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Sulfenato and Sulfinato Complex Formation via Oxidation of *OC*-6-3′2-Bis{2-[(2-pyridylmethyl)amino]ethanethiolato}cobalt(III) (1+) Complex by Molecular Dioxygen

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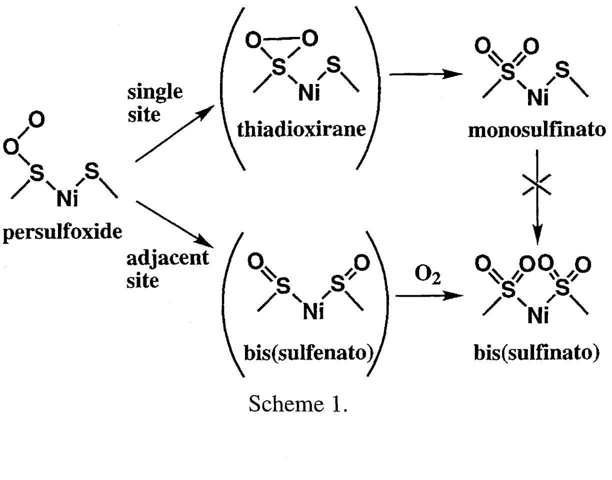
The first ligand oxidation of sulfur donors of *OC*-6-3′2-[Co(pyet)$_2$]$^+$ [pyet = 2-[(2-pyridylmethyl)amino]ethanethiolate (1−)] by molecular dioxygen is attained in the presence of active charcoal. The oxidation products are characterized as one (thiolato)(sulfinato) complex *OC*-6-3′2-[Co(pyet)(pyesi)]$^+$ (***b***; 82%), one (thiolato)(sulfenato) complex *OC*-6-3′2-[Co(pyet)(pyese)]$^+$ (***d***; 14%) and a mixture of four bis(sulfenato) complexes *OC*-6-3′2-[Co(pyese)$_2$]$^+$ (***h***, ***i***, ***j***, and ***k***; 4%), [pyese = 2-[(2-pyridylmethyl)amino]ethanesulfenate (1−); pyesi = 2-[(2-pyridylmethyl)amino]ethanesulfinate (1−)]. It is apparent that the route producing the monosulfinato complex is dominant in the dithiolatocobalt(III) complex as well as in the dithionickel(II) complexes. The isolation of *OC*-6-3′2-[Co(pyet)(pyese)]$^+$, however, is extremely interesting because this complex is the first example of an oxidation product free from an O$_2$.

The first ligand oxidation in a nickel(II) dithiolato complex by molecular oxygen O$_2$ was reported by M. J. Maroney et al. in 1989.[1] This reaction is very interesting because it will be a plausible chemical model for the deactivation of many hydrogenases having Ni centers with sulfur ligands by O$_2$. Since then, several examples of such oxidation reactions with O$_2$ have been reported for a bis(dithiolene)nickel(II) complex[2] and planar *cis*-dithiolatonickel(II) complexes.[3] Interestingly, the oxidation products characterized in those investigations were exclusively sulfinato complexes and no other oxidation products such as sulfenate ligands have been confirmed so far. A detailed mechanistic study of O$_2$ addition has been made by Darensbourg et al. through the isotopic labeling experiments and two oxidation routes via persulfoxide have been proposed in Scheme 1.[3] Namely, both oxygens in the monosulfinato complex [Ni(mese-daco)] [mese-daco = (mercaptoethyl)(sulfinatoethyl)diazacyclooctane] are derived from one dioxygen molecule. On the other hand, pairwise O$_2$ addition across *cis*-sulfur sites is the major pathway (91%) in the bis(sulfinato) complex [Ni(bse-daco)] [bse-daco = bis(sulfinatoethyl)diazacyclooctane].



Scheme 1.

In the cobalt(III) thiolato complexes, many papers concerning the preparation and characterization of various kinds of sulfur oxidation products such as thiolato, sulfenato, sulfinato and their derivatives have been reported so far.[4] However, there have been no reports concerning the direct ligand oxidation by molecular dioxygen. We previously observed some unknown products in the process of the synthesis and the column separation of [Co(pyet)$_2$]$^+$ [pyet = 2-[(2-pyridylmethyl)amino]ethanethiolate (1−)],[5] and at the present stage it is reasonable to consider them as the oxidation products of the bis(thiolato) complexes by O$_2$. Similar unidentified products, which may be oxidation products of the bis(thiolato) complexes, were observed also in [Co(*D*-pen)$_2$]$^-$ [*D*-pen = *D*-penycillaminate (2−)].[6]

We report here three kinds of oxidation products of *OC*-6-3′2-[Co(pyet)$_2$]$^+$.[7] They are the first examples of the oxidation of a cobalt(III) thiolate complex by molecular dioxygen and were characterized from elemental analysis, UV/vis absorption and ^{1}H and ^{13}C NMR spectra, and X-ray crystal analysis. The preliminary results have been reported elsewhere.[8]

Experimental

Synthesis. The tridentate ligand Hpyet was prepared according to the literature.[9] Abbreviations of the oxidized ligands are as follows; pyese = 2-[(2-pyridylmethyl)amino]ethanesulfenate (1−); pyesi = 2-[(2-pyridylmethyl)amino]ethanesulfinate (1−). Active charcoal was purchased from Wako Pure Chemical Industries Ltd.

Preparation of Complexes. **$[Co(pyet)_2]^+$ (Complexes 1 and 2).** To a solution of $[Co(NH_3)_6]Cl_3$ (1.3 g, 5 mmol) was added a solution of Hpyet (1.7 g, 10 mmol) and NaOH (0.4 g, 10 mmol) and the mixture was stirred at 70 °C for 2 h in the presence of active charcoal. The charcoal was removed by filtration and the filtrate was poured onto a column of SP-Sephadex C-25 resin (Na^+ form, 5×40 cm). Elution with 0.2 $mol\,dm^{-3}$ NaCl gave five bands, dark brown (**1**), dark green (**2**), blue and two dark yellow bands, in this order and there were no remaining complexes in the top of the column resin. The third blue band was very unstable and disappeared during the column separation. UV-vis absorption spectral measurements revealed that the first two bands **1** and **2** are the desired complexes containing a $[Co(thiolate)_2(N)_4]$ chromophore. Since the fourth and fifth bands were minor and may be oxidation products of the complexes **1** and/or **2**, they were not isolated. Each eluate was concentrated with a vacuum rotary evaporator and the white precipitate of NaCl filtered off. Addition of EtOH to the filtrate gave the chloride salt of the complex, which was recrystallized from water. The yield based on the starting cobalt(III) complex was 90% for **1** and 5% for **2**. Complex **1** {Found: C, 41.09; H, 5.74; N, 11.96%. Calcd for $[Co(pyet)_2]Cl\cdot 2H_2O$ ($C_{16}H_{26}ClCoN_4O_2S_2$): C, 41.33; H, 5.64, N, 12.05%}. Complex **2** {Found: C, 39.38; H, 5.88; N, 11.46%. Calcd for $[Co(pyet)_2]Cl\cdot 3.5H_2O$ ($C_{16}H_{29}ClCoN_4O_{3.5}S_2$): C, 39.06; H, 5.94; N, 11.39%}.

