Cobalt Thiolates with Organic $N,N,S$-Tridentate Ligand: Conversion of Thiolate Complex to Sulfinate Complex via Sulfenate

Takanori Kotera¹, Atsushi Fujita¹, Masahiro Mikuriya¹*, Daisuke Yoshioka¹, Takashi Shibahara², Kichisuke Nishimoto², Makoto Handa³

¹Department of Applied Chemistry for Environment and Research Center for Coordination Molecule-based Devices, School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen, Sanda 669-1337, Japan
²Department of Chemistry, Faculty of Science, Okayama University of Science, 1-1 Ridaicho, Kita-Ku, Okayama 700-0005, Japan
³Department of Chemistry, Graduate School of Natural Science and Technology, Shimane University, 1060 Nishikawatsu, Matsue 690-8504, Japan

junpei@kwansei.ac.jp

Abstract. Mononuclear cobalt(III) complex with 2-[(3-aminopropyl)amino]ethanethiol (Hapaet), [Co(apaet)₂]ClO₄ (1) and the sulfinate complex, [Co(apaetO₂)₂]ClO₄ (2) were synthesized and characterized by measurements of the elemental analysis, infrared and electronic spectra (UV-vis-NIR), and temperature dependence of magnetic susceptibilities (4.5—300 K), and DFT calculations. X-Ray crystal structure analysis of 1 and 2 revealed an octahedral CoS₂N₄ or Co(SO₂)₂N₄ chromophore with meridional chelation of two apaet⁻ or apaetO₂⁻. Conversion of 1 to the sulfinate complex 2 via the sulfenate complex was investigated by UV-vis spectra. Oxidation reaction of capsanthin with 1 was also examined.

1. Introduction

Organic thiols containing amino-nitrogen donors are useful to prepare metal thiolates [1-4]. Some $N,N,S$-tridentate thiolic ligands can be compared with the corresponding amino-alcoholic $N,N,O$-tridentate ligands which form dinuclear copper(II) species. Contrary to amino-alcoholic ligands, amino-thiolic ligands have a great affinity for many kinds of metal ions to form various metal thiolates from mononuclear to polynuclear species [5-20]. We focused on cobalt systems in the hope of obtaining new feature of metal thiolates, elucidating interesting crystal structures and spectral properties, although most metal thiolates are diamagnetic. An $N,N,S$-tridentate thiol, 2-[(3-aminopropyl)amino]ethanethiol (Hapaet), afforded mononuclear Co(III) and trinuclear Co(II)₃ species, [Co(apaet)₂]ClO₄ (1) and [{Co(apaet)₂}Co(ClO₄)₂ (1')], depending on the reaction condition [16]. Interestingly, the mononuclear Co(III) species underwent oxidation reaction with hydrogen peroxide to form another Co(III) species with the corresponding sulfinate ligand via the sulfenate ligand. Their conversion was monitored by UV-vis spectra and DFT calculations were performed. The oxidizing property of the Co(III) species was also tested for an orange-color dye, capsanthin.
2. Experimental

2.1 Synthesis
All the chemicals except for toluene and ethylenesulfide which were dehydrated and distilled, respectively, before using, were commercial products and were used as supplied. The thiolic ligand, 2-(3-aminopropylamino)ethanethiol (Hapaet), was synthesized according to a method reported in the literature [5]. Synthesis of [Co(apaet)$_2$]ClO$_4$.CH$_3$OH (1). To a methanol solution (4 cm$^3$) of Hapaet (34 mg, 0.25 mmol) and two drops of triethylamine, a methanol solution (4 cm$^3$) of cobalt(II) perchlorate hexahydrate (47 mg, 0.13 mmol) was added, and the reaction solution was left at room temperature for several days. The deposited dark purple crystals were filtered off and desiccated in vacuo. Yield: 21 mg, 37% (based on the Hapaet ligand). Found C 28.79, H 6.58, N 12.37%. Calcd for

$$
\text{[Co(apaet)$_2$]ClO}_4\cdot\text{CH}_3\text{OH, } C_{31}H_{27}ClO_7N_2(S)\cdot\text{H}_2\text{O, }}
$$

