Synthesis and Structures of the Doubly Bridged Dinuclear Cobalt(III) Peroxo Complexes $[(\mathrm{tren})\mathrm{Co}(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{SR})\mathrm{Co}(\mathrm{tren})]^{n+}$ [tren = Tris(2-aminoethyl)amine; SR = Thiosulfate(2−) and Benzenethiolate(1−)]

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Introduction

Many dinuclear dioxygen-bridged cobalt(III) complexes have been reported.[1] These compounds have been increasing in interest from the point of view of oxygen activation and selective or specific oxidation reactions for organic molecules.[2] Recently, we communicated the novel synthesis of the (μ-peroxo)(μ-thiosulfato)cobalt(III) complex $[(\mathrm{tren})\mathrm{Co}(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{S_2O_3})\mathrm{Co}(\mathrm{tren})]^{2+}$ [tren = tris(2-aminoethyl)amine] from $[\mathrm{CoCl_2(tren)}]\mathrm{Cl}$ and $\mathrm{NH_2(CH_2)_{\mathit{n}}NH_2{\cdot}H_2S_{\mathit{x}}}$ in the presence of activated charcoal.[3] The X-ray crystal structure reveals that the complex has an unprecedentedly large Co—O—O—Co torsion angle of 75.5(2)° as compared with those of the known doubly bridged peroxo complexes $[\mathrm{N_4Co}(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{X})\mathrm{CoN_4}]^{n+}$ ($\mathrm{X} = \mathrm{OH^-}$ and $\mathrm{NH_2^-}$).[1] It would be interesting to discover whether such a large torsion angle is essential for other μ-peroxo, μ-sulfur doubly bridged complexes.

Here we report the improved synthesis of $[(\mathrm{tren})\mathrm{Co}(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{S_2O_3})\mathrm{Co}(\mathrm{tren})]^{2+}$ and the related four peroxo complexes $[(\mathrm{tren})\mathrm{Co}(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{SR})\mathrm{Co}(\mathrm{tren})]^{n+}$ [SR = $\mathrm{SCH_2CH_2SO_3^{2-}}$, $\mathrm{SCH_2CH_2OH^-}$, $\mathrm{SC_6H_5^-}$, and $\mathrm{SCH_2CH_2N(CH_2CH_3)_2^-}$]. These complexes were obtained in relatively good yields and showed characteristic UV/vis absorption spectra. X-ray crystal structures were determined for the two complexes with $\mu\text{-}\mathrm{S_2O_3^{2-}}$ and $\mu\text{-}\mathrm{SC_6H_5^-}$.