$[Co(pyesi)_2]^+$ (Complexes 3 and 4). The corresponding bis(sulfinato) complexes **3** and **4** $[Co(pyesi)_2]^+$ were prepared through complete oxidation of $[Co(pyet)_2]^+$ (complexes **1** and **2**) by H_2O_2 as follows. To an 5 cm^3 aqueous solution of complex **1** (*OC*-6-3′2-$[Co(pyet)_2]Cl\cdot 2H_2O$, 0.1 g) was added 2 cm^3 of 20% H_2O_2 aq, and the mixed solution was kept standing at room temperature for 2 d. By adding an excess amount of $NaClO_4$ to the mixture, bright yellow fine crystals (complex **3**) were obtained. Complex **4** was obtained in a similar manner to complex **2**. Complex **3** {Found: C, 33.77; H, 4.02; N, 9.93%. Calcd for $[Co(pyesi)_2]ClO_4\cdot 0.5H_2O$ ($C_{16}H_{23}ClCoN_4O_{8.5}S_2$): C, 33.96; H, 4.10, N, 9.90%}. Complex **4** {Found: C, 34.37; H, 3.98; N, 10.12%. Calcd for $[Co(pyesi)_2]ClO_4$ ($C_{16}H_{22}ClCoN_4O_8S_2$): C, 34.51; H, 3.98, N, 10.06%}.

Oxidation Products (Complexes 5, 6, and 7) of Complex 1 (*OC*-6-3′2-$[Co(pyet)_2]Cl$) by Air. To an aqueous solution of complex **1** (1.0 g) was added active charcoal (0.5 g) and the mixed solution was stirred at room temperature for 21 h under air atmosphere. The charcoal was removed by filtration and the brown filtrate was poured onto a column of Dowex 50W×2 resin (Na^+ form, 4×8 cm). Elution with 0.4 $mol\,dm^{-3}$ NaCl gave three bands, orange (**5**, yield 4%), brown (**6**, 82%) and brown (**7**, 14%), in this order. Each eluate was concentrated with a vacuum rotary evaporator and the white precipitate of NaCl filtered off. After repeated removal of NaCl, each complex was converted to the corresponding perchlorate through a column of QAE-Sephadex A-25 (ClO_4^-) and was crystallized by standing at room temperature. Prismatic dark-red crystals were obtained from the front part of the second eluate (complex **6**). The thirdly eluted brown isomer partly overlaps the second brown isomer in the column separation and could not be isolated in a pure form. The single crystals, however, were obtained from this band and these orange plates CR **1** are clearly different from the dark-red prisms of complex **6**. The complex ratio in CR **1** was determined by the peak intensities of ^1H NMR spectrum, namely, complex **6** : complex **7** = 60% : 40%. Complex **5** {Found: C, 28.07; H, 3.91; N, 8.21%. Calcd for $[Co(pyese)_2]ClO_4\cdot NaClO_4\cdot 2H_2O$ ($C_{16}H_{26}Cl_2CoN_4NaO_{12}S_2$): C, 28.12; H, 3.83, N, 8.20%}. Complex **6** {Found: C, 36.76; H, 4.21; N, 10.68%. Calcd for $[Co(pyet)(pyesi)]ClO_4$ ($C_{16}H_{22}ClCoN_4O_6S_2$): C, 36.61; H, 4.22; N, 10.67%}. CR **1** {*OC*-6-3′2-$[Co(pyet)(pyesi)]ClO_4$ (**6**; 60%) and *OC*-6-3′2-$[Co(pyet)(pyese)]ClO_4$ (**7**; 40%)} {Found: C, 37.56; H, 4.31; N, 10.88%. Calcd for $[Co(pyet)(pyesi)_{0.6}(pyese)_{0.4}]ClO_4$ ($C_{16}H_{22}ClCoN_4O_{5.6}S_2$): C, 37.06; H, 4.28; N, 10.81%}.

Caution: In general, perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great care. The present ones ignite in a Bunsen burner flame but gave no hazard in solutions and in normal treatment of the solids.

Crystal Structure Determination of *OC*-6-3′2-$[Co(pyet)_2]Cl\cdot 2H_2O$ and *OC*-6-3′2-$[Co(pyet)(pyesi)]ClO_4$. The crystal data for *OC*-6-3′2-$[Co(pyet)_2]Cl\cdot 2H_2O$ (complex **1**) and *OC*-6-3′2-$[Co(pyet)(pyesi)]ClO_4$ (complex **6**) are collected in Table 1.

***OC*-6-3′2-$[Co(pyet)_2]Cl\cdot 2H_2O$ (Complex 1).** A total of 4835 reflections ($3 < 2\theta < 52.9°$) were measured on a Mac Science MXC3 diffractometer using graphite-monochromated Mo $K\alpha$ radiation. The reflections 3947 with $I > 3\sigma(I)$ were used in the refinement. An empirical absorption correction was applied (transmission factors ranging from 0.683 to 1.000). The data were corrected for Lorentz and polarization effects. The structure was solved by direct method and refined by full-matrix least squares. Non-hydrogen atoms were refined anisotropically. All hydrogen atom parameters were refined. The refinement converged at $R = 0.039$ ($R_w = 0.042$). All calculations were performed using the CRYSTAN[10)] crystallographic software package.