$\mu_{\text{eq}}/\mu_{\text{B}}: 0.68$. Synthesis of [Co(apaetO)$_2$]ClO$_4$.dmac (2) (dmac = N,N'-dimethylacetamide). To a solution of Hapaet (34 mg, 0.25 mmol) and two drops of triethylamine in methanol (4 cm$^3$)/dmac (2 cm$^3$) was added a methanol solution (4 cm$^3$) of cobalt(II) perchlorate hexahydrate (93 mg, 0.25 mmol). The mixture was allowed to stand for several days at room temperature. After the resulting crystals were removed by filtration, aqueous hydrogen peroxide (30%, 1 cm$^3$) was added to the filtrate. The mixture solution was allowed to stand for several days to give orange plates. These were collected by filtration (yield 16 mg, 22% based on the thiolic ligand). Found: C, 29.02; H, 6.62; N, 12.26%. IR (KBr) $\tilde{\nu}$/cm$^{-1}$: $\tilde{\nu}$(NH) 3313(m), 3223(m), 3148(m); $\tilde{\nu}$(CH) 2949(m), 2800(m); $\tilde{\nu}$(ClO) 1100(s), 1076(s), 1040(s), 622(s). Diffuse reflectance spectrum $\tilde{\alpha}$/nm: 270, 340, 480, 890, 1364, 1552, 1708, 1746 nm. Absorption spectrum in H$_2$O $\tilde{\alpha}$/nm ($\tilde{\alpha}$/M$^{-1}$cm$^{-1}$): 205 (20700), 276 (16500), 467 (590). Magnetic moment at room temperature $\mu_{\text{eq}}/\mu_{\text{B}}$: 0.68. Synthesis of [Co(apaetO)$_2$]ClO$_4$.dmac (2) (dmac = N,N'-dimethylacetamide). To a solution of Hapaet (34 mg, 0.25 mmol) and two drops of triethylamine in methanol (4 cm$^3$)/dmac (2 cm$^3$) was added a methanol solution (4 cm$^3$) of cobalt(II) perchlorate hexahydrate (93 mg, 0.25 mmol). The mixture was allowed to stand for several days at room temperature. After the resulting crystals were removed by filtration, aqueous hydrogen peroxide (30%, 1 cm$^3$) was added to the filtrate. The mixture solution was allowed to stand for several days to give orange plates. These were collected by filtration (yield 16 mg, 22% based on the thiolic ligand). Found: C, 29.02; H, 6.62; N, 12.26%. IR (KBr) $\tilde{\nu}$/cm$^{-1}$: $\tilde{\nu}$(NH) 3302(m), 3140(m); $\tilde{\nu}$(ClO) 1100(s), 1076(s), 1040(s), 622(s). Diffuse reflectance spectrum in H$_2$O $\tilde{\alpha}$/nm ($\tilde{\alpha}$/dm$^3$mol$^{-1}$cm$^{-1}$): 232 (11300), 294 (16600), 310 (15900), 456 (370).

2.2 Measurements and Methods
Elemental analyses for C, H, and N were performed using a Thermo-Finnigan FLASH EA1112 series CHNO-S analyzer. Infrared spectra were measured with a JASCO MFT-2000 FT-IR Spectrophotometer in the 4000—600 cm$^{-1}$ region. Diffused reflectance spectrum was measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer Model UV-3100 in the 200—1500 nm region. Magnetic susceptibilities were measured with a Quantum Design MPMS-XL7 SQUID susceptometer over a temperature range of 4.5—300 K. Cyclic voltammetric measurements were carried out on a Hokuto Denko HA-501 potentiostat equipped with a Hokuto Denko HB-104 function generator. A three-electrode cell consisting of a glassy carbon electrode, a platinum-wire counter electrode, and an SCE electrode was used. Single-crystal diffraction data were measured on a Bruker Smart APEX CCD diffractometer equipped with a graphite crystal and incident beam monochromator using Mo Kα radiation ($\lambda = 0.71073$ Å). Crystal data and the data collection details are listed in Table 1. The structures of 1 and 2 were solved by an intrinsic phasing method, and refined by full-matrix least-squares methods. The hydrogen atoms were inserted at their calculated positions and fixed there. All of the calculations were carried out utilizing the SHELXT-2014/4 and SHELXTL-2014/7 [21]. Crystallographic data of the structures of 1 and 2 have been deposited with Cambridge Crystallographic Data Centre: Deposit numbers CCDC-1953681 and 1953680, respectively. 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 336033; e-mail: deposit@ccdc.cam.ac.uk). DFT calculations were carried out by using the described method in the literature [22]. Single point energy calculation and time-dependent density functional theory (TD-DFT) calculation were conducted.