Experimental Section

Preparations. $[\{\mathrm{Co(tren)}\}_2(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{S_2O_3})]\mathrm{Cl_2}$ (1). To an aqueous solution (30 cm³) of $\mathrm{CoCl_2{\cdot}6H_2O}$ (4.76 g) were added the quadridentate ligand tren (2.92 g) and then an aqueous solution (40 cm³) of $\mathrm{Na_2S_2O_3{\cdot}5H_2O}$ (2.5 g). The color of the mixture became dark brown in 30 min by because of air oxidation. The resulting solution was poured onto a column of cation exchanger (SP-Sephadex C-25, $\mathrm{Na^+}$ form; o.d. 4 × 50 cm) and eluted with 0.2 mol dm⁻³ NaCl to give two dark brown bands. The first dominant dark brown band (complex **1**: yield 67%) was the desired band, and the complex was crystallized after removal of NaCl by evaporation. The second dark brown band was the authentic complex $[\{\mathrm{Co(tren)}\}_2(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{OH})]^{3+}$ based on its absorption spectrum.[4] Anal. Calcd for **1**, $[\{\mathrm{Co(tren)}\}_2(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{S_2O_3})]\mathrm{Cl_2{\cdot}5H_2O} = \mathrm{C_{12}H_{46}Cl_2Co_2N_8O_{10}S_2}$: C, 20.15; H, 6.48; N, 15.66. Found: C, 20.07; H, 6.50; N, 15.59. ^{13}C NMR, δ [$\mathrm{(CD_3)_2SO}$]: 60.7, 58.5, 45.2, 44.0 (tren). The corresponding iodide, perchlorate, and nitrate were obtained by using anion exchange resins (QAE-Sephadex A-25). Anal. Calcd for $[\{\mathrm{Co(tren)}\}_2(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{S_2O_3})]\mathrm{I_2{\cdot}3.5H_2O} = \mathrm{C_{12}H_{43}Co_2I_2N_8O_{8.5}S_2}$: C, 16.54; H, 4.97; N, 12.86. Found: C, 16.66; H, 5.16; N, 12.93. Calcd for $[\{\mathrm{Co(tren)}\}_2(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{S_2O_3})](\mathrm{ClO_4})_2{\cdot}\mathrm{2H_2O} = \mathrm{C_{12}H_{40}Cl_2Co_2N_8O_{15}S_2}$: C, 18.26; H, 5.11; N, 14.20. Found: C, 18.43; H, 5.32; N, 14.13. Calcd for $[\{\mathrm{Co(tren)}\}_2(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{S_2O_3})](\mathrm{NO_3})_2{\cdot}\mathrm{4.5H_2O} = \mathrm{C_{12}H_{45}Co_2N_{10}O_{15.5}S_2}$: C, 18.98; H, 5.97; N, 18.44. Found: C, 19.06; H, 5.97; N, 18.55.

Table 1. UV/vis Absorption Data (Solvent: Water)

complex	$\lambda_{\max}$/nm (ϵ/dm³ mol⁻¹ cm⁻¹)
1	510 sh (720), 350 (6810), 275 (20 700), 228 (22 000)
2	510 sh (690), 348 (8120), 276 (24 000), 209 (19 300)
3	510 sh (670), 345 (8040), 276 (24 100), 208 (18 800)
4	520 sh (740), 360 (8060), 299 (23 400), 220 sh (21 000)
5	510 sh (600), 351 (6800), 276 (20 300), 209 (17 500)

$[\{\mathrm{Co(tren)}\}_2(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{SCH_2CH_2SO_3})]\mathrm{Cl_2}$ (2). This complex was prepared and chromatographed as described above except for the use of equimolar amounts of $\mathrm{HSCH_2CH_2SO_3Na}$ and $\mathrm{N(C_2H_5)_3}$ instead of $\mathrm{Na_2S_2O_3{\cdot}5H_2O}$. The yield was 37%. Anal. Calcd for **2**, $[\{\mathrm{Co(tren)}\}_2(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{SCH_2CH_2SO_3})]\mathrm{Cl_2{\cdot}6H_2O} = \mathrm{C_{14}H_{52}Cl_2Co_2N_8O_{11}S_2}$: C, 22.08; H, 6.88; N, 14.71. Found: C, 22.06; H, 6.90; N, 14.56. ^{13}C NMR δ ($\mathrm{D_2O}$): 61.9, 59.4, 46.6, 45.6 (tren); 52.8, 23.6 ($\mathrm{SCH_2CH_2SO_3}$).

$[\{\mathrm{Co(tren)}\}_2(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{SCH_2CH_2OH})][\mathrm{ClO_4}]_3$ (3). The reaction solution was prepared in the same way as that for complex **1** except for the use of equimolar amounts of $\mathrm{HSCH_2CH_2OH}$ and $\mathrm{N(C_2H_5)_3}$ instead of $\mathrm{Na_2S_2O_3{\cdot}5H_2O}$. Complex **3** was partly overlapped with $[\{\mathrm{Co(tren)}\}_2(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{OH})]^{3+}$ and eluted first. The complex was converted to the perchlorate salt using a column of QAE-Sephadex A-25 (o.d. 4 × 20 cm, $\mathrm{ClO_4^-}$ form). Anal. Calcd for **3**, $[\{\mathrm{Co(tren)}\}_2(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{SCH_2CH_2OH})][\mathrm{ClO_4}]_3{\cdot}\mathrm{H_2O} = \mathrm{C_{14}H_{43}Cl_3Co_2N_8O_{16}S}$: C, 20.12; H, 5.19; N, 13.41. Found: C, 20.26, H, 5.20; N, 13.45. ^{13}C NMR δ [$\mathrm{(CD_3)_2SO}$]: 60.3, 58.0, 45.1, 43.7 (tren); 61.2, 30.1 ($\mathrm{SCH_2CH_2OH}$).

