Formations and structures of cobalt dithiolene complexes with nitrogen group-substituted cyclopentadienyl ligands

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Abstract

The cobalt dithiolene complex with the sulfonylamide-substituted Cp ligand $[(C_5H_4-NHTs)Co\{S_2C_2(COOMe)_2\}]$ (**1**, Ts = p-$SO_2C_6H_4Me$) reacted with TsOH · H_2O to give $[(C_5H_4-NH_2)Co\{S_2C_2(COOMe)(H)\}]$ (**2**), $[(C_5H_4-NHTs)Co(S_2C_2H_2)]$ (**3**) and $[(C_5H_4-NHTs)Co\{S_2C_2(COOMe)(H)\}]$ (**4**). Complex **1** was dissolved in a basic aqueous solution, and the anion reacted with Me_2SO_4 to form the N-methylated product $[\{C_5H_4-N(Me)Ts\}Co\{S_2C_2(COOMe)_2\}]$ (**5**); the carboxylic acid complex $[\{C_5H_4-N(Me)Ts\}Co\{S_2C_2(COOMe)(COOH)\}]$ (**6**) formed by a base hydrolysis. The X-ray crystal structures of complexes **4–6** and the methylsulfonylamide-substituted Cp complex $[(C_5H_4-NHMs)Co\{S_2C_2(COOMe)_2\}]$ (**7**, Ms = SO_2Me) were determined. In the crystal structures of complexes **4** and **7**, intermolecular hydrogen bondings of NH···O (ca. 2.1 Å) and NH···S (ca. 3.1 Å) were observed. Complex **6** showed the OH···O intermolecular hydrogen bonding (ca. 1.6 Å) of COOH moiety between two molecules, and these two molecules were assembling each other. Complexes **5** and **6** showed an intramolecular π–π interaction between the aromatic cobaltadithiolene and benzene rings, and complex **5** also has intermolecular π–π interactions between two benzene rings, and between two cobaltadithiolene rings.
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1. Introduction

Molybdenum cofactors (Moco) are consisted of a mononuclear molybdenum dithiolene structure with pterin ligands [1]. In many cases, the mononuclear molybdenum dithiolene complex has an active metal center for some important oxo-transfer reactions (e.g., xanthine oxidase [2], sulfite oxidase [3], DMSO reductase [4]). Garner et al. have reported some cobalt dithiolene complexes that can be formulated as [CpCo(dithiolene-HET)] (Cp = η⁵-cyclopentadienyl) having heterocycles (HET), and the HET group includes pterin or pteridine analogues for a model compound of Moco [5]. The pterin contains an amide structure having an affinity for an organism, and the amide group is interesting for study of a crystal structure study containing a hydrogen bonding interaction. The chemistry of a hydrogen bonding interaction has been investigated in the studies of a metal dithiolene [6] and a tetrathiafulvalene (TTF) compound [7].

We have reported the cobalt dithiolene complex (**1**) with the sulfonylamide-substituted cyclopentadienyl ligand $[(C_5H_4-NHTs)Co\{S_2C_2(COOMe)_2\}]$ (Ts = p-$SO_2C_6H_4Me$). An amide structure is included on the substituent of cobalt-adithiolene ring in the pterin complex reported by Garner [5] and other dithiolene complexes [6], but our complex **1** has an amide substituent on the Cp ring, which is also an interesting complex as an organometallic compound. Complex **1** can be synthesized by the phosphine- or phosphite-induced imido-migration reaction: the reaction of the imido-bridged cobalt dithiolene complex [CpCo{S_2C_2-

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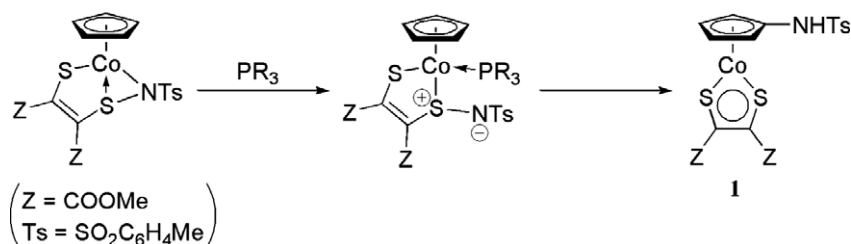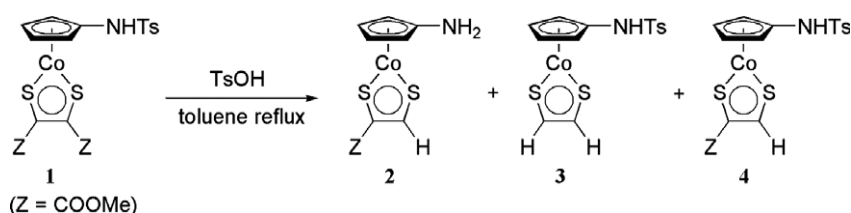
Scheme 1.

(COOMe)$_2$}(NTs)] with PR$_3$ undergoes an intramolecular imido-migration to the Cp ring, and this reaction forms the sulfonylamide-substituted Cp complex **1** (Scheme 1) [8]. This is the first case of a nitrogen group migration to the Cp ligand. Esteruelas et al. have later reported the migration of an amino ligand (NR$_2$) to the Cp ring in the reaction of the osmium complex [CpOs(H)(Cl)(NR$_2$)(PR$_3$)] [9]. These migration reactions are useful for the formation of a nitrogen group-substituted Cp ligand, because such a ligand is generally difficult to synthesize.

