	298	298	298	298	298
<i>a</i> (Å)	5.5617(19)	5.713(5)	10.887(2)	12.8160(4)	8.5458(8)	8.9747(7)	19.9964(11)	17.814(3)
<i>b</i> (Å)	9.836(4)	11.168(5)	6.1833(11)	6.1476(2)	11.8826(13)	10.9551(9)	9.1563(4)	8.0024(13)
<i>c</i> (Å)	11.442(17)	10.450(5)	18.342(4)	15.3332(5)	12.9164(13)	12.4152(11)	15.8428(9)	14.542(2)
<i>α</i> (°)	89.653(8)	90	90	90	90	107.219(3)	90	90
<i>β</i> (°)	84.857(7)	99.560(5)	97.2910(10)	92.434(2)	92.434(2)	103.656(3)	116.7950(10)	90
<i>γ</i> (°)	86.160(7)	90	90	91.936(2)	91.936(2)	91.936(2)	90	90
<i>V</i> (Å <sup>3</sup> )	622.0(10)	657.5(7)	1223.0(4)	1198.30(7)	1310.4(2)	1125.89(16)	2589.2(2)	2073.0(6)
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.700	1.669	1.827	1.842	1.685	1.795	1.818	1.950
<i>μ</i> (mm <sup>-1</sup> )	2.013	1.908	2.217	2.100	1.915	2.219	1.966	2.418
Total refls.	4921	5183	9087	8440	9848	8812	9180	14,934
Unique refls. ( <i>R</i> <sub>int</sub> )	2770 (0.0144)	2507 (0.0213)	2792 (0.0208)	2672 (0.0181)	2988 (0.0494)	4926 (0.0212)	2848 (0.0178)	2374 (0.023)
Unique refls. ( <i>I</i> > 2σ( <i>I</i> ))	2337	1975	2405	2435	2608	4158	2555	1897
<i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0727	0.0320	0.0331	0.0222	0.0453	0.0327	0.0319	0.0282
<i>wR</i> <sub>2</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.2430	0.0695	0.0858	0.0580	0.1121	0.0927	0.0808	0.0826
Goodness-of-fit	1.238	1.012	1.032	1.046	1.121	1.028	1.067	1.020

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

disordered with two possible orientations, and the refinement was not working well. [CpCo(pdtdt)] was refined in only 94% data completeness with alert A, because of poor crystal quality. In this work, no better crystal of it was obtained. Crystallographic data are summarized in Table 5.

## Appendix A. Supplementary material

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-772211 for [CpCo(F<sub>2</sub>pdtdt)], 772212 for [CpCo(bddt)], 772213 for [CpCo(dddt)], 772214 for [CpCo(dmid)], 772215 for [CpCo(dpdt)], 772216 for [CpCo(dttdt)], 772217 for [CpCo(pdtdt)] and 772218 for [CpCo(podtdt)]. Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336408; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.05.024.