$[\{\mathrm{Co(tren)}\}_2(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{SC_6H_5})][\mathrm{ClO_4}]_3$ (4). This complex was prepared and chromatographed as described for complex **3** except for the use of $\mathrm{C_6H_5SH}$ instead of $\mathrm{HSCH_2CH_2OH}$. Complex **4** was partly overlapped with $[\{\mathrm{Co(tren)}\}_2(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{OH})]^{3+}$ and eluted first. The yield was 40%. Anal. Calcd for **4**, $[\{\mathrm{Co(tren)}\}_2(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{SC_6H_5})][\mathrm{ClO_4}]_3 = \mathrm{C_{18}H_{41}Cl_3Co_2N_8O_{14}S}$: C, 25.44; H, 4.86; N, 13.18. Found: C, 24.91; H, 4.91; N, 13.24. ^{13}C NMR δ ($\mathrm{D_2O}$): 62.8, 59.8, 46.8, 46.7, 46.5, 45.6, 45.5, 45.4 (tren); 134.8, 131.4, 131.0, ($\mathrm{SC_6H_5}$).

$[\{\mathrm{Co(tren)}\}_2(\mu\text{-}\mathrm{O_2})\{\mu\text{-}\mathrm{SCH_2CH_2N(C_2H_5)_2}\}][\mathrm{ClO_4}]_3$ (5). The complex was prepared and chromatographed in the same way as that for complex **3** except for the use of $\mathrm{(C_2H_5)_2NCH_2CH_2SH}$ instead of $\mathrm{HSCH_2CH_2OH}$. Complex **5** was overlapped with $[\{\mathrm{Co(tren)}\}_2(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{OH})]^{3+}$ and eluted later. Anal. Calcd for **5**, $[\{\mathrm{Co(tren)}\}_2(\mu\text{-}\mathrm{O_2})\{\mu\text{-}\mathrm{SCH_2CH_2N(C_2H_5)_2}\}][\mathrm{ClO_4}]_3{\cdot}\mathrm{0.75NaClO_4{\cdot}H_2O} = \mathrm{C_{18}H_{52}Cl_3Co_2N_9O_{15}S{\cdot}0.75NaClO_4}$: C, 22.00; H, 5.33; N, 12.83. Found: C, 22.04; H, 5.40; N, 12.83. ^{13}C NMR δ [$\mathrm{(CD_3)_2SO}$]: 60.5, 58.0, 45.2, 44.0 (tren); 50.3, 46.7, 19.8, 9.2 [$\mathrm{SCH_2CH_2N(C_2H_5)_2}$].

X-ray Crystal Structure Determinations of $[(\mathrm{tren})\mathrm{Co}(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{S_2O_3})\mathrm{Co}(\mathrm{tren})]\mathrm{I_2{\cdot}3.5H_2O}$ (1) and $[(\mathrm{tren})\mathrm{Co}(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{SC_6H_5})\mathrm{Co}(\mathrm{tren})][\mathrm{ClO_4}]_3$ (4). Both crystals were obtained from aqueous solutions in a refrigerator. Diffraction data were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Crystallographic data for the complexes are listed in Table 2. Structures were solved using the Patterson method and parameters refined by block diagonal matrix least-squares methods. Anisotropic temperature factors were applied for the non-hydrogen atoms except for O(14A) of water in complex **1** and O(23A), O(23B), O(23C), O(24A), O(24B), O(24C), O(34A), and O(34B) of disordered perchlorate in complex **4**. All calculations were performed using the TEXSAN[5] crystallographic software package of Molecular Structure Corp.