In this work, the conversion of the sulfonylamide group (NHTs) in complex **1** was our strategy for other nitrogen group-substituted Cp cobalt dithiolene complexes. Using a hydrolysis reaction is one methodology for the conversion of a sulfonylamide group. We report on the acid and base hydrolysis of complex **1**. Furthermore, we found that complex **1** showed water-solubility at a basic condition. Recently, the synthesis and reactivity of an organometallic complex in an aqueous solution have been intensively investigated [10]. The reaction of complex **1** was performed in an aqueous solution. Moreover, we particularly report on the X-ray crystal structures of four cobalt dithiolene complexes with a nitrogen group-substituted cyclopentadienyl ligand, and we discuss a molecular stacking controlled by a hydrogen bonding and π–π interaction between aromatic rings.

2. Results and discussion

2.1. Reaction of complex 1 in acidic solution

The reaction of complex **1** with TsOH · H$_2$O in refluxing toluene (Scheme 2) gave [(C$_5$H$_4$-NH$_2$)Co{S$_2$C$_2$(COOMe)(H)}] (**2**, 6% yield), [(C$_5$H$_4$-NHTs)Co(S$_2$C$_2$H$_2$)] (**3**, trace amount), and [(C$_5$H$_4$-NHTs)Co{S$_2$C$_2$(COOMe)(H)}] (**4**, 26% yield (main product)). Complexes **2** and **3** were somewhat air-sensitive in both a solution and a solid states.

Although the only complex **2** was produced by a detosylation of complex **1**, the all products **2–4** lost one or two COOMe groups of cobaltadithiolene substituents. Proposed reaction mechanisms of the COOMe loss are the acid hydrolysis of the COOMe to form COOH group as a first reaction, and then carbon dioxide is eliminated from the COOH group when a heating is supplied. However, when this reaction was performed without heating (at room temperature), no reaction was confirmed. Therefore, in this reaction condition, the COOMe group of complex **1** is easier to be hydrolyzed than the NHTs group. An acid hydrolysis of complex **1** with H$_2$SO$_4$ was attempted in an aqueous solution, but a complicated decomposition was resulted.

2.2. Reaction of complex 1 in basic solution

When complex **1** was added into an aqueous solution containing excess NaOH, the complex was easily dissolved at room temperature. When Me$_2$SO$_4$ was added into this aqueous solution, and then a purple precipitation was formed immediately. After the reaction mixture was extracted with an organic solvent, products in the organic layer were separated by a silica-gel column chromatography. The *N*-methylated product [{C$_5$H$_4$-N(Me)Ts}-Co{S$_2$C$_2$(COOMe)$_2$}] (**5**) was obtained in 17% yield (Scheme 3). Complex **1** did not directly react with Me$_2$SO$_4$ in an organic solvent (e.g., benzene or dichloromethane), and complex **1** was not dissolved in a non-basic aqueous solution. These results suggest that the acidic NHTs group of complex **1** is deprotonated in a basic solution, and then the generated anion [(C$_5$H$_4$-NTs)Co{S$_2$C$_2$(COOMe)$_2$}]$^-$ is dissolved for the aqueous solution. Furthermore, the reaction described in Scheme 1 also produced the carboxylic acid complex which can be formulated as [{C$_5$H$_4$-N(Me)Ts}Co{S$_2$C$_2$(COOMe)(COOH)}] (**6**) as the main product in 48% yield. The complex **6** was a very polar

Scheme 2.

Scheme 3.
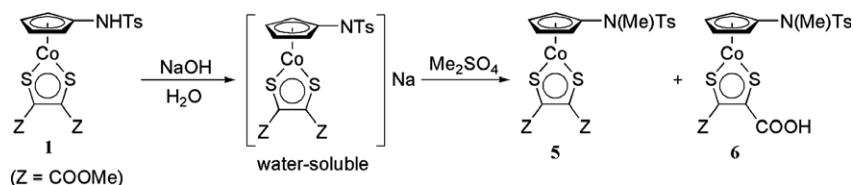
product, and it could be separated by acetone/methanol mixed-solvent using a silica-gel column chromatography. We assume that complex **6** was formed by a base hydrolysis of the COOMe group.

2.3. Product identifications and X-ray crystal structure analyses

The ^{1}H NMR spectra of complexes **2–6** showed two triplet signals in a cyclopentadienyl region, and these results indicate that there is a mono-substituted cyclopentadienyl ligand in complexes **2–6**. Complexes **2–4** resulted in singlet signals of low magnetic field of dithiolene protons at 8.46, 8.98 and 9.11 ppm (vs. TMS in CDCl$_3$), respectively. These δ values are lower than the magnetic field of a typical olefin proton. This result is explained by the effect of a strong ring current [11] in the five-membered cobalt-adithiolene ring.