***OC*-6-3′2-$[Co(pyet)(pyesi)]ClO_4$ (Complex 6).** A total of 6549 reflections ($3 < 2\theta < 60°$) were collected on a Rigaku AFC7R diffractometer using graphite-monochromated Mo $K\alpha$ radiation. The structure was solved by direct method. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 4056 observed reflections [$I > 3\sigma(I)$]. The linear absorp-

Table 1. Crystal Data for *OC*-6-3′2-$[Co(pyet)_2]Cl\cdot 2H_2O$ (Complex **1**) and *OC*-6-3′2-$[Co(pyet)(pyesi)]ClO_4$ (Complex **6**)

	Complex **1**	Complex **6**
Formula	$C_{16}H_{26}N_4O_2S_2ClCo$	$C_{16}H_{22}N_4O_6S_2ClCo$
Fw	464.93	524.88
Space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
Crystal system	Triclinic	Monoclinic
Cryst. size/mm	0.4 × 0.4 × 0.2	0.2 × 0.15 × 0.4
a/Å	8.971(2)	9.912(3)
b/Å	14.254(7)	6.960(5)
c/Å	8.411(2)	28.896(4)
α/deg	96.83(3)	
β/deg	105.35(2)	94.59(2)
γ/deg	105.01(3)	
V/Å^3	981.3(6)	1987(1)
Z	2	4
D_{calc}/g cm^{-3}	1.57	1.754
$2\theta_{max}$/deg	52.9	60.0
Temp/K	293	296
h, k, l	±11, +18, ±10	+14, +10, ±41
Variables	331	359
$I > 3\sigma(I)$	3947	4056
R[a)]	0.039	0.041
R_w[b)]	0.042	0.061

a) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

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

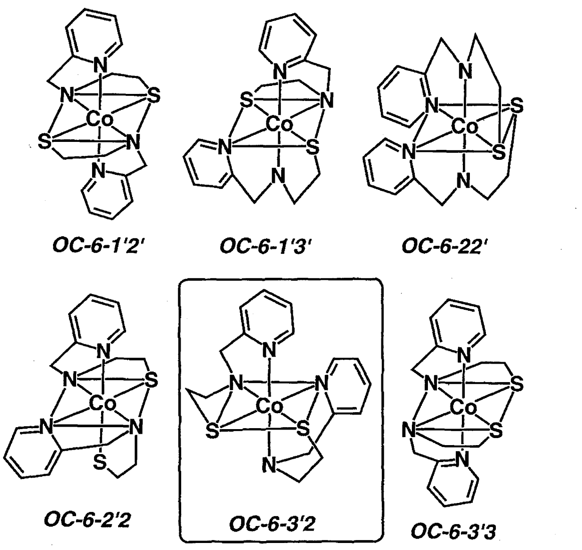
tion coefficient, μ, for Mo $K\alpha$ radiation is 12.5 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.89 to 1.00. The data were corrected for Lorentz and polarization effects. The refinement converged at $R = 0.041$ ($R_w = 0.061$). All calculations were performed using the TEXSAN[11] crystallographic software package.

The atomic coordinates, thermal parameters, complete bond lengths and angles, and $F_o - F_c$ data have been deposited as Document No. 71062 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Measurements. UV-vis absorption spectra were measured with a Hitachi 330 spectrophotometer and ^{1}H and ^{13}C NMR spectra with a JEOL JNM-GSX-400 spectrometer in D_2O and $(CD_3)_2SO$ at 30 °C. X-Ray crystal analysis was made at the X-ray Diffraction Service of the Department of Chemistry.

Results and Discussion

Characterizations of [Co(pyet)$_2$]$^+$ (1 and 2) and [Co(pyesi)$_2$]$^+$ (3 and 4). Six geometrical isomers, one bis(meridional) type and five bis(facial) types, are possible for [Co(pyet)$_2$]$^+$ as shown in Fig. 1. Only two complexes **1** and **2** were isolated in the column separation. The first d–d band appears at 570 nm (110 dm^3 mol^{-1} cm^{-1}) for complex **1** and 600 (117) and 497 nm (123 dm^3 mol^{-1} cm^{-1}) for complex **2** (Table 3). Two intense sulfur to metal charge-transfer (c.t.) bands appear at 290sh (23000) and 271 nm (26300 dm^3 mol^{-1} cm^{-1}) for complex **1** and at 287 (20400) and 267sh nm (18000 dm^3 mol^{-1} cm^{-1}) for complex **2**. These absorption spectra are characteristic of *cis(S)*-[CoS$_2$N$_4$] type complexes.[12] In the ^{13}C NMR spectra, complex **1** showed sixteen signals and complex **2** eight signals in $(CD_3)_2SO$ (Table 3). Thus complex **1** can be unequivocally assigned to *OC*-6-3′2-[Co(pyet)$_2$]$^+$ because only this isomer belongs to C_1 symmetry. On the other hand, complex **2** is considered to be one of three *cis(S)* isomers: *OC*-6-22′, *OC*-6-2′2 and *OC*-6-3′3.


OC-6-1′2′ OC-6-1′3′ OC-6-22′

OC-6-2′2 OC-6-3′2 OC-6-3′3

Fig. 1. Six possible geometrical isomers of [Co(pyet)$_2$]$^+$. The nomenclature is based on Ref. 7. The *OC*-6-3′2 isomer enclosed by a square is used as the starting material for the oxidation reaction by O_2.

Figure 2 shows an ORTEP[13] drawing of complex **1**. The crystal data and selected bond distances and angles are listed in Tables 1 and 2, respectively. The pyet ligand coordinates in a tridentate manner via the N(1), N(2), and S(1) atoms and forms two five-membered chelate rings. As expected by ^{13}C NMR and absorption spectra, the complex adopts a *OC*-6-3′2 geometry. The central cobalt(III) atom of complex **1** has a nearly regular octahedral structure: the S(1)–Co–N(11), N(1)–Co–N(12), and N(2)–Co–S(11) angles [177.0(1), 175.0(1), and 177.8(1)°, respectively] are close to 180°. The Co–S(1) length [2.235(1) Å] is shorter than the Co–S(11) length [2.251(1) Å], which reflects the steric repulsion between the pyridine ring of another pyet ligand and the S(11)

Table 2. Selected Bond Distances (Å) and Bond Angles (°) for *OC*-6-3′2-[Co(pyet)$_2$]Cl·2H$_2$O (Complex **1**) and *OC*-6-3′2-[Co(pyet)(pyesi)]ClO$_4$ (Complex **6**)