Measurements. UV/vis absorption spectra were measured with a Hitachi 330 spectrophotometer. Proton and ^{13}C NMR spectra were recorded with JEOL JNM-GSX-270 and GSX-400 spectrometers in $\mathrm{D_2O}$ and/or $\mathrm{(CD_3)_2SO}$. X-ray crystal structure analyses were performed by the X-ray Diffraction Service of the Department of Chemistry.

Results and Discussion

Preparation and Characterization. In all preparations containing $\mathrm{CoCl_2{\cdot}6H_2O}$, tren, and $\mathrm{RS^-}$ (mole ratio = 2:2:1) short

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(4) Zehnder, M.; Thewalt, U.; Fallab, S. *Helv. Chim. Acta* **1976**, *59*, 2290.
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Table 2. Crystallographic Data for $[(tren)Co(\mu\text{-}O_2)(\mu\text{-}S_2O_3)Co(tren)]I_2{\cdot}3.5H_2O$ (**1**) and $[(tren)Co(\mu\text{-}O_2)(\mu\text{-}SC_6H_5)Co(tren)][ClO_4]_3$ (**4**)

	1	**4**
chem formula	$C_{12}H_{43}Co_2I_2N_8O_{8.5}S_2$	$C_{18}H_{41}Cl_3Co_2N_8O_{14}S$
fw	871.32	849.85
crystal system	triclinic	triclinic
a, Å	11.078(1)	10.726(2)
b, Å	13.133(1)	15.538(2)
c, Å	10.163(1)	10.269(1)
α, deg	93.478(8)	96.69(1)
β, deg	105.289(9)	106.86(1)
γ, deg	79.438(8)	78.42(1)
V, Å^3	1402.0(2)	1601.4(4)
Z	2	2
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
T, °C	23	23
ϱ_c, g cm^{-3}	2.064	1.762
μ(Mo Kα), cm^{-1}	35.55	14.22
R^a	0.039	0.043
$R_w{}^b$	0.053	0.051

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2|F_o|$.

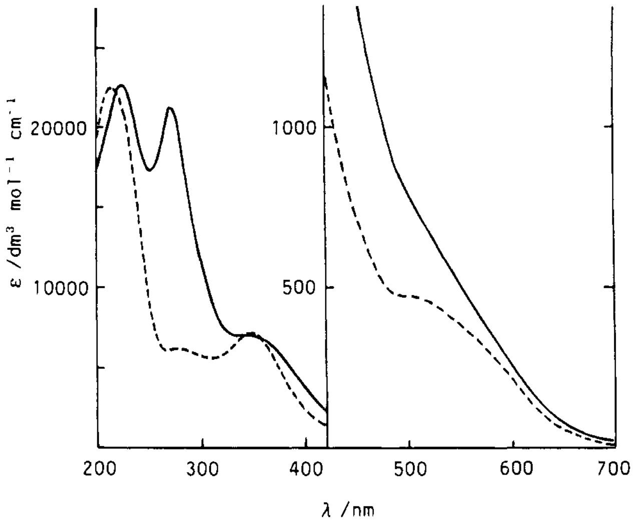
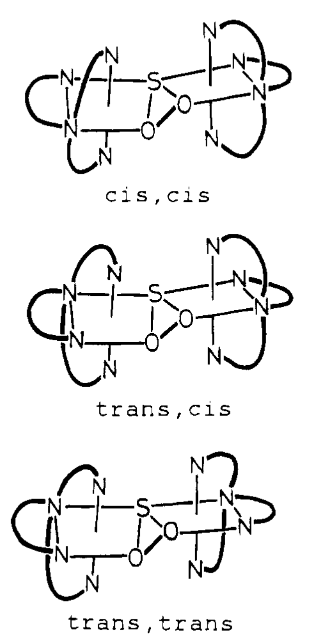