3. Results and discussion
When the reaction was done under the condition with the molar ratio of Hapaet:M = 1:1, trinuclear species $[\text{Co(apaet)}_3]^{2+}$ (1$^*$) was obtained [16]. Whereas, in the condition with the 2:1 ligand/metal ratio, mononuclear complex [Co(apaet)$_2$]ClO$_4$.CH$_3$OH (1) was isolated. The crystal structure of 1 consists of a mononuclear cation, [Co(apaet)$_2$]$^+$, perchlorate ion, and methanol molecule

$$
\text{[Co(apaet)$_2$]ClO}_4\cdot\text{CH}_3\text{OH, } C_{31}H_{27}ClO_7N_2(S)\cdot\text{H}_2\text{O, }}
$$

$\mu_{\text{eq}}/\mu_{\text{B}}: 0.68$. Synthesis of [Co(apaetO)$_2$]ClO$_4$.dmac (2) (dmac = N,N'-dimethylacetamide). To a solution of Hapaet (34 mg, 0.25 mmol) and two drops of triethylamine in methanol (4 cm$^3$)/dmac (2 cm$^3$) was added a methanol solution (4 cm$^3$) of cobalt(II) perchlorate hexahydrate (93 mg, 0.25 mmol). The mixture was allowed to stand for several days at room temperature. After the resulting crystals were removed by filtration, aqueous hydrogen peroxide (30%, 1 cm$^3$) was added to the filtrate. The mixture solution was allowed to stand for several days to give orange plates. These were collected by filtration (yield 16 mg, 22% based on the thiolic ligand). Found: C, 29.02; H, 6.62; N, 12.26%. IR (KBr) $\tilde{\nu}$/cm$^{-1}$: $\tilde{\nu}$(NH) 3302(m), 3140(m); $\tilde{\nu}$(ClO) 1100(s), 1076(s), 1040(s), 622(s). Diffuse reflectance spectrum in H$_2$O $\tilde{\alpha}$/nm ($\tilde{\alpha}$/dm$^3$mol$^{-1}$cm$^{-1}$): 232 (11300), 294 (16600), 310 (15900), 456 (370).
in the asymmetric unit. A perspective view of [Co(apaet)₂]⁺ is shown in Figure 1. The Co atom has a distorted octahedral geometry similar to those of the terminal octahedral cobalt atoms of the trinuclear complex 1’. The Co atom is coordinated by two apaet⁻ ligands in a meridional fashion with four amino-nitrogen atoms and two thiolate-sulfur atoms. The bond distances of Co-S [2.2612(19), Table 1.

| Crystal and experimental data. | [Co(apaet)₂]ClO₄·CH₃OH (1) | [Co(apaetO₂)₂]ClO₄·dmac (2) |
|--------------------------------|-----------------------------|-----------------------------|
| Chemical formula              | C₁₁H₃₀ClCoN₄O₅S₂⁻           | C₁₄H₂₁ClCoN₅O₉S₂²           |
| Formula weight                | 456.89                      | 571.94                      |
| T                              | 293                         | 293                         |
| Crystal system                | monoclinic                  | monoclinic                  |
| Space group                    | P₂₁/c                       | C₂/c                        |
| a                              | 14.039(16) Å               | 8.2072(12) Å                |
| b                              | 9.898(12) Å                | 27.374(4) Å                 |
| c                              | 14.145(17) Å               | 10.9117(16) Å               |
| α                              | 94.657(16)°                | 98.898(2)°                  |
| V                              | 1954(4) Å³                  | 2422.0(6) Å³                |
| Z                              | 4                           | 4                           |
| Dₐ                             | 1.549 g/cm³                 | 1.569 g/cm³                 |
| μ(Mo Kα)                       | 1.253 mm⁻¹                  | 1.044 mm⁻¹                  |
| F(000)                         | 960                         | 1192                        |
| Crystal size                   | 0.19×0.20×0.40 mm³          | 0.10×0.32×0.40 mm³          |
| No. of reflections collected   | 11469                       | 7575                        |
| No. of independent reflections | 4496                        | 2865                        |
| □□range for data collection   | 2.51 to 28.46°              | 1.49 to 28.62°              |
| Data/Restraints/Parameters     | 4496/0/219                  | 2865/0/140                  |
| Goodness-of-fit on F²          | 1.157                       | 1.522                       |
| R indices [I>2□(I)]            | R₁ = 0.0533, wR₂ = 0.1614   | R₁ = 0.0713, wR₂ = 0.2262   |
| R indices (all data)           | R₁ = 0.0739, wR₂ = 0.1725   | R₁ = 0.0929, wR₂ = 0.2368   |
| (□□)max                        | 0.001                       | 0.000                       |
| (□□)min                        | −0.417 eÅ⁻³                 | −0.572 eÅ⁻³                 |
| (□□)min                        | 0.754 eÅ⁻³                  | 1.409 eÅ⁻³                  |