	Complex **1**	Complex **6**
Bond distances		
Co–S(1)	2.235(1)	2.1929(9)
Co–S(11)	2.251(1)	2.2630(9)
Co–N(1)	1.934(1)	1.945(3)
Co–N(2)	2.021(1)	2.032(3)
Co–N(11)	1.993(1)	2.000(2)
Co–N(12)	1.987(1)	1.989(3)
S(1)–O(1)		1.473(4)
S(1)–O(2)		1.410(4)
S(1)–C(9)	1.813(1)	1.816(4)
S(11)–C(19)	1.814(1)	1.817(4)
N(1)–C(2)	1.342(1)	1.350(4)
N(1)–C(6)	1.350(1)	1.354(4)
N(2)–C(7)	1.484(2)	1.478(4)
N(2)–C(8)	1.486(1)	1.499(4)
N(11)–C(12)	1.342(1)	1.338(4)
N(11)–C(16)	1.353(1)	1.342(4)
N(12)–C(17)	1.485(2)	1.481(4)
N(12)–C(18)	1.490(2)	1.494(4)
Bond angles		
S(1)–Co–S(11)	89.0(1)	90.87(4)
S(1)–Co–N(2)	88.9(1)	87.69(8)
S(1)–Co–N(11)	177.0(1)	176.21(8)
S(11)–Co–N(2)	177.8(1)	178.56(8)
S(11)–Co–N(11)	91.3(1)	91.29(7)
S(11)–Co–N(12)	88.5(1)	87.88(8)
N(1)–Co–N(2)	84.0(1)	84.4(1)
N(1)–Co–N(12)	175.0(1)	175.5(1)
N(11)–Co–N(12)	83.3(1)	84.1(1)
Co–S(1)–C(9)	96.6(1)	98.4(1)
Co–S(11)–C(19)	96.6(1)	96.4(1)
Co–S(1)–O(1)		110.2(1)
Co–S(1)–O(2)		116.6(2)
O(1)–S(1)–O(2)		117.7(2)
Co–N(2)–C(7)	107.3(1)	107.0(2)
Co–N(2)–C(8)	112.5(1)	112.2(2)
C(7)–N(2)–C(8)	113.0(1)	112.7(3)
Co–N(12)–C(17)	109.2(1)	108.1(2)
Co–N(12)–C(18)	112.9(1)	113.2(2)
C(17)–N(12)–C(18)	113.1(1)	112.8(3)

Table 3. Carbon-13 NMR and UV-vis Absorption Spectral Data of the Present Complexes

Compound	Solvent	^{13}C NMR	UV-vis absorption$^{d)}$		
		δ	nm (ε/dm^3 mol^{-1} cm^{-1})		
[Co(pyet)$_2$]$^+$ (**1**)	$(CD_3)_2SO^{a)}$	163.3 162.6 154.7 148.8 138.5$^{c)}$ 125.3 124.8 120.5	570sh (110)	450 (288)	390sh (630)
		120.1 61.5 59.5 59.2 57.9 30.9 24.5	290sh (23000)	271 (26300)	225sh (20000)
[Co(pyet)$_2$]$^+$ (**2**)	$D_2O^{b)}$	153.3 140.1 125.7 122.5 60.7 59.4 30.2	600sh (117)	497 (123)	390sh (400)
	$(CD_3)_2SO$	163.7 152.7 138.1 123.3 120.3 59.9 57.9 29.3	287 (20400)	270sh (18000)	220sh (17000)
[Co(pyesi)$_2$]$^+$ (**3**)	D_2O	164.3 163.2 154.6 151.2 142.6 142.4 127.5 127.4		425sh (400)	320 (19500)
		124.0 123.6 62.9 62.3 60.7 59.2 50.7 49.6	295sh (16000)	263 (10500)	230sh (15000)
[Co(pyesi)$_2$]$^+$ (**4**)	D_2O	163.6 154.4 142.1 126.7 124.3 62.6 59.2 49.9		405sh (1300)	321 (17000)
			295sh (11000)	262 (20900)	225sh (20900)
[Co(pyese)$_2$]$^+$ (**5**)	$(CD_3)_2SO$	163.9 163.8 163.6 163.5 163.4 162.7 162.6 162.4		480sh (840)	389 (11200)
		153.8 153.7 152.0 151.7 151.0 149.9 148.6$^{c)}$	294 (23400)	270sh (21400)	
		140.2 139.9 139.8$^{c)}$ 139.4$^{c)}$ 139.2 138.6			
		125.6 125.4 125.1$^{c)}$ 125.0$^{c)}$ 124.5 124.4 124.0 122.3			
		121.9$^{c)}$ 121.8 121.5$^{c)}$ 121.2 61.3$^{c)}$ 60.7$^{c)}$ 60.1$^{c)}$ 59.3			
		59.1$^{c)}$ 57.8$^{c)}$ 57.2$^{c)}$ 56.9 56.6$^{c)}$ 51.6 51.4 50.5 50.4			
		49.9 49.7 48.8 48.1			
[Co(pyet)(pyesi)$^+$ (**6**)	$(CD_3)_2SO$	164.4 162.5 155.4 148.8 139.8 139.3 125.5 125.0	590sh (52)	480sh (320)	380sh (2000)
		121.6 120.9 61.4 60.2 59.1 58.2 49.5 26.0	293 (15700)	267 (15300)	220sh (17600)
[Co(pyet)(pyese)]$^+$ (**7**)	$(CD_3)_2SO$	164.6 162.7 153.5 148.7 139.4 138.7 125.4 125.3	600sh (150)	485sh (650)	370sh (7700)
		122.1 121.0 61.0 58.2 57.9 53.8 50.8 25.4	295 (16500)	266 (18100)	230sh (17000)

a) Downfield relative to $SiMe_4$ in $(CD_3)_2SO$. b) Downfield relative to $SiMe_4$ by use of dioxane (δ = 67.40) as an internal reference. c) Relatively strong signal. d) All spectra were measured in H_2O.

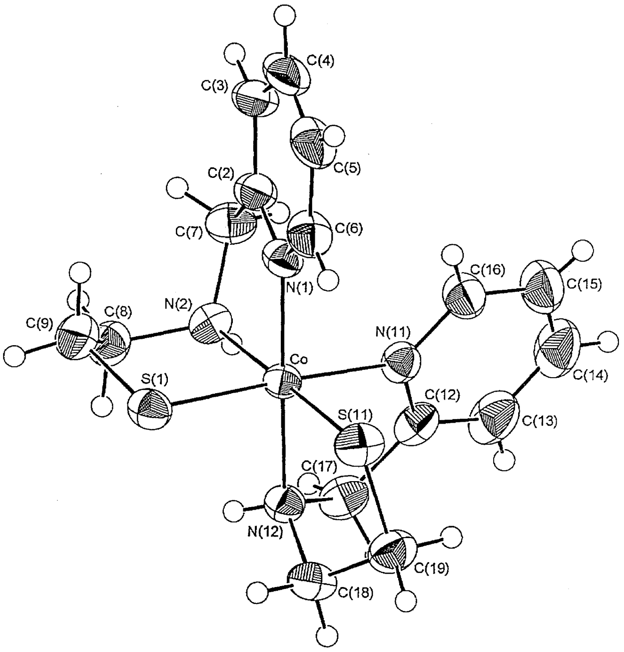


Fig. 2. An ORTEP drawing of the cation of *OC*-6-3′2-[Co(pyet)$_2$]Cl·2H$_2$O (complex **1**).

