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Synthesis, Characterization, and Stereochemistry of Oxorhenium(V) Complexes with 2-Aminoethanethiolate

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A series of oxorhenium(V) complexes with 2-aminoethanethiolate (aet), [ReO(aet-*N,S*)(D-pen-*N,O,S*)] (**2**), [{ReO(aet-*N,S*)$_2$}$_2$O] (**3**), [ReO(Cl)(aet-*N,S*)$_2$] (**4**), and [ReO(aet-*N,S*)(Haet-*S*)$_2$]Cl$_2$ ([**5**]Cl$_2$) was newly prepared starting from ReO_4^-. The reaction of NH_4ReO_4 with a 1:1 mixture of Haet·HCl and D-H$_2$pen (D-penicillamine) in the presence of $SnCl_2 \cdot 2H_2O$ in water gave **2**, **3**, and the known complex [ReO(D-Hpen-*N,S*)(D-pen-*N,O,S*)] (**1**). These complexes were fractionally precipitated by controlling the pH of the reaction solution. The complex **2** was also prepared in a higher yield by a similar reaction using methanol as a solvent. The crystal structure of **2** was determined by X-ray crystallography; **2** crystallizes in the tetragonal space group $P4_3$ with $a = 9.621(1)$, $c = 12.911(1)$ Å, $V = 1195.0(3)$ Å^3, and $Z = 4$. The oxorhenium(V) core in **2** is coordinated by a bidentate-*N,S* aet ligand and a tridentate-*N,O,S* D-pen ligand, having a distorted octahedral geometry with a *cis-N cis-S* configuration in the equatorial plane perpendicular to the O−Re−O axis. The 1:2 reaction of NH_4ReO_4 with Haet·HCl in the presence of $SnCl_2 \cdot 2H_2O$ in methanol produced **4**, which is interconvertible with **3**, while the corresponding 1:3 reaction resulted in the isolation of [**5**]Cl$_2$. The complexes **4** and **5** were also structurally characterized; **4** crystallizes in the monoclinic space group $P2_1/c$ with $a = 6.839(1)$, $b = 10.0704(6)$, $c = 14.1075(8)$ Å, $\beta = 91.729(8)°$, $V = 971.2(2)$ Å^3, and $Z = 4$, while [**5**]Cl$_2$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.938(3)$, $b = 12.366(3)$, $c = 5.819(1)$ Å, $\alpha = 102.71(2)$, $\beta = 101.28(2)$, $\gamma = 75.41(2)°$, $V = 802.0(3)$ Å^3, and $Z = 2$. In **4**, the oxorhenium(V) core is octahedrally coordinated by two bidentate-*N,S* aet ligands, which form a *cis-N cis-S* configurational equatorial plane with a Cl^- ion trans to the oxo ligand. On the other hand, the oxorhenium(V) core in [**5**]$^{2+}$ is coordinated by one bidenate-*N,S* aet and two monodentate-*S* Haet ligands, having a distorted trigonal-bipyramidal geometry with S and N donors at the apical positions.

Introduction

Oxorhenium(V) complexes with thiolato donor groups have attracted much interest because of the chemical similarity with Tc congeners that are used in nuclear medicine as imaging agents and have potential applications in radiotherapy.[2−9] In many cases, tetradentate-*S,N,N,S* thiolate ligands, which contain two inner amine(or amido) and two terminal thiolate groups, have been employed in the preparation of thiolato oxorhenium(V) complexes.[3] It has been shown that these oxorhenium(V) complexes commonly adopt a five-coordinate square-pyramidal

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geometry having a restricted *cis-N cis*-S configuration in a basal plane. Similar five-coordinate oxorhenium(V) complexes with a N_2S_2O donor set have also been prepared by using bidentate-*N,S* thiolate ligands, 1-(4′-methoxyphenyl)amino-2-methylpropane-2-thiolate and pyridine-2-methanethiolate, although they prefer to form a basal plane with a *trans-N trans-S* configuration.[5a] On the other hand, examples of six-coordinate oxorhenium(V) complexes with thiolate ligands are much less common,[6−9] and thus, their fundamental stereochemical and spectroscopic properties have not been well understood.