Figure 1. UV/vis absorption spectra of $[(tren)Co(\mu\text{-}O_2)(\mu\text{-}S_2O_3)Co(tren)]^{2+}$ (solid line) and $[(tren)Co(\mu\text{-}O_2)(\mu\text{-}OH)Co(tren)]^{3+}$ (dotted line).

air oxidation produced a dark brown solution, which was composed of two dark brown bands detected by the column separation. The fact that complex **1** in the thiosulfate system wsa eluted before the authentic complex $[\{Co(tren)\}_2(\mu\text{-}O_2)(\mu\text{-}OH)]^{3+}$ [4] indicates that complex **1** has a divalent net electric charge: the dioxygen group O_2 is a peroxo(2−) form. Elemental analysis agrees well with the formulation $[\{Co(tren)\}_2(\mu\text{-}O_2)(\mu\text{-}S_2O_3)]X_2$. The UV/vis absorption spectrum of complex **1** is shown in Figure 1 as wel as that of $[\{Co(tren)\}_2(\mu\text{-}O_2)(\mu\text{-}OH)]^{3+}$. Both complexes have no absorption at 680 nm indicating a bridging superoxo group, which is consistent with the above formulation. Two characteristic intense bands with almost equal molar absorption coefficients have been observed at 348 (ϵ = 7210) and 277 nm (ϵ = 6330) for $[\{Co(tren)\}_2(\mu\text{-}O_2)(\mu\text{-}OH)]^{3+}$. These bands are considered to be due to the peroxo group.[6] Complex **1** shows two similar intense bands at 350 (ϵ = 6810) and 275 nm (ϵ = 20 700). However, the molar absorption coefficient at 275 nm is 3 times larger than that at 350 nm because an intense sulfur-to-metal charge transfer band overlaps the second peroxo band.[7] The UV/vis absorption spectra of the other complexes **2**−**5** are analogous to that of complex **1**, though small red shifts were observed for complex **4** with the benzenethiolato bridge (Table 1). The change of the bridging sulfur ligands among $S_2O_3{}^{2-}$, $SCH_2CH_2SO_3{}^{2-}$, $HOCH_2CH_2S^-$, and $Et_2NCH_2CH_2S^-$ seems to have little influence on the UV/vis absorption spectra.


cis,cis

trans,cis

trans,trans

Figure 2. Three possible geometrical isomers of $[(tren)Co(\mu\text{-}O_2)(\mu\text{-}SR)Co(tren)]^{n+}$.

Three geometrical isomers are possible for $[(tren)Co(\mu\text{-}O_2)(\mu\text{-}X)Co(tren)]^{n+}$. They are designated as cis,cis, cis,trans, and trans,trans with regard to the relationship between the two tertiary amines of tren and the peroxo group as shown in Figure 2. Only the cis,cis isomer was found in the hydroxo complex (X = OH^-) in the crystal state.[4] A molecular model consideration indicates that both cis,trans and trans,trans structures are sterically unfavorable because they have one or two chelate rings in the crowded sulfur bridging side. The ^{13}C NMR spectrum of the hydroxo complex showed only four signals, two [δ (D_2O): 62.7, 60.4] for $N(CH_2CH_2NH_2)_3$ and two [δ (D_2O): 45.2, 45.1) for $N(CH_2CH_2NH_2)_3$. The same spectral patterns were obtained for complexes **1**−**3** and **5**. This means that only the cis,cis isomer exists even in D_2O or $(CD_3)_2SO$ and the structure is symmetrical not only at the top and bottom but also at the right and left. It is reasonable to consider that the peroxo group is exchanging at a faster rate than the NMR time scale. However, complex **4** showed eight signals, two in the $N(CH_2CH_2NH_2)_3$ region and six in the $N(CH_2CH_2NH_2)_3$ region. This indicates that complex **4** adopts the cis,cis structure with C_1 symmetry and the exchange rate of the peroxo group is relatively slow for this complex.