The crystal structures of complexes **4–6** were determined by X-ray structure analyses. The ORTEP drawings together with selected bond lengths and angles are shown in Figs. 1a, 2a and 3a, respectively. The packing diagrams are given in Figs. 1b, 2b and 3b. This paper also reports on the X-ray crystal structure (Figs. 4a and b) of the meth-
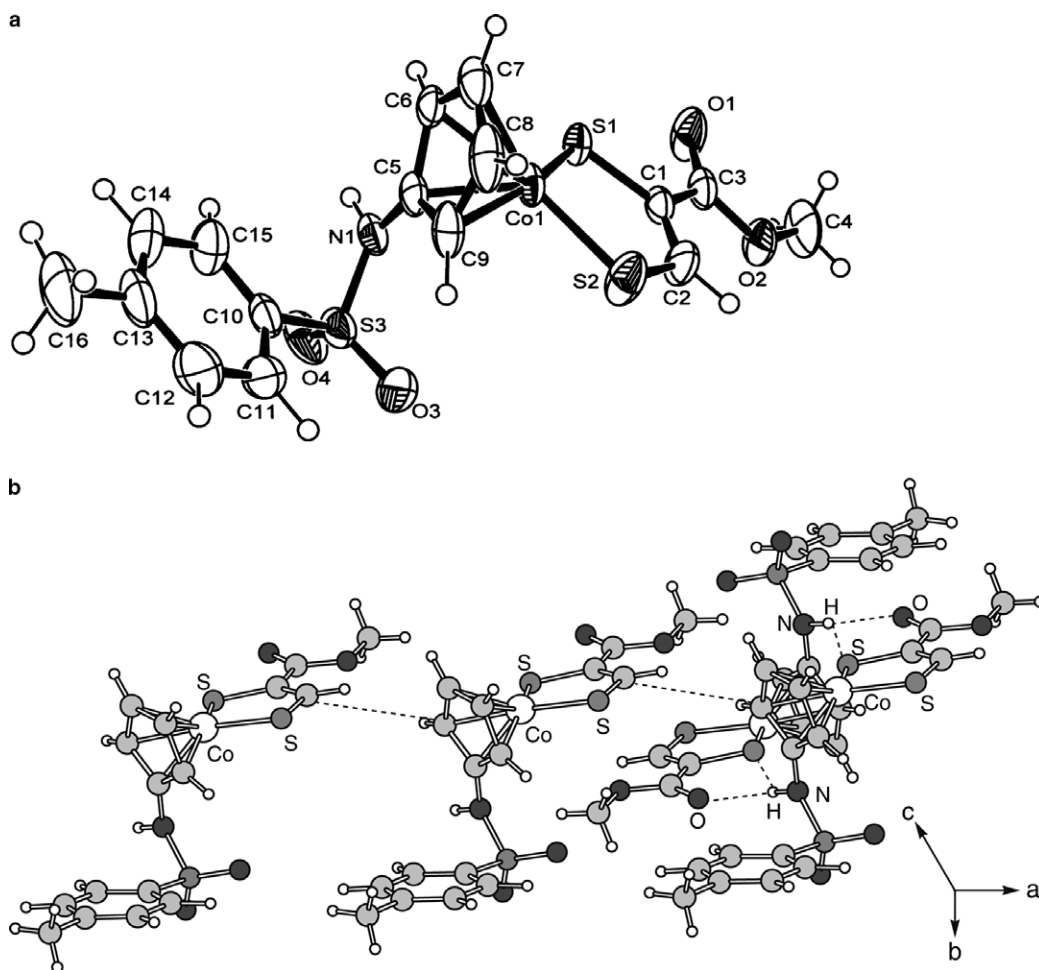

Fig. 1. (a) ORTEP drawing of [(C$_5$H$_4$-NHTs)Co{S$_2$C$_2$(COOMe)(H)}] (**4**). The thermal ellipsoids are drawn at 50% probability level. Selected bond lengths (Å): Co1–S1 = 2.1770(7), Co1–S2 = 2.1800(9), S1–C1 = 1.703(2), S2–C2 = 1.676(3), C1–C2 = 1.485(4). Selected bond angles (°): S1–Co1–S2 = 101.86(3), Co1–S1–C1 = 94.79(9), Co1–S2–C2 = 95.0(1), S1–C1–C2 = 123.6(2), S2–C2–C1 = 124.8(2). (b) Packing diagram of [(C$_5$H$_4$-NHTs)Co{S$_2$C$_2$(COOMe)(H)}] (**4**) showing NH···O and NH···S hydrogen bondings and head-to-tail arrangement.
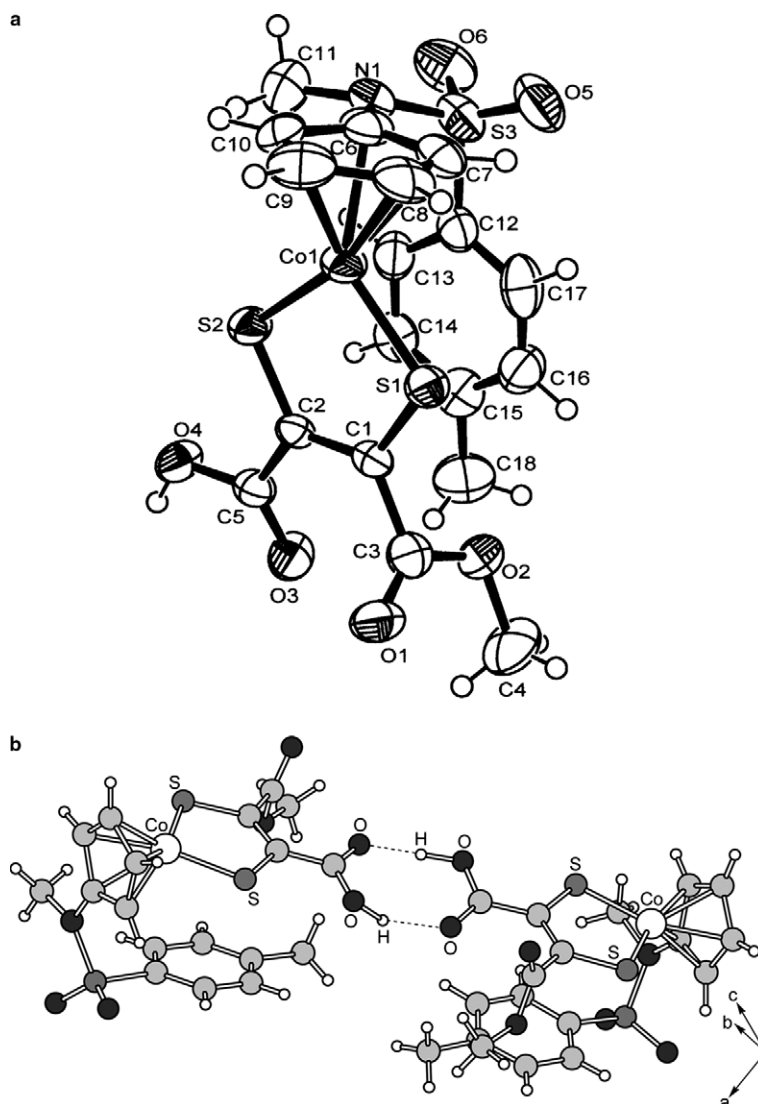
Fig. 2. (a) ORTEP drawing of [{C$_5$H$_4$-N(Me)Ts}Co{S$_2$C$_2$(COOMe)$_2$}] (5). One of two independent molecules is shown. The thermal ellipsoids are drawn at 50% probability level. Selected bond lengths (Å): Co1–S1 = 2.101(1), Co1–S2 = 2.118(1), S1–C1 = 1.714(4), S2–C2 = 1.710(4), C1–C2 = 1.358(5). Selected bond angles (°): S1–Co1–S2 = 91.98(4), Co1–S1–C1 = 104.9(1), Co1–S2–C2 = 104.4(1), S1–C1–C2 = 119.1(3), S2–C2–C1 = 119.6(3). (b) Packing diagram of [{C$_5$H$_4$-N(Me)Ts}Co{S$_2$C$_2$(COOMe)$_2$}] (5) showing π–π stacking of molecules.