Figure 1. ORTEP drawing of the complex cation of 1. Selected bond lengths (Å) and angles (°): Co1-S1 2.2612(19), Co1-S2 2.271(2), Co1-N1 2.010(4), Co1-N2 2.028(3), Co1-N3 2.002(3), Co1-N4 2.010(4); S1-Co1-S2 92.04(9), S1-Co1-N1 86.26(12), S1-Co1-N2 179.10(10), S1-Co1-N3 88.71(12), S1-Co1-N4 88.34(12), S2-Co1-N1 86.93(11), S2-Co1-N2 87.58(13), S2-Co1-N3 88.13(11), S2-Co1-N4 179.03(11), N1-Co1-N2 94.53(15), N1-Co1-N3 172.82(14), N1-Co1-N4 92.21(15), N2-Co1-N3 90.47(15), N2-Co1-N4 92.05(16), N3-Co1-N4 92.76(15).
Figure 2. ORTEP drawing of the complex cation of 2. Selected bond lengths (Å) and angles (°): Co1-S1 2.2164(13), Co1-N1 2.026(4), Co1-N2 2.014(4), S1-O1 1.469(4), S1-O2 1.461(4), S1-Co1-S1 91.36(7), S1-Co1-N1 85.20(12), S1-Co1-N1' 90.74(12), S1-Co1-N2 176.85(12), S1-Co1-N2' 88.82(14), N1-Co1-N1' 174.2(2), N1-Co1-N2 91.66(16), N1-Co1-N2' 92.41(16), N2-Co1-N2 91.2(3). Symmetry code; i (1 – x, y, 1/2 – z).

2.271(2) Å and Co-N [2.002(3)—2.031(4) Å] are significantly shorter than the corresponding distances for the terminal Co(II) atoms of 1' [16]. These values are comparable to those of octahedral Co(III) complexes [4]. The bond distances of the Co-N located at trans positions of the sulfur donor are elongated, suggesting a trans influence of the thiolate-sulfur donor. The five-membered chelate rings, Co1-S1-C1-C2-N1 and Co1-S2-C6-C7-N3, take a gauche form which is common for five-membered ring, whereas the six-membered chelate rings, Co1-N1-C3-C4-C5-N2 and Co1-N3-C8-C9-C10-N4, take a chair form. The methanol molecule is located near the amino-nitrogen atom as indicated by the distance O5(MeOH)···N3 2.935 Å which suggests the occurrence of hydrogen bonding. The magnetic susceptibility measurement shows that the complex 1 is essentially diamagnetic throughout the 4.5—300 K temperature region, which is consistent with the low-spin cobalt(III) formulation. Although, the driving force of the oxidation of cobalt(II) is uncertain, the octahedral coordination environment around the Co atom may be important for the stable low-spin Co(III) electronic configuration. The complex 2 was obtained from a reaction solution of 1 by air oxidation or reaction with hydrogen peroxide. The crystal structure of 2 consists of mononuclear cations, [Co(apaetO2)2]2+, perchlorate ions, and dmac molecules. A perspective view of [Co(apaetO2)2]2+ is shown in Figure 2. The complex cation has a crystallographic C2 axis. Now, each sulfur atom of thiolic ligands, apaet–, was added by two oxygen atoms to form the sulfinato ligands, apaetO2–. The Co has a distorted octahedral geometry, coordinated by two sulfinate apaetO2– ligands with four amino-nitrogen atoms and two sulfinate-sulfur atoms in a meridional fashion. The bond distances of Co-S [2.2164(13) Å], Co-N [2.026(4), 2.014(4) Å], and S-O [1.461(4), 1.469(4) Å] are comparable to those of octahedral Co(III) sulfinato complexes [23]. As the electron density of S atoms would be higher by addition of oxygen atoms, the bond distances of Co-S are slightly shorter than those of the thiolate complex 1. The bond distances of Co-N located at trans positions of sulphur atoms are not elongated, in contrast with the case for the thiolate complex 1, where the trans influence was observed. This reflects the weaker donor property of the sulfinate-sulfur compared with that of the thiolate-sulfur. The five-membered chelate rings, Co1-S1-C1-C2-N1, take an envelope form which is not common for five-member chelate ring [24], whereas the six-membered chelate rings, Co1-N1-C3-C4-C5-N2, take a chair form. This mononuclear Co(III) sulfinato complex may be a model for nitrile hydratases (NHase) which was shown to have noncorrinoid cobalt center with nitrogen and thiolate-sulfur donors. The Fe-containing NHase has the bound Cys-S centers, and at least, two of those are modified to Cys-sulfenic and -sulfinic groups [23]. The Co-containing NHase must have a comparable configuration to that of Fe.
3.1 Electronic spectra and reactions of complexes