Crystal Structures of $[(tren)Co(\mu\text{-}O_2)(\mu\text{-}S_2O_3)Co(tren)]I_2{\cdot}3.5H_2O$ (1) and $[(tren)Co(\mu\text{-}O_2)(\mu\text{-}SC_6H_5)Co(tren)][ClO_4]_3$ (4). An ORTEP[8] projection of the dinuclear cation **1** is shown in Figure 3. Crystallographic data, atomic parameters, and selected bond distances and angles are listed in Tables 2, 3 (supplement), and 5, respectively. Complex **1** adopts the cis,cis geometry as found in $[(tren)Co(\mu\text{-}O_2)(\mu\text{-}OH)Co(tren)]^{3+}$.[4] The two cobalt ions are bridged by a thiosulfato sulfur and a peroxo group, thus completing the octahedral coordination sphere of the cobalt(III) ions. The $Co-O_2$ distances 1.902(2) and 1.893(2) Å, the O−O distance 1.456(3) Å, and the Co−O−O angles 111.7(2) and 111.7(2)° are quite normal for peroxo-bridged

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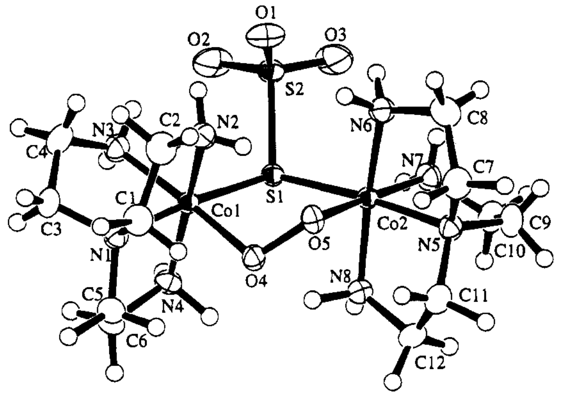

Figure 3. ORTEP drawing of the cation in $[(\mathrm{tren})\mathrm{Co}(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{S_2O_3})\mathrm{Co}(\mathrm{tren})]\mathrm{I_2}\cdot 3.5\mathrm{H_2O}$ (**1**).

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for $[(\mathrm{tren})\mathrm{Co}(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{S_2O_3})\mathrm{Co}(\mathrm{tren})]\mathrm{I_2}\cdot 3.5\mathrm{H_2O}$ (**1**) and $[(\mathrm{tren})\mathrm{Co}(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{SC_6H_5})\mathrm{Co}(\mathrm{tren})][\mathrm{ClO_4}]_3$ (**4**)