ylsulfonylamide-substituted Cp complex [(C$_5$H$_4$-NHMs)-Co{S$_2$C$_2$(COOMe)$_2$}] (7, Ms = SO$_2$Me) analogous to complex 1, whose synthesis and spectroscopic data have been reported previously [8a]. In complexes 4–7, the Co–S bond lengths of the cobaltadithiolene ring were 2.086–2.180 Å (Table 1), and such values are shorter than the typical bond lengths of Co(III)–S (2.25–2.48 Å) [12]. This can be explained if the shorter bond length of the cobaltadithiolene ring is due to a π-electron donation from sulfur to metal center [13]. Such π-electron donation undergoes a delocalization of 6π electrons, and the electronic effect gives a strong ring current [11] in a cobaltadithiolene ring. In

other words, there is an pseudo-aromaticity in the cobaltadithiolene ring [14].

The mean deviations from the cobaltadithiolene plane are 0.0045 (4), 0.0048 (5), 0.0264 (6) and 0.0154 (7) Å (Table 1). Therefore, these cobaltadithiolene rings are extremely planar. The dihedral angles between the cobaltadithiolene and Cp planes are almost right angles (87.369 (4), 92.654 (5), 95.038 (6) and 90.713 (7) in Table 1). Namely, these complexes have typical two-legged piano-stool geometries identical to those of the 16-electron CpCo^{III} [15], CpRh^{III} [16] and CpIr^{III} [17] dithiolene complexes. In other cases, (η^6-arene)Ru^{II} [18] and CpNi^{III}

Fig. 3. (a) ORTEP drawing of [{C₅H₄-N(Me)Ts}Co{S₂C₂(COOMe)(COOH)}] (6). One of two independent molecules is shown. The thermal ellipsoids are drawn at 50% probability level. Selected bond lengths (Å): Co1–S1 = 2.112(3), Co1–S2 = 2.100(2), S1–C1 = 1.693(7), S2–C2 = 1.709(8), C1–C2 = 1.37(1). Selected bond angles (°): S1–Co1–S2 = 92.83(9), Co1–S1–C1 = 103.8(3), Co1–S2–C2 = 103.9(2), S1–C1–C2 = 120.0(6), S2–C2–C1 = 119.3(5). (b) Packing diagram of [{C₅H₄-N(Me)Ts}Co{S₂C₂(COOMe)(COOH)}] (6) showing an assembly of two molecules in those COOH moieties.

[19] dithiolene complexes have similar two-legged piano-stool structures as half-sandwich metal dithiolene complexes.

Complex 4 was regularly arranged in head-to-tail positions (Fig. 1b), and the intermolecular distance between the Cp carbons and the dithiolene carbon (C2) is close (ca. 3.7 Å). In complexes 5 and 6, the benzene rings and cobaltadithiolene rings are placed face-to-face at a distance of ca. 3.5 Å (Figs. 2b and 3b), and especially both rings are quite parallel in complex 6 because the dihedral angle of benzene/cobaltadithiolene is 2.845° (Table 1). This tendency is also found in the crystal structure of complex 1 [8a]. We assume that there are intramolecular π–π interactions between the two aromatic rings. Furthermore, intermolecular π–π interactions between two benzene rings (ca. 3.7 Å) and between two cobaltadithiolene rings (ca. 4.5 Å) were found in complex 5 (Fig. 2b). Unexpectedly,

complex 4 showed neither intramolecular nor intermolecular π–π interaction (Figs. 1a and b) though both aromatic rings are located in parallel position (the dihedral angle of benzene/cobaltadithiolene = 8.018° in Table 1).