The crystal structure of the mononuclear complex 1 is quite similar to those of octahedral parts of the trinuclear complex 1' except for the oxidation state. To clear the relationship between the structural configuration and oxidation states, we attempted to oxidize the aqueous solution of 1'. The diffuse reflectance spectra of 1' show absorption bands at 350, 675, 735, 783, and 1333 nm, where the absorption at 350 nm and the other absorptions in the visible and near-infrared region can be assigned to thiolate-to-cobalt(II) charge transfer transition and ligand field absorptions for high-spin tetrahedral cobalt(II) species \(^{4}A_2 \rightarrow ^{4}T_{1}(P)\) and \(^{4}A_2 \rightarrow ^{4}T_{1}(F)\), respectively [16]. The electronic absorption spectra in aqueous solution are essentially the same as the diffused reflectance spectra, which means that the trinuclear species in the solid is maintained in the aqueous solution. However, the absorption spectra of the aqueous solution of 1' show a gradual change with time upon exposure to air at room temperature [16]. The spectra obtained after one day show a broad absorption at 470 nm and intense one at 274 nm similar to those of 1 (276 nm (\(\varepsilon = 16500 \text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}\)), 467 nm (590)). This result shows that the trinuclear cobalt(II) species was oxidized to the mononuclear cobalt(III) species, where octahedral environment is stable for low-spin \(d^6\) species rather than tetrahedral geometry. On the reaction of 1 with hydrogen peroxide, an interesting change occurred in the electronic absorption spectra as shown in Figure 3. At the beginning of the reaction, the absorption band at 276 nm (\(\varepsilon = 16500 \text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}\)) which can be assigned as thiolate-sulfur to cobalt charge transfer transition was decreasing and then increasing the intensity of the absorption band at 376 nm which is attributed to sulfenate-sulfur to cobalt charge transfer transition, molar absorption coefficient became up to 10500 dm\(^3\)mol\(^{-1}\)cm\(^{-1}\). This reaction should be a first order and rate constants in decomposition of thiolate complex \((8.1 \times 10^{-5} \text{ s}^{-1}, 25 \degree \text{C})\) and formation of sulfenate complex \((8.1 \times 10^{-5} \text{ s}^{-1})\) are almost same. The intensity of this sulfenate-sulfur to cobalt charge transfer transition band was weakened with the successive time, the absorption at 294 nm, which may be identified as sulfinate-sulfur to cobalt charge transfer transition was arisen (\(\varepsilon = 13300 \text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}\)) and is compatible with the absorption spectra of 2. The rate constant for the formation of sulfinate complex is \(6.1 \times 10^{-4} \text{ s}^{-1}\), more than 10 times slower than that for the formation of sulfenate complex. In this manner, the sulfinate cobalt complex was obtained from oxidation of thiolate complex via sulfenate complex as an intermediate.

![Figure 3. Spectral change for the reaction of 1 with hydrogen peroxide.](image-url)
3.2 DFT calculations

To explain the mechanism of oxidation by hydrogen peroxide, we performed the DFT calculations for 1 and 2. The MO energy diagrams are shown in Figure 4. In 1, unoccupied Co(III) d-orbitals \( (dx^2-y^2, dz^2) \) are almost degenerated and are located at LUMO. While, the energy levels of occupied d-orbitals \( (d_{xy}, d_{zx}, d_{zy}) \) are separated and are divided into two parts by influences of coordinated S atoms. Since the HOMO of 1 exists at the lone pair of thiolate sulfur atoms, the sulfur atoms have considerable nucleophilic character. Whereas, the HOMO of 2 is not located at S atoms but also lone pairs of oxygen atoms, the sulfur atoms are no longer so called “activation sites”. It is generally accepted that \( \text{H}_2\text{O}_2 \) oxidation of nucleophilic substrates occurs via nucleophilic attack of the substrate on the O-O bond of \( \text{H}_2\text{O}_2 \). The oxidation reaction scheme from thiolate complex to sulfinate complex seems to be as follows (Scheme 1). (1) \( \text{H}_2\text{O}_2 \) molecule reacts with nucleophilic attack to the coordinated thiolate sulfur atom and this is deprotonated to form terminal bonded S=O-OH species. (2) As the oxygen atom connected to sulfur atom has a negative \( \square \) charge, terminal hydrogen atom moves to the oxygen atom connected to sulfur atom. (3) The O-O bonding of \( \text{O}_2^2^- \) is weakened and terminal oxygen is disconnected. The electron of oxygen atom is localized toward sulfur atom, oxygen atom is deprotonated, and then sulfenate intermediate is formed. The leaving oxygen atom may oxidize other sulfur atom, generate dioxygen or \( \text{H}_2\text{O} \) molecule. (4) A similar nucleophilic attack of \( \text{H}_2\text{O}_2 \) molecule to sulfenate oxygen atom forms sulfinate complex. Because of the steric hindrance around sulfenate sulfur atom, the reaction from sulfenate to sulfinate complex may be slower than that from thiolate complex to sulfenate complex.