donor. The Co–N(2) and Co–N(11) lengths [2.021(1) and 1.993(1) Å] are longer than the corresponding Co–N(12) and Co–N(1) lengths [1.987(1) and 1.934(1) Å], respectively, because of the *trans* influence of sulfur atom on the former bonds.[14]

The bis(sulfinato) complex was prepared from the complete oxidation of the corresponding bis(thiolato) complex by an excess amount of H_2O_2; complex **3** was obtained from complex **1** and complex **4** from complex **2**. Since each sulfinato complex showed the same number of the ^{13}C NMR signals as the starting material, it is reasonable that the geometry is retained during the H_2O_2 oxidation. Thus the geometry of complex **3** is *OC*-6-3′2 and that of complex **4** is one of three *cis(S)* isomers, *OC*-6-22′, *OC*-6-2′2 and *OC*-6-3′3.[7] Both complexes showed characteristic UV/vis absorption spectra. The first d–d absorption bands of the complexes **3** and **4** appeared at shorter wavelength region compared with those of the corresponding thiolato and/or sulfenato complexes, because the sulfinato group occupies a very much higher position in the spectrochemical series (Table 3).[4] Two intense sulfur to metal c.t. bands are characteristic of the complexes with the *cis(S)* geometry:[15] 320 (19500) and 295sh nm (16000 dm^3 mol^{-1} cm^{-1}) for complex **3** and 321 (17000) and 295sh nm (11000 dm^3 mol^{-1} cm^{-1}) for complex **4**.

Oxidation of *OC*-6-3′2-[Co(pyet)$_2$]$^+$ by O$_2$. The Ni(II) thiolato complexes undergo oxidation to the sulfinato complexes simply upon exposure to air[1] or under an oxygen atmosphere.[2,3] However, the oxidation reaction of the present Co(III) thiolato complex did not proceed at all under the same conditions. We found that the coexistence of active charcoal was indispensable, though the role of active charcoal is not still clear. There has been a report that active charcoal catalyzes the formation of cobalt(II) species,[16] but the labile Co(II) intermediate is not consistent with the results of the present reaction, which gives no isomerized products of *OC*-6-3′2-[Co(pyet)$_2$]$^+$.

The oxidation reaction is much faster in a bis(thiolato) Co(III) complex than in a monothiolato one. For example, an aqueous solution of *OC*-6-3′2-[Co(pyet)$_2$]$^+$ in the presence of active charcoal was spontaneously oxidized by air in several hours at room temperature, whereas an aqueous solution of [Co(aet)(en)$_2$]$^{2+}$ or [Co(aet)(tren)]$^{2+}$ [aet = 2-aminoethanethiolate (1−), en = 1,2-ethanediamine and tren = tris(2-aminoethyl)amine] showed almost no sign of oxidation in the presence of active charcoal irrespective of air bubbling for 1 week. Such a large difference may be related to the oxidation mechanism. Since O_2 addition occurs as a O_2 unit, the uptake of O_2 is more advantageous for a *cis(S)*-dithiolato complex than for a monothiolato one. The former has large probability for a single site addition in Scheme 1 than the latter and an adjacent site addition is possible only for the former.

Characterization of Oxidation Products (Complexes 5—7). Possible oxidation products of *OC*-6-3′2-[Co(pyet)$_2$]$^+$ are shown in Fig. 3 which displays only the enantiomers with the same C (clockwise) chirality.[7] Since this complex has C_1 symmetry, two thiolato atoms are chemically nonequivalent. Fifteen racemic pairs, one bis(sulfinato), two (thiolato)(sulfinato), four (thiolato)(sulfenato), four bis(sulfenato), and four (sulfenato)(sulfinato) complexes, are expected in total. In the column separation of the oxidation products of *OC*-6-3′2-[Co(pyet)$_2$]$^+$, three bands were found. The yields are 4% for the first orange band (**5**), 82% for the second brown one (**6**), and 14% for the last one (**7**).

***OC*-6-3′2-[Co(pyet)(pyesi)]$^+$ (Complex 6).** The secondly eluted main band showed sixteen signals, ten in the pyridine chemical shift region and six in the higher magnetic region (Table 3), which means that this band is composed of a single isomer. The signal at $\delta = 26.0$ indicates the presence of a thiolato group, because a carbon signal bonded to a sulfenato or a sulfinato group shifts to low magnetic field by more than 20 ppm. The presence of a thiolato group is also confirmed by UV/vis absorption spectrum in Fig. 4: A shoulder near 600 nm is characteristic of a thiolato group.[4] Complex **6** exhibited a shoulder at 590 nm and the molar absorption coefficient is half the molar absorption coefficient of *OC*-6-3′2-[Co(pyet)$_2$]$^+$. Another criterion is an intense band at 370—390 nm, which is characteristic for the sulfenato group; the molar absorption coefficient (dm^3 mol^{-1} cm^{-1}) is estimated to be ca. 7000 per one sulfenato group.[4] Complex **6** exhibited a similar band at 380sh nm (2000 dm^3 mol^{-1} cm^{-1}) but this band is assigned to a sulfinato group because of its small molar absorption coefficient. Thus complex **6** can be assigned to *OC*-6-3′2-[Co(pyet)(pyesi)]$^+$.