In complexes 4 and 7 having an amide group, intermolecular hydrogen bondings were observed. The N1H···O (carbonyl oxygen) distances were 2.072(3) Å in complex 4, and 2.172(7) Å in complex 7, and the N1H···S (dithiolene sulfur) distances were 3.130(2) Å in complex 4 and 3.110(5) Å in complex 7 (Table 1). Complex 7 has an alternate stacking structure with the intermolecular hydrogen bonding (Fig. 4b). In previous reports, we already reported an intermolecular hydrogen bonding in complex 1 (N1H···O = 1.946(23) Å and N1H···S = 2.877(34) Å) [8a] and in the cobalt dithiolene complex formulated as [CpCo{S₂C₂(COOMe)(CONHTs)}] (N1H···O = 2.144-(2) Å and N1H···S = 3.5419(7) Å) [20]. Mashima et al.
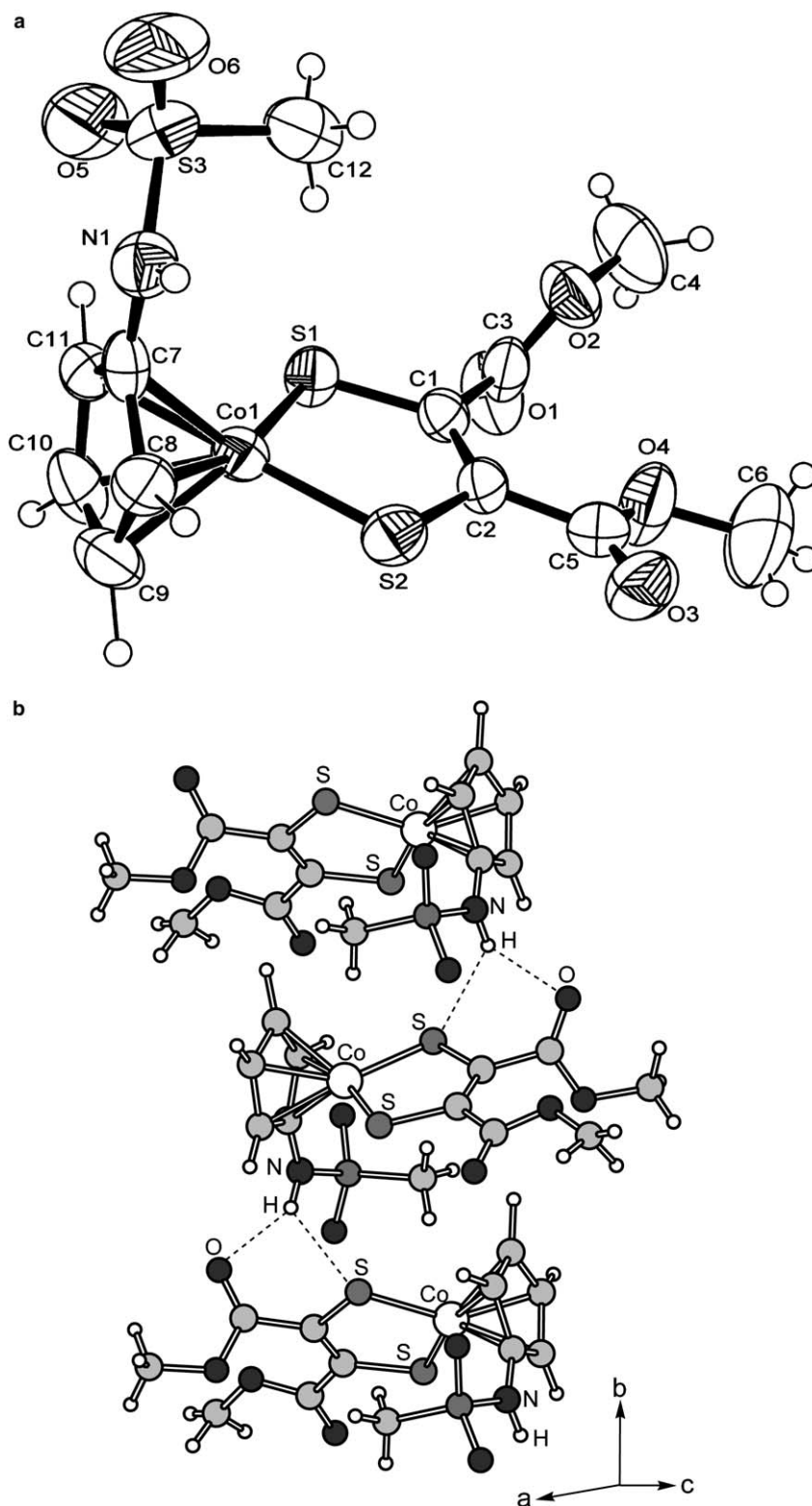
Fig. 4. (a) ORTEP drawing of $[(C_5H_4\text{-}NHMs)Co\{S_2C_2(COOMe)_2\}]$ (**7**). The thermal ellipsoids are drawn at 50% probability level. Selected bond lengths (Å): Co1–S1 = 2.107(2), Co1–S2 = 2.096(2), S1–C1 = 1.718(5), S2–C2 = 1.719(6), C1–C2 = 1.355(7). Selected bond angles (°): S1–Co1–S2 = 92.45(7), Co1–S1–C1 = 104.5(2), Co1–S2–C2 = 104.5(2), S1–C1–C2 = 119.0(4), S2–C2–C1 = 119.5(4). (b) Packing diagram of $[(C_5H_4\text{-}NHMs)Co\{S_2C_2\text{-}(COOMe)_2\}]$ (**7**) showing NH···O and NH···S hydrogen bondings and a molecular stacking.

have reported the binuclear ruthenium dithiolene complex bridged by the η^2-hydrazine ligand $[(\eta^6\text{-}C_6Me_6)Ru\text{-}(S_2C_6H_4)]_2$ ($\eta^2\text{-}NH_2NH_2$), which has the NH···S hydrogen

bonding (3.18 and 3.22 Å) [21]. Recently, the square-planar nickel bisdithiolene complexes with amide groups have been reported; they show NH···O intermolecular hydrogen