![Figure 4. MO diagrams of 1 and 2.](image-url)

![Scheme 1. Reaction mechanism of reaction of 1 with hydrogen peroxide.](image-url)
Figure 5. Diffused reflectance spectra of 1 and 2 with the TD-DFT calculated transition energies as absorption wavelengths in nm and oscillator strengths indicated by vertical lines for comparison.

To assign electronic absorption spectra, we perform time-dependent density functional theory (TD-DFT) calculations for 1 and 2. The calculated and experimental spectra of the complexes 1 and 2 are shown in Figure 5. The calculated spectra exhibit good agreement with experimental spectra. For the electronic absorption spectra of 1 show two large absorption bands at 220(sh) and 276 nm, calculated peaks are located at 223 and 277 nm. The calculated peak at 223 nm may be corresponding to the experimental shoulder absorption at 220 nm is arisen mainly by the transition from HOMO-6 (consists of Co d_{xy} + s(α)) to LUMO+1 (Co d_{x^2-y^2}) , which can be assigned S(α)→Co charge transfer. The calculated peaks around at 276nm are consists of many transitions. In particular, the peak at 291 nm can be attributed to S(α)→Co charge transfer. Because the calculated peaks around at 276 nm are divided some peaks in calculation, intensity of this peak would be lower than that of experimental peak at 276 nm. Whereas, the electronic absorption spectra of complex 2 show intense absorption bands at 232, 294 and 310 nm, calculated peaks are positioned at 245 and 280 nm. Although, the two intense calculated peaks are mainly consists of the same transition from HOMO-1 (lone pair of O + Co d_{z^2} + S(α)) to LUMO (d_{z^2}) and from HOMO (lone pair of O + Co d_{xy} + S(α)) to LUMO+1 (dx^2-y^2), the transition moments of them are pointed opposite or same directions. As the transition moments calculated at 245 nm are pointed opposite directions, the intensity of peak becomes weak, whereas those of calculated at 280 nm are pointed the same direction and strong intensity can be observed. Because of the electron configuration interaction, the two calculated peaks apart each other. The observed peak at 232, 294, and 310 nm can be assigned S(α)→Co charge transfer.

3.3 Reaction of 1 and H_{2}O_{2} with carotenoids

As we assumed that an active O atom forms in the reaction of 1 and H_{2}O_{2}, we examined oxidation reaction of a dye like carotenoids by using 1. The "orange color 100" is one of the carotenoid dyes used as food additives, which is a mixture of capsanthine, glycerin, and so on. When an aqueous solution of orange color 100 (ca. 140 μmol/L as capsanthine), was reacted with the complex 1 (24.3 μmol/L) and hydrogen peroxide (3.65 mmol/L) in alkaline aqueous condition (pH10.8), the
electronic absorption spectra shows the decomposition of the carotenoid. The spectral change of orange color 100 with time upon the reaction is shown in Figure 6. The reaction constant of this reaction is $5.14 \times 10^{-5}$ s$^{-1}$ at 20$^\circ$C, $25.0 \times 10^{-5}$ s$^{-1}$ at 30$^\circ$C, and $59.5 \times 10^{-5}$ s$^{-1}$ at 40$^\circ$C and activation energy for decomposition of orange color 100 was calculated to 216 kJ/mol. No spectral change was occurred in the reaction condition without I or with cobalt(II) chloride hexahydrate instead of I in the similar time range (one week at 25$^\circ$C). This result shows that the complex I reacts as an oxidant and may has a DTI (dye-transfer inhibition) effect during laundering.