In 1984, Johnson et al. reported that the $SnCl_2$ reduction of ReO_4^- in the presence of a potentially tridentate-*N,O,S* ligand D-penicillamine (D-H_2pen) forms a six-coordinate oxorhenium(V) complex [ReO(D-Hpen)(D-pen)] (**1**).[7] Recently, this complex was structurally characterized and found to have a distorted octahedral geometry with a *cis-N cis-S trans-O* configuration, in which one D-pen ligand chelates to oxorhenium(V) core through S, N, and O atoms and the other through S and N atoms.[8] Furthermore, an analogous oxorhenium(V) complex, [Ph_4P][{ReO(L-cys-*N,S*)(L-cys-*N,O,S*)}{ReO(L-Hcys-*N,S*)(L-cys-*N,O,S*)}], has been prepared by using L-cysteine (L-H_2cys) as a potentially tridentate-*N,O,S* ligand, and X-ray analysis demonstrated that each of the [ReO(L-cys-*N,S*)(L-cys-*N,O,S*)]$^-$ and [ReO(L-Hcys-*N,S*)(L-cys-*N,O,S*)] units adopts a distorted octahedral coordination geometry with a *cis-N cis-S trans-O* configuration,[9] which is consistent with the structure for **1**. Since in these D-pen or L-cys oxorhenium(V) complexes one ligand acts as a bidentate chelator through amine-*N* and thiolato-*S* groups, we expected that similar six-coordinate oxorhenium(V) complexes are created by using a simple bidentate-*N,S* aminothiolate ligand in place of D-pen or L-cys. The most representative ligand of this class is 2-aminoethanethiolate (aet), which has been used for preparing a wide range of metal complexes.[10] In this paper, we report on the first syntheses and chemical and structural characterizations of a series of oxorhenium(V) complexes with one, two, or three aet ligands, [ReO(aet-*N,S*)(D-pen-*N,O,S*)] (**2**), [ReO(Cl)(aet-*N,S*)$_2$] (**4**), and [ReO(aet-*N,S*)(Haet-*S*)$_2$]Cl_2 ([**5**]Cl_2), along with those of an oxo-bridged dimer, [{ReO(aet-*N,S*)$_2$}$_2$O] (**3**). Since the properties of oxorhenium(V) complexes containing bidentate-*N,S* ligands have been studied little,[5,8] systematic investigations of aet oxorhenium(V) complexes will contribute significantly not only to our understanding of the fundamental coordination chemistry of oxorhenium(V) complexes with thiolate ligands, but also to the development of Re and Tc nuclear medicine.

Experimental Section

[ReO(aet-*N,S*)(D-pen-*N,O,S*)] (2). Method A. To a solution containing 1.60 g (5.96 mmol) of NH_4ReO_4, 0.90 g (7.92 mmol) of Haet·HCl, and 1.20 g (8.04 mmol) of D-H_2pen in 300 cm^3 of water was added a solution containing 1.50 g (6.65 mmol) of $SnCl_2$·$2H_2O$ in 100 cm^3 of water. The mixture was stirred at room temperature for 1 day, and then it gave a cloudy dark red−purple solution. After filtration through Celite, the reaction solution was adjusted to ca. pH 9 with 1 mol dm^{-3} aqueous ammonia; this was followed by allowing it to stand at room temperature for 1 day. The resulting red−brown powder of [{ReO(aet-*N,S*)$_2$}$_2$O] (**3**) (0.46 g) was removed by filtration. The filtrate was then adjusted to ca. pH 7 with 1 mol dm^{-3} aqueous HCl then concentrated to ca. 100 cm^3 with a rotary evaporator. The concentrated solution was allowed to stand at room temperature for 4 days, which produced a brown powder of [ReO(aet-*N,S*)(D-pen-*N,O,S*)] (**2**). This product was collected by filtration and washed with ethanol. Yield: 0.66 g (26%). Anal. Calcd for [ReO(aet)(D-pen)], $C_7H_{15}N_2O_3ReS_2$: C, 19.76; H, 3.55; N, 6.58%. Found: C, 19.78; H, 3.49; N, 6.57%. Brown rod crystals of **2** suitable for X-ray analysis were obtained by recrystallization of the brown powder from water at room temperature.