1		**4**	
Co(1)−S(1)	2.2672(8)	Co(1)−S(1)	2.2411(9)
Co(2)−S(1)	2.2642(8)	Co(2)−S(1)	2.2448(9)
Co(1)−O(4)	1.902(2)	Co(1)−O(4)	1.894(2)
Co(2)−O(5)	1.893(2)	Co(2)−O(5)	1.887(2)
O(4)−O(5)	1.456(3)	O(4)−O(5)	1.449(3)
Co(1)−N(1)	1.968(3)	Co(1)−N(1)	1.980(3)
Co(1)−N(2)	1.946(3)	Co(1)−N(2)	1.952(4)
Co(1)−N(3)	1.971(3)	Co(1)−N(3)	1.990(3)
Co(1)−N(4)	1.979(3)	Co(1)−N(4)	1.974(4)
Co(2)−N(5)	1.971(3)	Co(2)−N(5)	1.971(3)
Co(2)−N(6)	1.966(4)	Co(2)−N(6)	1.963(4)
Co(2)−N(7)	1.975(3)	Co(2)−N(7)	1.994(3)
Co(2)−N(8)	1.956(4)	Co(2)−N(8)	1.951(3)
S(1)−S(2)	2.095(1)	S(1)−C(21)	1.775(4)
S(2)−O(1)	1.439(3)		
S(2)−O(2)	1.442(3)		
S(2)−O(3)	1.444(3)		
S(1)−Co(1)−O(4)	84.60(7)	S(1)−Co(1)−O(4)	84.37(7)
S(1)−Co(2)−O(5)	88.07(6)	S(1)−Co(2)−O(5)	88.06(7)
Co(1)−S(1)−Co(2)	104.54(3)	Co(1)−S(1)−Co(2)	105.28(4)
Co(1)−O(4)−O(5)	111.7(2)	Co(1)−O(4)−O(5)	112.2(2)
Co(2)−O(5)−O(4)	111.7(2)	Co(2)−O(5)−O(4)	112.7(2)
S(1)−Co(2)−O(5)	88.07(6)	S(1)−Co(2)−O(5)	88.06(7)
S(1)−Co(1)−N(1)	174.5(1)	S(1)−Co(1)−N(1)	171.5(1)
N(2)−Co(1)−N(4)	169.3(1)	N(2)−Co(1)−N(4)	167.4(1)
N(3)−Co(1)−O(4)	178.1(1)	N(3)−Co(1)−O(4)	179.4(1)
S(1)−Co(2)−N(5)	174.1(1)	S(1)−Co(2)−N(5)	174.1(1)
N(6)−Co(2)−N(8)	169.8(1)	N(6)−Co(2)−N(8)	168.7(1)
N(7)−Co(2)−O(5)	178.0(1)	N(7)−Co(2)−O(5)	178.9(1)
N(1)−Co(1)−N(2)	85.2(1)	N(1)−Co(1)−N(2)	85.5(1)
N(1)−Co(1)−N(3)	86.3(1)	N(1)−Co(1)−N(3)	86.2(1)
N(1)−Co(1)−N(4)	85.9(1)	N(1)−Co(1)−N(4)	84.5(1)
N(5)−Co(2)−N(6)	86.5(1)	N(5)−Co(2)−N(6)	85.6(1)
N(5)−Co(2)−N(7)	85.7(1)	N(5)−Co(2)−N(7)	86.1(1)
N(5)−Co(2)−N(8)	85.0(1)	N(5)−Co(2)−N(8)	85.7(1)
Co(1)−O(4)−O(5)−Co(2)	75.5(2)	Co(1)−O(4)−O(5)−Co(2)	73.2(2)

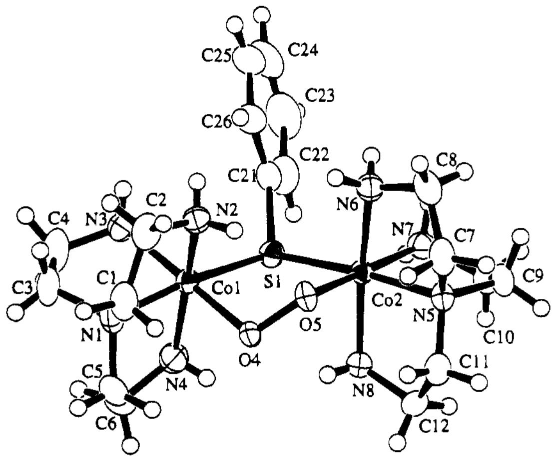

Figure 4. ORTEP drawing of the cation in $[(\mathrm{tren})\mathrm{Co}(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{SC_6H_5})\mathrm{Co}(\mathrm{tren})][\mathrm{ClO_4}]_3$ (**4**).