**Figure 6.** Spectral change for oxidation of orange color 100 by I and H$_2$O$_2$.

3.4 Electrochemistry

The cyclic voltammograms of I and 2 are shown in Figure 7. The first reduction processes have the characteristic of an electrochemically quasi-reversibl e couple and assigned for Co(III)/Co(II) redox couple. Half-wave potentials ($E_{1/2}$) of them are $+1.19$ V (210 mV) vs SCE for I and $+0.61$ V ($50$ mV) for 2. This result show that Co(III) species of I is more stable than that of 2 and they go hand-in-hand with the LUMO of I ($-3.6157$ eV) has higher energy than that of 2 ($-4.4651$ eV) in DFT calculation.

**Figure 7.** Cyclic voltammograms of I and 2 (1 mM) in MeOH [(n-(C$_4$H$_9$)$_4$NClO$_4$, scan rate 100 mV/s).
4. Conclusion
In this study, we have isolated and characterized two kinds of mononuclear Co(III) complexes with apaet and apaetO\textsuperscript{2–}. The mononuclear thiolate complex can react with hydrogen peroxide, resulting in sulfinate mononuclear Co(III) complex via the sufenate Co(III) species, which may be relevant to a model for bacterial enzymes, nitrile hydratase (NHase).

Acknowledgement
The present work was partially supported by the MEXT-Supported Program for the Strategic Research Foundation at Private Universities and Grants-in-Aid for Scientific Research No. 17K05820 from the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

References
[1] B. Krebs, G. Henkel, “Transition-metal thiolates: from molecular fragments of sulfidic solids to models for active centers in biomolecules,” Angew. Chem. Int. Ed. Engl., vol. 30, 769-788, 1991.
[2] J. A. Garcia-Vazquez, J. Romero, A. Sousa, “Electrochemical synthesis of metallic complexes of bidentate thiolates containing nitrogen as an additional donor atom,” Coord. Chem. Rev., vol. 212, 691-745, 1999.
[3] M. Mikuriya, S. Kida, S. Ueno, I. Murase, “Crystal and molecular structure of a triply-thiolate-bridged binuclear cobalt(III) complex, [Co\textsubscript{2}(SCH(CH\textsubscript{2}CH\textsubscript{2}NH\textsubscript{2})\textsubscript{2}]\textsubscript{3}(ClO\textsubscript{4})\textsubscript{3}·H\textsubscript{2}O,” Bull. Chem. Soc. Jpn., vol. 58, pp. 1857-1858, 1985.
[4] M. Mikuriya, S. Kida, I. Murase, “Crystal and molecular structure of a thiolato-bridged binuclear nickel(II) complex, [Ni\textsubscript{2}(SCH(CH\textsubscript{2}CH\textsubscript{2}NH\textsubscript{2})\textsubscript{2}]\textsubscript{2}Br\textsubscript{2},” Bull. Chem. Soc. Jpn., vol. 60, pp. 1180-1182, 1987.
[5] M. Handa, M. Mikuriya, J.-Z. Zhong, H. Okawa, S. Kida, “Synthesis, properties, and crystal structure of binuclear nickel(II) and palladium(II) complexes of tridentate thiolic ligands with NNS-donor set,” Bull. Chem. Soc. Jpn., vol. 61, pp. 3883-3887, 1988.
[6] M. Mikuriya, F. Adachi, H. Iwasawa, M. Handa, M. Koikawa, H. Okawa, “A novel thiolate-bridged polynuclear manganese(II) complex with 2-[2-(2-pyridyl)ethylamino]ethanethiol,” Inorg. Chim. Acta, vol. 179, pp. 3-4, 1991.
[7] M. Mikuriya, F. Adachi, H. Iwasawa, M. Handa, M. Koikawa, H. Okawa, “Synthesis and characterization of thiolate-bridged manganese(II) complexes with NNS-donor sets,” Bull. Chem. Soc. Jpn., vol. 67, 3263-3270, 1994.
[8] M. Mikuriya, T. Kotera, F. Adachi, M. Handa, M. Koikawa, H. Okawa, “Syntheses and structural characterization of dinuclear and trinuclear iron(II) complexes of tridentate thiolic ligands with an NNS donor set,” Bull. Chem. Soc. Jpn., vol. 68, pp. 574-580, 1995.
[9] M. Mikuriya, H. Tsutsu, R. Nukada, M. Handa, Y. Sayama, “Synthesis and characterization of thiolate-bridged trinuclear heteromatal complexes with 2-[(3-aminopropyl)amino]ethanethiol,” Bull. Chem. Soc. Jpn., vol. 69, pp. 3489-3498, 1996.
[10] T. Kawahashi, H. Tsutsu, M. Mikuriya, “A novel tetranuclear palladium(II) complex with 2-[(3-aminopropyl)amino]ethanethiol,” Polyhedron, vol. 15, pp. 169-171, 1996.
[11] M. Mikuriya, X. Jian, S. Ikemi, T. Kawahashi, H. Tsutsu, “Synthesis and structural characterization of thiolato-bridged zinc(II) complexes with NNS-tridentate ligands,” Bull. Chem. Soc. Jpn., vol. 71, pp. 2161-2168, 1998.
[12] T. Kawahashi, M. Mikuriya, R. Nukada, J.-W. Lim, “Synthesis and structural characterization of thiolato-bridged tetranuclear palladium(II) complexes with N,N,S-tridentate ligands,” Bull. Chem. Soc. Jpn., vol. 74, pp. 323-329, 2001.
[13] M. Mikuriya, X. Jian, S. Ikemi, T. Kawahashi, H. Tsutsu, A. Nakasone, J.-W. Lim, “Synthesis and characterization of thiolato-bridged cadmium(II) complexes with N,N,S-chelating thiolic ligands,” Inorg. Chim. Acta, vol. 312, pp. 183-187, 2001.
[14] T. Kotera, M. Mikuriya, “Thiolato-bridged hexanuclear Cu\textsuperscript{II}Cu\textsuperscript{II} mixed-valence complex,” Chem. Lett., vol. 31, pp. 654-655, 2002.
[15] T. Kotera, A. Fujita, M. Mikuriya, M. Handa, “Thiolato-bridged copper complexes with N,N,S-
tridentate ligands,” Materials Science (Poland), vol. 21, pp. 171-179, 2003.