Table 1
Bond lengths, intermolecular hydrogen bonding distances, mean deviations from cobaltadithiolene plane, and dihedral angles of cobalt dithiolene complexes

	1[a]	**4**	**5**[b]	**6**[b]	**7**
Bond length (Å)					
Co1–S1	2.112(3)	2.1770(7)	2.101(1)	2.112(3)	2.107(2)
Co1–S2	2.102(3)	2.1800(9)	2.118(1)	2.100(2)	2.096(2)
S1–C1	1.697(10)	1.703(2)	1.714(4)	1.693(7)	1.718(5)
S2–C2	1.726(9)	1.676(3)	1.710(4)	1.709(8)	1.719(6)
C1–C2	1.35(1)	1.485(4)	1.358(5)	1.37(1)	1.355(7)
Hydrogen bonding (Å)					
NH···O	1.946(23)	2.072(3)	–	–	2.172(7)
NH···S	2.877(34)	3.130(2)	–	–	3.110(5)
OH···O	–	–	–	1.695(5)	–
				1.580(5)	
Mean deviation (Å) from cobaltadithiolene plane	0.005	0.0045	0.0048	0.0264	0.0154
Dihedral angle (°) of Cp/cobaltadithiolene	88.84	87.369	92.654	95.038	90.713
Dihedral angle (°) of benzene/cobaltadithiolene	12.35	8.018	15.982	2.845	–

[a] Ref. [8a].
[b] Data of one of two independent molecules.

bondings (ca. 2.02–2.08 Å) [6a]. In addition, the NH···S hydrogen bonding has also been reported in some complexes with bulky thiolato ligands; (Me_2NHCH_2-CH_2NHMe_2)[$Pd(SC_6F_5)_4$] (3.256(6) Å) [22], (Me_3NCH_2-$CONH_2$)$_2$[$Co(SPh)_4$] (3.316(3)–3.453(3) Å) [23], and [$Mo(O)(S$-o-$C_6H_4CONHMe)$]$^-$ (2.97–3.03 Å) [24]. Furthermore, complex **6** has OH···O (carbonyl oxygen) intermolecular hydrogen bondings of 1.580(5) and 1.695(5) Å in COOH moiety between two molecules, and two molecules were assembling each other like a typical carboxylic acid (Fig. 3b). The TTF compounds having carboxylic acid were also reported, and the structure of the carboxylic acid dimer has been observed [25].

2.4. Conclusion

In this work, we found interesting π–π interactions: the intramolecular π–π interaction between benzene ring and cobaltadithiolene ring in complexes **5** and **6**, the intermolecular π–π interactions between two benzene rings, and between two cobaltadithiolene rings in complex **5**. These results indicate one of remarkable features of aromatic metalladithiolene rings. We have reported electrophilic and radical substitution reactions of metalladithiolene ring due to its aromaticity [26]. Moreover, some intermolecular hydrogen bondings were observed in the NH···O and NH···S moieties of complexes **4** and **7**, and in the OH···O moiety of complex **6**. These π–π interactions and the hydrogen bondings formed a molecular stacking and a molecular assembling. Interestingly, the only complex **5** which does not have a strong hydrogen bonding, showed both intramolecular and intermolecular interactions between aromatic rings. In this case, we assume that the hydrogen bonging interferes with the π–π stacking of aromatic rings.

The products in this work were obtained by the hydrolysis of the cobalt dithiolene complex (**1**) with the sulfonyamide-substituted cyclopentadienyl ligand [(C_5H_4-

NHTs)Co{S_2C_2(COOMe)$_2$}]. The sulfonylamide group was converted to amino group (–NH_2) by an acid hydrolysis, or was converted to the *N*-metylamide group (–N(Me)Ts) by a methylation in a basic aqueous solution. The base hydrolysis of COOMe group in complex **1** produced the cobalt dithiolene complex with carboxylic acid. Although a nitrogen group-substituted Cp ligand is generally difficult to synthesize, we could obtain some nitrogen group-substituted Cp cobalt dithiolene complexes by the imido-migration [8] and by the conversion of the sulfonylamide group in complex **1**.

3. Experimental section

3.1. General remarks

All reactions were carried out under argon atmosphere by means of standard Schlenk techniques. Organic solvents were dried by known procedures and distilled before use. TsOH · H_2O, NaOH and Me_2SO_4 were obtained from Wako Pure Chemical Industries, Ltd. and these were used without further treatment. Complexes **1** and **7** were prepared by literature methods [8a]. Silica gel (Wakogel C-300) was obtained from Wako Pure Chemical Industries, Ltd. Mass and IR spectra were recorded on a JEOL JMS-D300 and Shimadzu model FT-IR 8600PC, respectively. NMR spectra were measured with a JEOL LA500 spectrometer. UV–Vis were recorded on Hitachi model UV-2500PC. Elemental Analyses were determined by using a Shimadzu PE2400-II instrument. Melting points were measured by Yanaco model Micro melting point apparatus.

3.2. Reaction of complex 1 in acidic solution

A solution of complex **1** (100 mg, 0.2 mmol) and TsO-H · H_2O (380 mg, 2.0 mmol) in toluene (40 mL) was refluxed

for 24 h. The reaction mixture was extracted by CH_2Cl_2/H_2O, and the organic layer was dried with $MgSO_4$. After the organic solvent was removed under reduced pressure, the residue was separated by a column chromatography (silica-gel, eluent = dichloromethane). The purple products noted below were obtained: $[(C_5H_4-NH_2)Co\{S_2C_2(COOMe)(H)\}]$ (**2**, 3 mg, 0.012 mmol, 6% yield), $[(C_5H_4-NHTs)Co(S_2C_2H_2)]$ (**3**, a trace amount) and $[(C_5H_4-NHTs)Co\{S_2C_2(COOMe)(H)\}]$ (**4**, 23 mg, 0.052 mmol, 26% yield). Complex **4** was further purified by recrystallization from CH_2Cl_2/n-hexane.