When the remaining solution, after removal of **2**, was adjusted to ca. pH 1 with 1 mol dm^{-3} aqueous HCl followed by allowing it to stand at room temperature for 10 days, a purple powder of [ReO(D-Hpen-*N,S*)(D-pen-*N,O,S*)] (**1**) (0.89 g) appeared, which was collected by filtration. This complex was also prepared by the reaction of NH_4ReO_4 with D-H_2pen and $SnCl_2$·$2H_2O$ in aqueous HCl, according to a method similar to that described in a literature.[7a]

Method B. To a solution containing 0.32 g (1.19 mmol) of NH_4ReO_4, 0.14 g (1.23 mmol) of Haet·HCl, and 0.18 g (1.21 mmol) of D-H_2pen in 30 cm^3 of methanol was added a solution containing 0.30 g (1.33 mmol) of $SnCl_2$·$2H_2O$ in 10 cm^3 of methanol. The mixture was stirred at room temperature overnight, and the resulting brown powder of [ReO(aet-*N,S*)(D-pen-*N,O,S*)] (**2**) was collected by filtration and washed with ethanol. Yield: 0.22 g (43%).

[{ReO(aet-*N,S*)$_2$}$_2$O] (3). To a solution containing 1.60 g (5.96 mmol) of NH_4ReO_4 and 2.00 g (17.60 mmol) of Haet·HCl in 250 cm^3 of water was added a solution containing 1.50 g (6.65 mmol) of $SnCl_2$·$2H_2O$ in 50 cm^3 of water. The mixture was stirred at room temperature for 1 day, which gave a cloudy dark purple solution. After filtration through Celite, the reaction solution was adjusted to ca. pH 9 with 1 mol dm^{-3} aqueous ammonia; this was followed by allowing it to stand at room temperature for 10 min. The resulting red−brown powder was collected by filtration and washed with water. Yield: 1.78 g (82%). Anal. Calcd for [{ReO(aet)$_2$}$_2$O], $C_8H_{24}N_4O_3Re_2S_4$: C, 13.25; H, 3.34; N, 7.73%. Found: C, 13.08; H, 3.47; N, 7.59%.

[ReO(Cl)(aet-*N,S*)$_2$] (4). To a solution containing 0.16 g (0.60 mmol) of NH_4ReO_4 and 0.14 g (1.23 mmol) of Haet·HCl in 50 cm^3 of methanol was added a solution containing 0.15 g (0.66 mmol) of $SnCl_2$·$2H_2O$ in 10 cm^3 of methanol. The mixture was stirred at room temperature for 2 h; this was followed by allowing it to stand at room temperature for 4 days. The resulting dark purple crystals were collected by filtration. Yield: 0.08 g (34%). Anal. Calcd for [ReO(Cl)(aet)$_2$], $C_4H_{12}ClN_2OReS_2$: C, 12.32; H, 3.10; N, 7.18%. Found: C, 12.40; H, 3.10; N, 7.08%. One of the crystals thus obtained was used for X-ray analysis.

[ReO(aet-*N,S*)(Haet-*S*)$_2$]Cl_2 ([5]Cl_2). To a solution containing 0.16 g (0.60 mmol) of NH_4ReO_4 and 0.20 g (1.76 mmol) of Haet·HCl in 40 cm^3 of methanol was added a solution containing 0.15 g (0.66 mmol) of $SnCl_2$·$2H_2O$ in 10 cm^3 of 1 mol dm^{-3} methanolic HCl. The mixture was stirred at room temperature for 1 day, which gave a red−purple solution. The reaction solution was adjusted to ca. pH 4 with 1 mol dm^{-3} aqueous ammonia. After a white powder that precipitated was removed by filtration through Celite, the red−purple filtrate was concentrated to dryness. The purple residue was then dissolved in 5 cm^3 of water; this was followed by allowing the solution to stand at room temperature for 4 days. The resulting black crystals were collected by filtration. Yield: 0.13 g (43%). Anal. Calcd for [ReO(aet)(Haet)$_2$]-

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Table 1. Crystallographic Data for **2**, **4**, and [**5**]Cl$_2$

	2	**4**	[**5**]Cl$_2$
empirical formula	$C_7H_{15}N_2O_3ReS_2$	$C_4H_{12}ClN_2OReS_2$	$C_6H_{20}Cl_2N_3OReS_3$
fw	425.54	389.94	503.55
space group	$P4_3$ (no. 78)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a, Å	9.621(1)	6.839(1)	11.938(3)
b, Å		10.0704(6)	12.366(3)
c, Å	12.911(1)	14.1075(8)	5.819(1)
α, deg			102.71(2)
β, deg		91.729(8)	101.28(2)
γ, deg			75.41(2)
V, Å^3	1195.0(3)	971.2(2)	802.0(3)
Z	4	4	2
T, K	296	291	291
radiation λ, Å	0.7107	0.7107	0.7107
ρ_{calcd} g cm^{-3}	2.365	2.667	2.085
μ(Mo $K\alpha$) cm^{-1}	105.12	131.71	82.89
R^a	0.019	0.026	0.021
$R_w{}^b$	0.021	0.025	0.027

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

Cl$_2$, $C_6H_{20}Cl_2N_3OReS_3$: C, 14.31; H, 4.00; N, 8.34%. Found: C, 14.28; H, 4.13; N, 8.35%. One of the crystals thus obtained was used for X-ray analysis.