## References

- (a) S.D. Cummings, R. Eisenberg, *Prog. Inorg. Chem.* 52 (2003) 315; (b) M. Hissler, J.E. McGarrah, W.B. Connick, D.K. Geiger, S.D. Cummings, R. Eisenberg, *Coord. Chem. Rev.* 208 (2000) 115; (c) H. Kisch, *Coord. Chem. Rev.* 159 (1997) 385.
- (a) M. Fourmigué, *Acc. Chem. Res.* 37 (2004) 179; (b) C. Faulmann, P. Cassoux, *Prog. Inorg. Chem.* 52 (2003) 399; (c) M. Fourmigué, *Top. Organomet. Chem.* 27 (2009) 161.
- (a) R. Kato, *Chem. Rev.* 104 (2004) 5319; (b) A. Kobayashi, E. Fujiwara, H. Kobayashi, *Chem. Rev.* 104 (2004) 5243.
- C.L. Beswick, J.M. Schulman, E.I. Stiefel, *Prog. Inorg. Chem.* 52 (2003) 55.
- (a) W. Paw, S.D. Cummings, M.A. Mansour, W.B. Connick, D.K. Geiger, R. Eisenberg, *Coord. Chem. Rev.* 171 (1998) 125; (b) S.-K. Lee, K.-S. Shin, D.-Y. Noh, O. Jeannin, F. Barriere, J.-F. Bergamini, M. Fourmigué, *Chem. Asian J.* 5 (2010) 169.
- M. Fourmigué, *Coord. Chem. Rev.* 178 (1998) 823.
- M. Nomura, S. Horikoshi, M. Kajitani, *J. Jpn. Soc. Colour Mater.* 82 (2009) 296.
- M. Nomura, T. Cauchy, M. Fourmigué, *Coord. Chem. Rev.* 254 (2010) 1406.
- A. Sugimori, T. Akiyama, M. Kajitani, T. Sugiyama, *Bull. Chem. Soc. Jpn.* 72 (1999) 879.
- (a) M. Kajitani, G. Hagino, M. Tamada, T. Fujita, M. Sakurada, T. Akiyama, A. Sugimori, *J. Am. Chem. Soc.* 118 (1996) 489; (b) A. Sugimori, N. Tachiya, M. Kajitani, T. Akiyama, *Organometallics* 15 (1996) 5664; (c) M. Nomura, H. Oguro, K. Maeshima, S. Iida, S. Horikoshi, T. Sugiyama, A. Sugimori, M. Kajitani, *J. Organomet. Chem.* 695 (2010) 1613.
- (a) M. Nomura, H. Hatano, T. Fujita, Y. Eguchi, R. Abe, M. Yokoyama, C. Takayama, T. Akiyama, A. Sugimori, M. Kajitani, *J. Organomet. Chem.* 689 (2004) 993; (b) M. Nomura, T. Yagisawa, C. Takayama, T. Sugiyama, Y. Yokoyama, K. Shimizu, A. Sugimori, M. Kajitani, *J. Organomet. Chem.* 611 (2000) 376.
- M. Fourmigué, T. Cauchy, M. Nomura, *Cryst. Eng. Comm.* 11 (2009) 1491.
- C. Takayama, M. Kajitani, T. Sugiyama, A. Sugimori, *J. Organomet. Chem.* 563 (1998) 161.
- M. Nomura, R. Okuyama, C. Fujita-Takayama, M. Kajitani, *Organometallics* 24 (2005) 5110.
- E.J. Miller, T.B. Brill, A.L. Rheingold, W.C. Fultz, *J. Am. Chem. Soc.* 105 (1983) 7580.
- M. Nomura, T. Cauchy, M. Geoffroy, P. Adkine, M. Fourmigué, *Inorg. Chem.* 45 (2006) 8194.
- H.W. Baird, B.M. White, *J. Am. Chem. Soc.* 88 (1966) 4744.
- T. Cauchy, E. Ruiz, O. Jeannin, M. Nomura, M. Fourmigué, *Chem. Eur. J.* 13 (2007) 8858.
- M. Nomura, D. Takeuchi, Y. Toyota, E. Suzuki, C. Fujita-Takayama, T. Sugiyama, M. Kajitani, *J. Organomet. Chem.* 694 (2009) 4261.
- M. Nomura, M. Fourmigué, *New J. Chem.* 31 (2007) 528.
- M. Nomura, M. Fourmigué, *J. Organomet. Chem.* 692 (2007) 2491.
- M. Fourmigué, V. Perrocheau, *Acta Crystallogr. C53* (1997) 1213.
- (a) C. Faulmann, F. Delpéch, I. Malfant, P. Cassoux, *J. Chem. Soc., Dalton Trans.* (1996) 2261; (b) M. Fourmigué, N. Avarvari, *Dalton Trans.* (2005) 1365.
- M. Nomura, M. Geoffroy, P. Adkine, M. Fourmigué, *Eur. J. Inorg. Chem.* (2006) 5012.
- T.B. Rauchfuss, *Prog. Inorg. Chem.* 52 (2003) 1.
- R.P. Singh, D.T. Meshri, J.M. Shreeve, *Adv. Org. Synth.* 2 (2006) 291.
- H. Ushijima, S. Sudoh, M. Kajitani, K. Shimizu, T. Akiyama, A. Sugimori, *Appl. Organomet. Chem.* 5 (1991) 221.
- (a) M. Nomura, C. Fujita-Takayama, T. Sugiyama, A. Sugimori, M. Kajitani, *Inorg. Chem. Commun.* 12 (2009) 711;