Figure 5 shows an ORTEP[13] drawing of complex **6**. The crystal data and selected bond distances and angles are listed in Tables 1 and 2, respectively. The N,N,S ligand adopts a *facial* arrangement and forms two five-membered chelate rings. Complex **6** takes the *OC*-6-3′2 structure, whose struc-

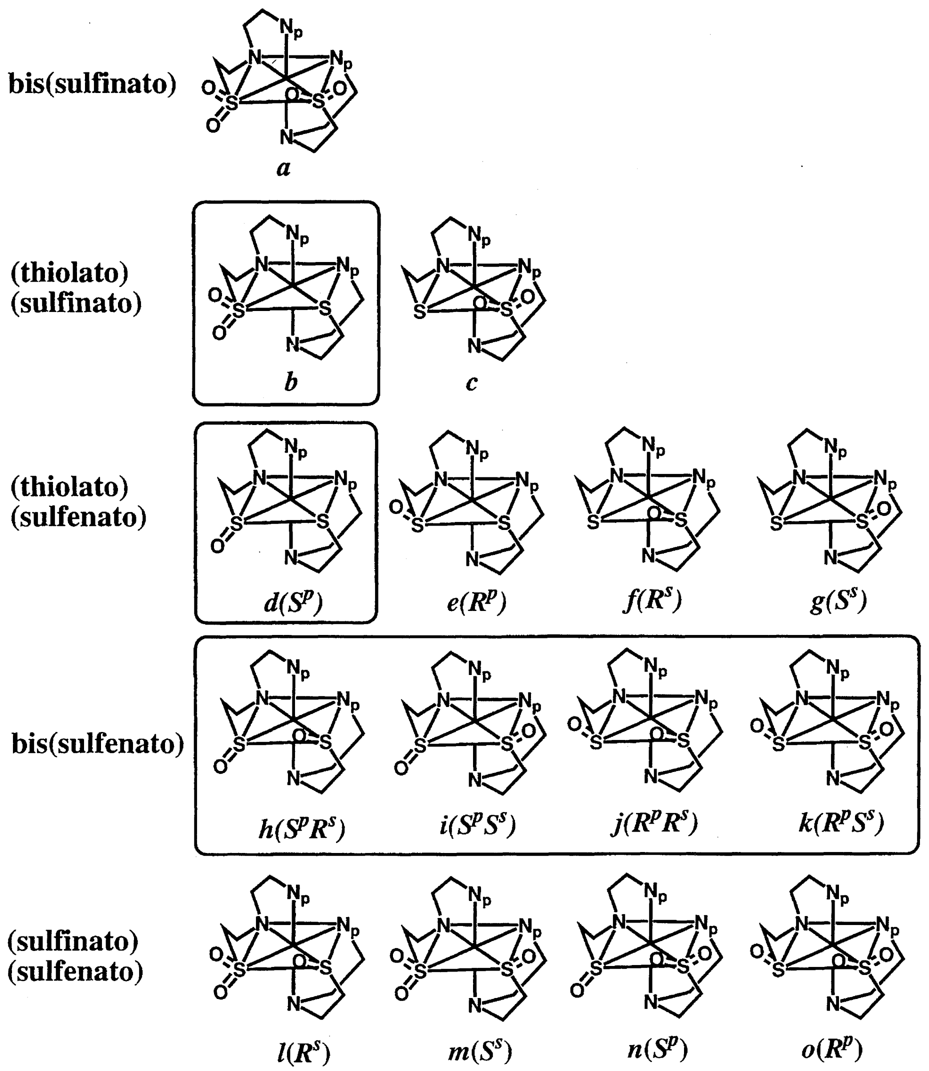


Fig. 3. Fifteen possible oxidation products (*a*—*o*) of *OC*-6-3′2-[Co(pyet)$_2$]$^+$ (complex **1**); only C (clockwise)[7] isomers are shown. The character *R* or *S* in parenthesis means the chirality of the sulfenato group and the superscripts *p* (pyridine *trans*) and *s* (secondary nitrogen *trans*) are used to discriminate two sulfur donors. The isomers enclosed by squares are oxidation products to be formed.

ture is similar to that in *OC*-6-3′2-[Co(pyet)$_2$]$^+$ as shown in Fig. 2. As expected from ^{13}C NMR and UV-vis absorption spectra, complex **6** is a (thiolato)(sulfinato) complex *OC*-6-3′2-[Co(pyet)(pyesi)]$^+$. Though two isomers, ***b*** and ***c***, are possible in *OC*-6-3′2-[Co(pyet)(pyesi)]$^+$ as shown in Fig. 3, the isolated isomer is a ***b*** isomer having a sulfinato group at the S(1) site and a thiolato group at the S(11) site. The oxidation reaction may be difficult at the S(11) site because there is considerable steric repulsion between the pyridine ring of another pyet ligand and the S(11) donor. It is important that an intramolecular hydrogen bond [O(1)···N(12) = 2.865(4) Å, O(1)–H(12)–N(12) = 110(3)°] between O(1) and H–N(12) becomes possible in this structure. This may be the reason why only one isomer is formed in *OC*-6-3′2-[Co(pyet)(pyesi)]$^+$. The central cobalt(III) ion of complex **6** has a nearly regular octahedral structure: the N(1)–Co–N(12), N(2)–Co–S(11), and S(1)–Co–N(11) angles [175.5(1), 178.56(8), and 176.21(8)°, respectively] are close to 180°. The Co–S(1) length [2.1929(9) Å] is shorter than the Co–S(11) length [2.2630(9) Å], which are normal as a sulfinato and a thiolato group, respectively. The Co–N(2) and Co–N(11) lengths [2.032(3) and 2.000(2) Å] are considerably longer than the corresponding Co–N(12) and Co–N(1) lengths [1.989(3) and 1.945(3) Å], respectively, because of the *trans* influence of sulfur atoms for the former bonds.[14]

***OC*-6-3′2-[Co(pyet)(pyese)]$^+$ (Complex 7).** The plate crystals CR **1** were obtained from the third eluted brown band and they are clearly different from the prismatic crystals of complex **6**. The ^{13}C NMR spectrum of CR **1** showed thirty-two signals in total, as shown in Fig. 6. The sixteen signals are completely the same as those of complex **6** and the remaining sixteen signals are due to complex **7**. The ratio of both complexes was determined by the peak intensities of ^{1}H NMR spectrum, namely, Complex **6** : Complex **7** = 60% : 40%. Complex **7** shows a signal at δ = 25.4 which is characteristic of a thiolato group. The pure UV-vis absorption spectrum of complex **7** was calculated by subtracting the contribution of complex **6** from the molar absorption coeffi-