Interconversion of 3 and 4. To a stirred suspension of **3** (0.10 g) in 50 cm^3 of ethanol was added dropwise 1 mol dm^{-3} aqueous HCl until the suspension became a clear yellow−brown solution. When this solution was stirred at room temperature for several minutes, a dark-brown crystalline solid of **4** precipitated. Yield: 0.06 g (56%).

To a suspension of **4** (0.05 g) in 10 cm^3 of water was added 1 mol dm^{-3} aqueous ammonia until the pH of the solution became ca. 9. This suspension was stirred at room temperature for several minutes, which gave a red−brown powder of **3**. Yield: 0.04 g (86%).

Measurements. The electronic absorption spectra were recorded with a JASCO Ubest-55 spectrophotometer, and the CD spectra were recorded with a JASCO J-700 spectropolarimeter at room temperature. The IR spectra were measured with a JASCO FT/IR-5000 infrared spectrophotometer using KBr disks at room temperature. The ^{1}H NMR spectra were recorded with a JEOL JNM-A500 NMR spectrometer at probe temperature in D_2O. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as the internal reference. The elemental analyses (C, H, N) were performed by the Analysis Center of the University of Tsukuba.

Crystal Structure Determination. Single-crystal X-ray diffraction experiments for **2**, **4**, and [**5**]Cl$_2$ were performed on a Rigaku AFC-7S diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). Crystallographic data are summarized in Table 1. Unit cell parameters were determined by a least-squares refinement, using the setting angles of 25 (28° < 2θ < 30°), 25 (29° < 2θ < 30°), and 24 (29° < 2θ < 30°) reflections for **2**, **4**, and [**5**]Cl$_2$, respectively. The intensity data were collected by the $\omega-2\theta$ scan technique (2θ < 55°). The intensities were corrected for Lorentz and polarization effects. Empirical absorption corrections based on a series of ψ scans were also applied. The 1340, 1879, and 3447 independent reflections with $I > 2\sigma(I)$ of the measured 1593, 2548, and 3871 reflections were considered as "observed" and used for structure determinations of **2**, **4**, and [**5**]Cl$_2$, respectively.

The positions of Re, S, and some other atoms for **2** and **4** were determined by direct methods, and those for [**5**]Cl$_2$ were determined by the Patterson method. The remaining non-H atom positions were found by successive difference Fourier techniques. The structures were refined by full-matrix least-squares techniques using anisotropic thermal parameters for non-H atoms. All H atoms for **2** were located and added to calculations but not refined. For **4** and [**5**]Cl$_2$, H atoms were found from difference Fourier maps and refined using isotropic thermal parameters. All calculations were performed using the teXsan crystallographic software package.[11]

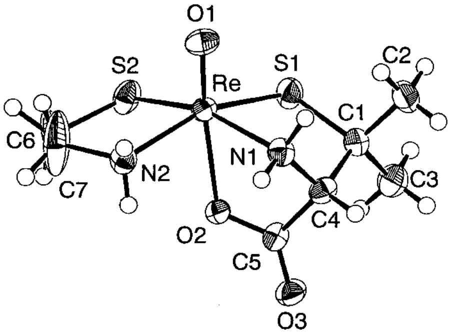

Figure 1. A perspective view of [ReO(aet-*N,S*)(D-pen-*N,O,S*)] (**2**) with the atomic labeling scheme. Ellipsoids represent 50% probability.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **2**