compounds.[1] However, the Co−O−O−Co torsion angle [75.5(2)°] is large and the Co- -Co distance [3.5838(7) Å] is very long compared with 60.7° and 3.294 Å, respectively, in $[(\mathrm{tren})\mathrm{Co}(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{OH})\mathrm{Co}(\mathrm{tren})]^{3+}$.[4] The bridging mode of the thiosulfato ion $\mu\text{-}\mathrm{S_2O_3}\text{-}S$ in the complex has been known in $[\mathrm{Cu}_n(\mu\text{-}\mathrm{S_2O_3}\text{-}S)_{2n}]^{3n-}$.[9] The Co−S bond distances are 2.2672(8) and 2.2642(8) Å, which are normal for a Co−S bond. The S−S bond distance of the thiosulfato ion is 2.095(1) Å, which is longer than 2.013(3) Å, in $\mathrm{MgS_2O_3}$,[10] 2.046(3) Å in $[\mathrm{Cu}_n(\mu\text{-}\mathrm{S_2O_3}\text{-}S)_{2n}]^{3n-}$,[9] and 2.066(6) Å in *cis*(*S*)-$[\mathrm{Pd}(\mathrm{S_2O_3}\text{-}S)_2(\mathrm{en})]^{2-}$ (en = ethane-1,2-diamine).[11] On the contrary, the average S−O distance is 1.442 Å, which is shorter than 1.48(1) Å in $\mathrm{MgS_2O_3}$, 1.474(12) and 1.463(13) Å in $[\mathrm{Cu}_n(\mu\text{-}\mathrm{S_2O_3})_{2n}]^{3n-}$, and 1.457(7) Å in *cis*(*S*)-$[\mathrm{Pd}(\mathrm{S_2O_3})_2(\mathrm{en})]^{2-}$.

An ORTEP projection of the cation in complex **4** is shown in Figure 4. The crystallographic data, the atomic parameters, and the selected bond distances and angles are listed in Tables 2, 4 (supplement), and 5, respectively. This complex also has the same cis,cis structure as complex **1**. The Co−$\mathrm{O_2}$ distances 1.894(2) and 1.887(2) Å, the O−O distance 1.449(3) Å, and the Co−O−O angles 112.2(2) and 112.7(2)° are very similar to those of complex **1**. The Co−O−O−Co torsion angle 73.2(2)° is also quite large, and the Co- -Co distance 3.5656(8) Å is long.

The difference between complexes **1** and **4** is in the μ-SR moiety. The torsion angles N(3)−Co(1)−S(1)−S(2) and N(7)−Co(2)−S(1)−S(2) in complex **1** are 42.6(1) and −66.5(1)°, respectively, whereas the corresponding angles N(3)−Co(1)−S(1)−C(21) and N(7)−Co(2)−S(1)−C(21) in complex **4** are 27.8(2) and −50.7(2)°: the benzenethiolato ligand is closer to the plane composed of Co, S, Co, and $\mathrm{O_2}$ than is the thiosulfato ligand.

The unprecedentedly large Co−O−O−Co torsion angles 75.5(2)° in complex **1** and 73.2(2)° in complex **4** are found in the present (μ-$\mathrm{O_2}$)(μ-SR) doubly bridged complexes. The average Co−O−O−Co torsion angle is only 61.7° in the known four structures of analogous compounds $[(\mathrm{N})_4\mathrm{Co}(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{OH})\mathrm{Co}(\mathrm{N})_4]^{n+}$.[4,12-14] The difference may be responsible for the Co- -Co distance: it is 3.5838(7) Å in complex **1** and 3.5656(8) Å in complex **4**, whereas the corresponding distance is quite shorter in $[(\mathrm{N})_4\mathrm{Co}(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{OH})\mathrm{Co}(\mathrm{N})_4]^{n+}$ (3.272−3.321 Å).[4,12-14] Therefore, the (μ-$\mathrm{O_2}$)(μ-SR) doubly bridged complexes uncommonly have large Co−O−O−Co torsion angles because of the long Co- -Co distances.

Supplementary Material Available: Tables of non-hydrogen positional parameters (Tables 3 and 4), full crystal data, complete hydrogen positional and isotropic thermal parameters, anisotropic thermal parameters for non-hydrogen atoms, and bond distances and angles (28 pages). Ordering information is given on any current masthead page.

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