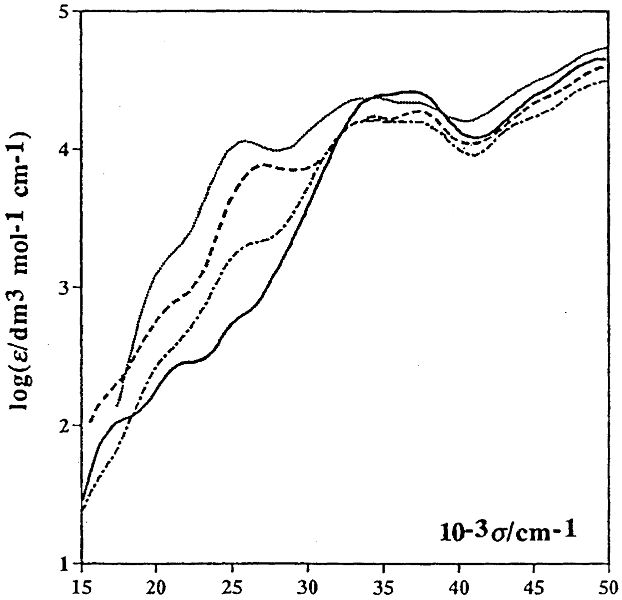


Fig. 4. UV-vis absorption spectra of *OC*-6-3′2-[Co(pyet)$_2$]$^+$ (—) and its oxidation products [complexes **5** (····), **6** (– · –), and **7** (- - -)] by O$_2$.

cients of the mixed samples (Fig. 4). Complex **7** exhibited a shoulder at 600 nm; this band means the presence of a thiolato group.[4] This complex showed an intense band at 370sh nm (7700 dm^3 mol^{-1} dm^{-1}) which can be assigned to a sulfenato group because of its high molar absorption coefficient.[4] Thus, complex **7** can be assigned to *OC*-6-3′2-[Co(pyet)(pyese)]$^+$. Though four isomers, ***d*—*g***, are possible in *OC*-6-3′2-[Co(pyet)(pyese)]$^+$, as shown in Fig. 3, the above ^{13}C NMR spectrum confirms the existence of only one isomer.

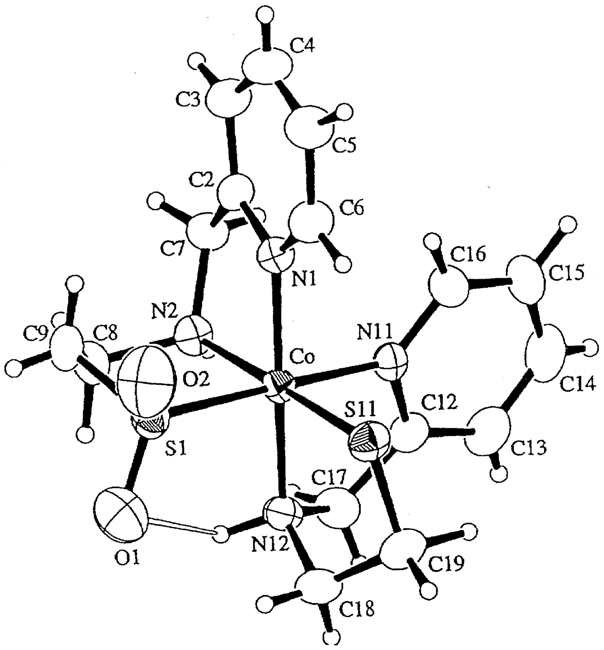


Fig. 5. An ORTEP drawing of the cation of *OC*-6-3′2-[Co(pyet)(pyesi)]ClO$_4$ (complex **6**). The line between O(1) and N(12)–H means an intramolecular hydrogen bond.

The crystal data of CR **1** are shown in Ref. 17. The crystal CR **1** is composed of both complexes (complex **6** : complex **7** = 60% : 40%) and is crystallographically isomorphous to the crystal of complex **6**. Hence an ORTEP[13] drawing of CR **1** is quite similar to that of complex **6** in Fig. 5. The most important point of CR **1** is the electron density differences of two oxygen atoms, O(1) and O(2) in Fig. 5. The occupancy of O(1) as well as those of the other all atoms

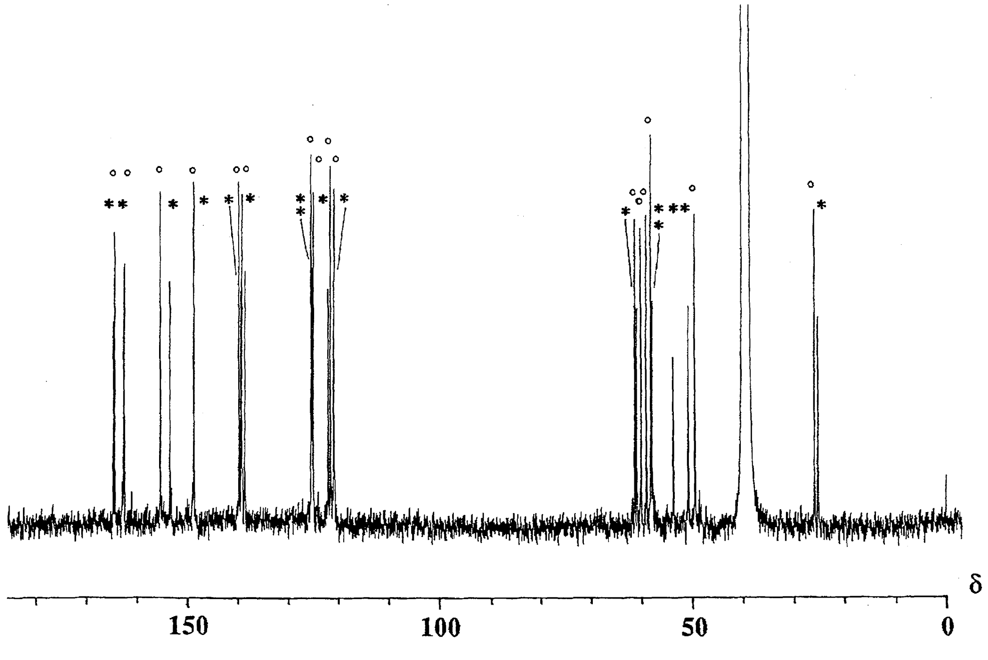


Fig. 6. Carbon-13 NMR spectrum of CR **1** [*OC*-6-3′2-[Co(pyet)(pyesi)]$^+$ (°; 60%) and *OC*-6-3′2-[Co(pyet)(pyese)]$^+$ (*; 40%)] in (CD$_3$)$_2$SO.

was 100%, but the converged occupancy value of O(2) was only ca. 60% in CR **1**. The occupancy ratio is extremely consistent with the value obtained by the ^{1}H NMR spectrum. These results indicate that complex **7** occupies completely the same sites as complex **6**; that is, forming a solid solution. The oxygen site of the sulfenato group in complex **7** is the O(1) site and hence complex **7** can be assigned to a $\boldsymbol{d}(\boldsymbol{S}^{\boldsymbol{p}})$ isomer in Fig. 3. The O(1) site is more preferable because an intramolecular hydrogen bond [O(1)···N(12) = 2.87(2) Å, O(1)–H(12)–N(12) = 108.7°] between S(1)–O(1) and H–N-(12) becomes possible. This is the reason why only the $\boldsymbol{d}(\boldsymbol{S}^{\boldsymbol{p}})$ isomer was formed though four isomers, $\boldsymbol{d}(\boldsymbol{S}^{\boldsymbol{p}})$, $\boldsymbol{e}(\boldsymbol{R}^{\boldsymbol{p}})$, $\boldsymbol{f}(\boldsymbol{R}^{\boldsymbol{s}})$, and $\boldsymbol{g}(\boldsymbol{S}^{\boldsymbol{s}})$, are possible in *OC*-6-3′2-[Co(pyet)(pyese)]$^+$.