$[(C_5H_4-NH_2)Co\{S_2C_2(COOMe)(H)\}]$ (**2**). Mass (EI$^+$, 70 eV) m/z (rel. intensity) 287 (M$^+$, 100), 203 ($(C_5H_4-NH_2)CoS_2^+$, 69.9), 139 ($(C_5H_4-NH_2)Co^+$, 12.7), 80 ($C_5H_4-NH_2^+$, 53.4). ^1H NMR (500 MHz, CDCl$_3$, vs. TMS) δ 8.98 (s, 1H, dithiolene-H), 5.33 (t, $J = 2.01$ Hz, 2H, Cp), 5.04 (t, $J = 2.01$ Hz, 2H, Cp), 4.71 (broad, 2H, NH$_2$), 3.83 (s, 3H, OMe). HR-Mass (EI$^+$) m/z: Anal. Calc. for $C_9H_{10}N_1O_2S_2Co_1$: 286.9485. Found: 286.9487.

$[(C_5H_4-NHTs)Co(S_2C_2H_2)]$ (**3**). Mass (EI$^+$, 70 eV) m/z (rel. intensity) 383 (M$^+$, 70.7), 91 ($C_6H_4Me^+$, 100). ^1H NMR (500 MHz, CDCl$_3$, vs. TMS) δ 8.46 (s, 2H, dithiolene-H), 7.44 (d, $J = 8.22$ Hz, 2H, C_6H_4), 6.98 (d, $J = 8.22$ Hz, 2H, C_6H_4), 5.47 (t, $J = 2.05$ Hz, 2H, Cp), 4.99 (t, $J = 2.05$ Hz, 2H, Cp), 2.32 (s, 3H, Me). HR-Mass (EI$^+$) m/z. Anal. Calc. for $C_{14}H_{14}N_1O_2S_3Co_1$: 382.9519. Found: 382.9515.

$[(C_5H_4-NHTs)Co\{S_2C_2(COOMe)(H)\}]$ (**4**). M.p. 229–230 °C. Mass (EI$^+$, 70 eV) m/z (rel. intensity) 441 (M$^+$, 100), 357 ($(C_5H_4-NHTs)CoS_2^+$, 3.3), 155 (Ts$^+$, 22.5), 91 ($C_6H_4Me^+$, 74.1). ^1H NMR (500 MHz, CDCl$_3$, vs. TMS) δ 9.11 (s, 1H, dithiolene-H), 7.37 (d, $J = 8.50$ Hz, 2H, C_6H_4), 6.90 (d, $J = 8.50$ Hz, 2H, C_6H_4), 5.63 (t, $J = 2.05$ Hz, 2H, Cp), 5.04 (t, $J = 2.05$ Hz, 2H, Cp), 3.87 (s, 3H, OMe), 2.25 (s, 3H, Me). UV–Vis (CH_2Cl_2) λ_{max} (ε) 575 (6500), 354 (4000), 288 (16000). IR (KBr disk) 3157, 1676, 1506, 1356, 1281, 1165, 862 cm^{-1}. Anal. Calc. for $C_{16}H_{16}N_1O_4S_3Co_1$: C, 43.53; H, 3.65; N, 3.17. Found: C, 43.80; H, 3.71; N, 3.32%.

3.3. Reaction of complex 1 in basic solution

Complex **1** (100 mg, 0.2 mmol) was added into a 20 mL aqueous solution containing NaOH (160 mg, 4.0 mmol). After the complex was dissolved, Me$_2$SO$_4$ (3.78 mL, 40 mmol) was added into this solution. The reaction mixture was stirred at room temperature for 30 min, and then a purple precipitation was formed. The reaction mixture was extracted by CH_2Cl_2/H_2O, and the organic layer was dried with MgSO$_4$. After the organic solvent was removed under reduced pressure, the residue was separated by a silica-gel column chromatography. The products, $[\{C_5H_4-N(Me)Ts\}Co\{S_2C_2(COOMe)_2\}]$ (**5**, eluent = dichloromethane) and $[\{C_5H_4-N(Me)Ts\}Co\{S_2C_2(COOMe)(COOH)\}]$ (**6**, eluent = acetone/methanol = 1:1 (v/v)), were obtained as purple solids in 17% (17 mg, 0.034 mmol) and 48% (48 mg, 0.096 mmol) yields, respectively. Complexes **5** and **6** were

further purified by recrystallization from CH_2Cl_2/n-hexane. Complex **1** was recovered in 32% yield.