[16] T. Kotera, A. Fujita, M. Mikuriya, H. Tsutsumi, M. Handa, “Cobalt complexes with 2-[(3-aminopropyl)amino]ethanethiol,” Inorg. Chem. Commun., vol. 6, pp. 322-324, 2003.

[17] T. Kotera, T. Sugimoto, M. Mikuriya, “A thiolato-bridged octanuclear copper(I,II) mixed-valence complex with N,N,S-tridentate ligand,” Chem. J. Moldova, vol. 2, pp. 102-107, 2007.

[18] M. Mikuriya, T. Watanabe, A. Suyama, D. Yoshioka, “Rhenium complex with 2-[(2-pyridylmethyl)amino]ethanethiol,” X-ray Struct. Anal. Online, vol. 31, pp.3-4, 2015.

[19] M. Mikuriya, K. Kusunoki, T. Kotera, D. Yoshioka, and K. Ogasawara, “Synthesis, crystal structure, and DFT calculation of a dioxido-bridged dinuclear oxidomolybdenum(V) complex with 2-(2-aminoethyl)aminoethanethiol,” X-ray Struct. Anal. Online, vol. 33, pp.37-39, 2017.

[20] M. Mikuriya, K. Kusunoki, T. Kotera, D. Yoshioka, S. Takemura, and K. Ogasawara, “Synthesis, crystal structure, and relativistic DV-Xα calculation of a µ-oxido-µ-molybdato(VI)-bridged dinuclear oxidomolybdenum(V) complex with 2-(3-aminopropyl)aminoethanethiol,” X-ray Struct. Anal. Online, vol. 34, pp.19-21, 2018.

[21] G. M. Sheldrick, “Crystal structure refinement with SHELXL,” Acta Crystallogr., Sect. C, vol. 71, pp. 1-8, 2015.

[22] S. Wada, T. Kotera, M. Mikuriya, “Synthesis and structural characterization of a dinuclear palladium(II) complex with N,N,N,N'-tetakis(2-p-toluenesulfonamidoethyl)cyclam,” Bull. Chem. Soc. Jpn., vol.81, pp.1454-1460, 2008.

[23] I. Kung, D. Schweitzer, J. Shearer, W. D. Taylor, H. L. Jackson, S. Lovell, J. A. Kovacs, “How do oxidized thiolate ligands affect the electronic and reactivity properties of a nitrile hydratase model compound?,” J. Am. Chem. Soc., vol. 122, pp. 8299-8300, 2000.

[24] M. Mikuriya, H. Okawa, S. Kida, “Binuclear metal complexes. XLIV. Crystal structures and magnetic properties of alkoxy-bridged binuclear copper(II) complexes with 2-[2-(dialkylamino)ethylthio]ethanol,” Bull. Chem. Soc. Jpn., vol. 55, pp. 1086-1091, 1982.