- (b) K. Kawabata, M. Nakano, H. Tamura, G. Matsubayashi, *J. Organomet. Chem.* 689 (2004) 405.
- [29] (a) C.-X. Ren, Y.-Q. Ding, *Acta Crystallogr. E* 63 (2007) m249;  
(b) G.-X. Jin, M. Herberhold, A.L. Reingold, *New J. Chem.* 22 (1998) 1035;  
(c) W.-G. Jia, Y.-F. Han, J.-S. Zhang, G.-X. Jin, *Inorg. Chem. Comm.* (2007) 1222.
- [30] M. Nomura, E. Tsukano, C. Fujita-Takayama, T. Sugiyama, M. Kajitani, *J. Organomet. Chem.* 694 (2009) 3116.
- [31] (a) O.J. Dautel, M. Fourmigué, E. Canadell, P. Auban-Senzier, *Adv. Funct. Mater.* 12 (2002) 693;  
(b) O.J. Dautel, M. Fourmigué, *Inorg. Chem.* 40 (2001) 2083.
- [32] (a) O.J. Dautel, M. Fourmigué, E. Faulques, *Cryst. Eng. Comm.* 4 (2002) 249;  
(b) O. Jeannin, M. Fourmigué, *C. R. Chim* 9 (2006) 1287.
- [33] O. Jeannin, M. Fourmigué, *Chem. Eur. J.* 12 (2006) 2994.
- [34] (a) R. Kato, A. Tajima, A. Nakao, M. Tamura, *J. Am. Chem. Soc.* 128 (2006) 10016;  
(b) S. Ohira, M. Tamura, R. Kato, *Mol. Cryst. Liq. Cryst.* 379 (2002) 41.
- [35] (a) J.S. Pap, F.L. Bedito, E. Bothe, E. Bill, S. DeBeer George, T. Weyhermueller, K. Wieghardt, *Inorg. Chem.* 46 (2007) 4187;  
(b) M. Nomura, M. Fujii, K. Fukuda, T. Sugiyama, Y. Yokoyama, M. Kajitani, *J. Organomet. Chem.* 690 (2005) 1627.
- [36] F. Guyon, D. Lucas, I.V. Jourdain, M. Fourmigué, Y. Mugnier, H. Cattey, *Organometallics* 20 (2001) 2421.
- [37] (a) B.-H. Zhu, Y. Shibata, S. Muratsugu, Y. Yamanoi, H. Nishihara, *Angew. Chem. Int. Ed.* 48 (2009) 3858;  
(b) Y. Shibata, B. Zhu, S. Kume, H. Nishihara, *Dalton Trans.* (2009) 1939.
- [38] B. Zhou, M. Shimamura, E. Fujiwara, A. Kobayashi, T. Higashi, E. Nishibori, M. Sakata, H.B. Cui, K. Takahashi, H. Kobayashi, *J. Am. Chem. Soc.* 128 (2006) 3872.
- [39] A. Fukaya, R. Kato, *J. Phys. Soc. Jpn.* 77 (2008) 094710.
- [40] R.B. King, *Inorg. Chem.* 5 (1966) 82.
- [41] T.S. Piper, F.A. Cotton, G. Wilkinson, *J. Inorg. Nucl. Chem.* 1 (1955) 313.
- [42] G. Steimecke, H. Sieler, R. Kirmse, E. Hoyer, *Phosphorus, Sulfur Silicon Relat. Elem.* 7 (1979) 49.
- [43] S.-G. Liu, P.-J. Wu, Y.-Q. Liu, D.-B. Zhu, *Phosphorus, Sulfur Silicon Relat. Elem.* 106 (1995) 145.
- [44] M. Kumasaki, H. Tanaka, A. Kobayashi, *J. Mater. Chem.* 8 (1998) 301.
- [45] O.J. Dautel, M. Fourmigué, *J. Org. Chem.* 65 (2000) 6479.
- [46] A. Charlton, A.E. Underhill, A. Kobayashi, H. Kobayashi, *J. Chem. Soc., Dalton Trans.* (1995) 1285.
- [47] H. Mueller, Y. Ueba, *Bull. Chem. Soc. Jpn.* 66 (1993) 1773.
- [48] M.R. Bryce, G.J. Marshall, *Tetrahedron Lett.* 32 (1991) 6033.
- [49] S.K. Kumar, H.B. Singh, J.P. Jasinski, E.S. Paight, R.J. Butcher, *J. Chem. Soc., Perkin Trans. 1* (1991) 3341.
- [50] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits, C. Smykala, The DIRDIF Program System, Technical Report of the Crystallography Laboratory, University of Nijmegen, Nijmegen, The Netherlands, 1992.
- [51] WINGX 1.70 L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837.
- [52] Crystal Structure 3.6.0, Single Crystal Structure Analysis Software. Molecular Structure Corporation and Rigaku Corporation, The Woodlands, TX; Tokyo, Japan, 2004.