***OC*-6-3′2-[Co(pyese)$_2$]$^+$ (Complex 5).** The first eluted minor complex **5** (4%) has orange color. The ^{13}C NMR spectrum exhibis 50 signals, 14 of which are significantly larger than the others due to overlapping of peaks (Table 3). In the chemical shift region of 162—164 ppm, eight signals were observed. These results indicate the co-existence of four kinds of complexes with C_1 symmetry. Since there is no signal at $\delta = 25$—30, the original thiolato groups were oxidized completely into the sulfenato or sulfinato groups. The UV-vis absorption spectrum of complex **5** was shown in Fig. 4. This complex showed an intense band at 389 nm (11200 dm^3 mol^{-1} cm^{-1}) which can be assigned to a sulfenato group.[4] Its molar absorption coefficients are approximately twice the molar absorption coefficients of the monosulfenato complex *OC*-6-3′2-[Co(pyet)(pyese)]$^+$ (**7**) and hence complex **5** can be assigned to the bis(sulfenato) complex *OC*-6-3′2-[Co(pyese)$_2$]$^+$. The above ^{13}C NMR spectrum of complex **5** confirms the co-existence of four isomers, $\boldsymbol{h}(\boldsymbol{S}^{\boldsymbol{p}}\boldsymbol{R}^{\boldsymbol{s}})$, $\boldsymbol{i}(\boldsymbol{S}^{\boldsymbol{p}}\boldsymbol{S}^{\boldsymbol{s}})$, $\boldsymbol{j}(\boldsymbol{R}^{\boldsymbol{p}}\boldsymbol{R}^{\boldsymbol{s}})$, and $\boldsymbol{k}(\boldsymbol{R}^{\boldsymbol{p}}\boldsymbol{S}^{\boldsymbol{s}})$, of *OC*-6-3′2-[Co(pyese)$_2$]$^+$ as shown in Fig. 3.

Oxidation Mechanism of the Present Complexes. As shown above, the three oxidation products of *OC*-6-3′2-[Co(pyet)$_2$]$^+$ by molecular dioxygen are assigned to the mixture of four bis(sulfenato) complexes *OC*-6-3′2-[Co(pyese)$_2$]$^+$ (complex **5**; ***h***, ***i***, ***j***, and ***k***), one (thiolato)(sulfinato) complex *OC*-6-3′2-[Co(pyet)(pyesi)]$^+$ (complex **6**; ***b***) and one (thiolato)(sulfenato) complex *OC*-6-3′2-[Co(pyet)(pyese)]$^+$ (complex **7**; ***d***).

The formation of a (thiolato)(sulfinato) complex *OC*-6-3′2-[Co(pyet)(pyesi)]$^+$ (***b***; 82%) as a main product is compatible with the conventional single site mechanism for nickel(II) complexes, as shown in Scheme 1. The route resulting in the monosulfinato complex is dominant in the Co(III) thiolato complex and the result is quite analogous to those in the Ni(II) thiolato complexes.[1—3]

A further important point is the characterization of bis(sulfenato) complexes *OC*-6-3′2-[Co(pyese)$_2$]$^+$ (***h***—***k***; 4%). The pairwise O_2 addition mechanism across *cis*-sulfur sites in Scheme 1 has been proposed in the formation of the bis(sulfinato)nickel(II) complexes,[2] but intermediate bis(sulfenato) complexes have never been found in the dithionickel(II) complexes. The formation of bis(sulfenato) complexes is first confirmed in the present Co(III) system. This route, however, is minor in the Co(III) thiolato complex and hence no bis(sulfinato) complex *OC*-6-3′2-[Co(pyesi)$_2$]$^+$ was found in the present system.

The most interesting result concerns the isolation of the (thiolato)(sulfenato) complex *OC*-6-3′2-[Co(pyet)(pyese)]$^+$ (***d***; 14%). This complex is the first example of an oxidation product free from a O_2 unit and its formation is incompatible with the above two intramolecular mechanisms in Scheme 1. Since there has been no concrete evidence of scrambling reactions from a (thiolato)(sulfinato) complex to a bis(sulfenato) one and/or from a bis(sulfenato) complex and a bis(thiolato) one to a (thiolato)(sulfenato) complex in the Ni(II) complexes[2] and in the Co(III) complexes,[4] it is reasonable that a new route, e.g. an intermolecular mechanism, is necessary to explain the formation of the (thiolato)(sulfenato) complex. We would like to try further oxidation reactions in other Co(III) complex systems and reveal their oxidation mechanisms.

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17) Crystal data of CR **1** [*OC*-6-3′2-[Co($C_8H_{11}N_2S_2$)($C_8H_{11}O_2N_2S$)]ClO_4 (60%) and *OC*-6-3′2-[Co($C_8H_{11}N_2S_2$)($C_8H_{11}ON_2S$)]ClO_4 (40%)] at 296 K: $M = 518.48$, $0.15\times0.07\times0.20$ mm, monoclinic, $P2_1/c$ (no. 14), $a = 9.912(4)$, $b = 6.983(2)$, $c = 28.909(9)$ Å, $\beta = 94.51(3)^\circ$, $V = 1994(1)$ Å^3, $Z = 4$, and R (R_w) = 0.074 (0.100) for 1247 independent reflections with $I > 3\sigma(I)$. The structure was solved by direct methods and refined by full-matrix least-squares. All calculations were performed using the TEXSAN[11)] crystallographic software package. The plate CR **1** was crystallographically isomorphous to the prismatic crystal of *OC*-6-3′2-[Co(pyet)(pyesi)]ClO_4 (complex **6**) and the bond lengths and angles of *OC*-6-3′2-[Co(pyet)(pyese)]ClO_4 (complex **7**) are omitted because of low quality of its crystal analysis.