$[\{C_5H_4-N(Me)Ts\}Co\{S_2C_2(COOMe)_2\}]$ (**5**). M.p. 137–138 °C. Mass (EI$^+$, 1.3 kV) m/z (rel. intensity) 513 (M$^+$, 100), 371 ($\{C_5H_4-N(Me)Ts\}CoS_2^+$, 13), 356 ($(C_5H_4-NTs)$-$CoS_2^+$, 47), 91 ($C_6H_4Me^+$, 88), 59 (Co$^+$, 43). ^1H NMR (500 MHz, CDCl$_3$, vs. TMS) δ 7.24 (d, $J = 8.24$ Hz, 2H, C_6H_4), 6.98 (d, $J = 8.24$ Hz, 2H, C_6H_4), 5.72 (t, $J = 2.67$ Hz, 2H, Cp), 5.13 (t, $J = 2.67$ Hz, 2H, Cp), 3.88 (s, 6H, OMe), 3.23 (s, 3H, NMe), 2.25 (s, 3H, Me). ^{13}C NMR (125 MHz, CDCl$_3$, vs. TMS) δ 165.1 (C=O), 159.0 (dithiolene carbon), 145.1, 129.6, 129.5, 127.0 (benzene carbon), 114.0, 76.0, 71.1 (Cp), 52.9 (OMe), 37.9 (NMe), 21.3 (Me). UV–Vis (CH_2Cl_2) λ_{max} (ε) 571 (6900), 367 (4100), 292 (18000). IR (KBr disk) 1707, 1474, 1242, 1165 cm^{-1}. Anal. Calc. for $C_{18}H_{18}N_1O_6S_3Co_1$: C, 44.44; H, 3.93; N, 2.73. Found: C, 44.19; H, 3.83; N, 2.51%.

$[\{C_5H_4-N(Me)Ts\}Co\{S_2C_2(COOMe)(COOH)\}]$ (**6**). M.p. 176–177 °C (dec.). Mass (EI$^+$, 70 eV) m/z (rel. intensity) 499 (M$^+$, 3.0), 455 (M$^+$−CO$_2$, 6.9), 249 ($C_5H_5NMeTs^+$, 22.4), 155 (Ts$^+$, 14.3), 94 ($C_5H_5NMe^+$, 100), 91 ($C_6H_4Me^+$, 89.8). ^1H NMR (500 MHz, CDCl$_3$, vs. TMS) δ 7.25 (d, $J = 8.41$ Hz, 2H, C_6H_4), 6.96 (d, $J = 8.41$ Hz, 2H, C_6H_4), 5.76 (t, $J = 2.30$ Hz, 2H, Cp), 5.17 (t, $J = 2.30$ Hz, 2H, Cp), 3.99 (s, 6H, OMe), 3.23 (s, 3H, NMe), 2.26 (s, 3H, Me). ^{13}C NMR (125 MHz, CDCl$_3$, vs. TMS) δ 166.7 (C=O), 156.3 (dithiolene carbon), 145.1, 129.7, 129.5, 127.1 (benzene carbon), 114.6, 76.9, 71.0 (Cp), 53.9 (OMe), 38.0 (NMe), 21.4 (Me). UV–Vis (CH_2Cl_2) λ_{max} (ε) 566 (6200), 402 (4200), 384 (4200), 297 (20000). IR (KBr disk) 1717, 1670, 1474, 1254, 1173 cm^{-1}. Anal. Calc. for $C_{18}H_{18}N_1O_6S_3Co_1$: C, 43.28; H, 3.63; N, 2.80; S, 19.26. Found: C, 43.47; H, 3.50; N, 2.79; S, 19.17%.

3.4. X-ray diffraction study

Single crystals of complexes **4**–**7** were obtained by recrystallization from the dichloromethane solutions and then vapor diffusion of n-hexane into those solutions. Each measurement was made on a Rigaku MERCURY diffractometer with graphite-monochromated Mo Kα radiation. The data were corrected for Lorentz and polarization effects. Each structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All the calculations were carried out using the Crystal Structure crystallographic software package. Crystallographic data of complexes **4**–**7** are summarized in Table 2.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 282968 (**4**), 282969 (**5**), 282970 (**6**) and 282971 (**7**). Copies of the data can be obtained, free

Table 2
Crystallographic data of complexes **4**–**7**

	4	**5**	**6**	**7**
Formula	$C_{16}H_{16}NO_4S_3Co$	$C_{19}H_{20}NO_6S_3Co$	$C_{18}H_{18}NO_6S_3Co$	$C_{12}H_{14}NO_6S_3Co$
Formula weight/g · mol^{-1}	441.42	513.50	499.46	423.36
Crystal color	Purple	Purple	Purple	Violet
Crystal habit	Block	Block	Block	Block
Crystal size (mm)	$0.12 \times 0.10 \times 0.10$	$0.12 \times 0.10 \times 0.10$	$0.09 \times 0.06 \times 0.03$	$0.15 \times 0.10 \times 0.05$
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P-1(#2)	$P2_1/a$(#14)	$P2_1$(#4)	$P2_1/c$(#14)
a (Å)	8.2039(5)	10.698(2)	12.0859(9)	11.2644(8)
b (Å)	8.2667(5)	22.285(3)	14.0984(7)	10.4810(7)
c (Å)	13.7612(10)	18.117(3)	13.1486(10)	14.5621(11)
α (°)	90.945(3)			
β (°)	99.903(3)	91.4391(5)	113.9469(8)	95.2284(11)
γ (°)	91.572(3)			
V (Å^3)	918.81(10)	4317.7(11)	2047.6(2)	1712.1(2)
Z	2	8	4	4
D_{calc} (g · cm^{-3})	1.595	1.543	1.620	1.642
μ (Mo Kα)/cm^{-1}	12.95	11.19	11.80	13.94
T (K)	296	296	296	296
$2\theta_{max}$/°	55.0	55.0	55.0	55.0
Unique data (R_{int})	3744 (0.014)	9832 (0.033)	6752 (0.026)	3911 (0.043)
No. of observations	3061	5294	3971	1596
No. of variables	242	581	559	222
R_1, wR_2 ($I > 3.00 \sigma(I)$)	0.033, 0.044	0.036, 0.050	0.036, 0.047	0.035, 0.031
Goodness-of-fit on F^2	0.898	1.193	1.014	1.472
Largest difference peak and hole (e Å^{-3})	0.43, −0.42	0.42, −0.34	0.53, −0.29	0.35, −0.29

of charge, on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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