	Distances		
Re−S1	2.305(3)	Re−O2	2.177(5)
Re−S2	2.291(2)	Re−N1	2.189(6)
Re−O1	1.680(6)	Re−N2	2.171(7)
	Angles		
S1−Re−S2	92.3(1)	S2−Re−N2	82.2(2)
S1−Re−O1	106.0(2)	O1−Re−O2	159.0(3)
S1−Re−O2	82.6(2)	O1−Re−N1	91.0(3)
S1−Re−N1	83.2(2)	O1−Re−N2	95.6(3)
S1−Re−N2	158.4(2)	O2−Re−N1	70.6(2)
S2−Re−O1	107.8(2)	O2−Re−N2	76.6(2)
S2−Re−O2	90.7(2)	N1−Re−N2	95.3(3)
S2−Re−N1	161.2(2)		

Results and Discussion

Crystal Structures. [ReO(aet-*N,S*)(D-pen-*N,O,S*)] (2). X-ray analysis indicated that **2** is a neutral oxorhenium(V) complex with mixed chelating ligands, D-pen and aet. The molecular structure of **2** is shown in Figure 1, and its selected bond distances and angles are listed in Table 2. The D-pen ligand coordinates to the oxorhenium core through N, O, and S atoms and the aet ligand though N and S atoms, forming a six-coordinate structure in [ReO(aet-*N,S*)(D-pen-*N,O,S*)]. The two thiolato S and two amine N donor atoms are situated in an equatorial plane with a *cis-N cis-S* arrangement. The remaining coordination site trans to the oxo ligand is occupied by a carboxylato O atom from the tridentate-*N,O,S* D-pen ligand. Therefore, the arrangement of donor atoms in **2** is *cis-N*, *cis-S*, and *trans-O*, which is consistent with that found in each of [ReO(D-Hpen-*N,S*)(D-pen-*N,O,S*)] (**1**) and (Ph$_4$P)[{ReO(L-cys-*N,S*)(L-cys-*N,O,S*)}{ReO(L-Hcys-*N,S*)(L-cys-*N,O,S*)}].[8,9] The coordination environment around the Re atom in **2** is highly distorted from a regular octahedron, as reflected in the three trans angles (S1−Re−N2 = 158.4(2), S2−Re−N1 = 161.2(2), and O1−Re−O2 = 159.0(3)°). Furthermore, the Re atom lies 0.40 Å out of the N_2S_2 equatorial plane toward the oxo ligand. A similar distortion from regular octahedron has been observed in **1** (S−Re−N = 155.9(2) and 163.0(2)°, and O−Re−O = 157.3(3)°; 0.30 Å out of the N_2S_2 plane).[8] The bond distances and angles associated with the oxo and the tridentate D-pen ligand in **2** are essentially the same as those in **1**. Furthermore, the bond distances and angles for the aet ligand in **2** (Re−S2 = 2.291(2), Re−N2 = 2.171(7) Å, and S2−Re−N2 = 82.2(2)°) are quite similar to those found for the bidentate-*N,S* D-Hpen ligand in **1** (Re−S = 2.286(2), Re−N2 = 2.186(6)

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[11] Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1992.

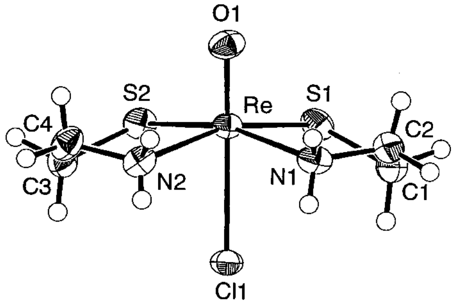

Figure 2. A perspective view of [ReO(Cl)(aet-*N,S*)$_2$] (**4**) with the atomic labeling scheme. Ellipsoids represent 50% probability.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **4**

	Distances		
Re−Cl	2.595(2)	Re−O	1.686(4)
Re−S1	2.294(2)	Re−N1	2.193(6)
Re−S2	2.298(2)	Re−N2	2.176(6)
	Angles		
S1−Re−S2	91.84(6)	S2−Re−N2	83.4(2)
S1−Re−O	106.8(2)	O−Re−Cl	161.4(2)
S1−Re−Cl	86.20(6)	O−Re−N1	91.3(2)
S1−Re−N1	83.2(2)	O−Re−N2	91.5(2)
S1−Re−N2	161.7(2)	Cl−Re−N1	76.8(2)
S2−Re−O	105.5(2)	Cl−Re−N2	75.9(2)
S2−Re−Cl	86.82(6)	N1−Re−N2	96.3(2)
S2−Re−N1	163.2(2)		

Å, and S−Re−N = 83.0(2)°). Accordingly, **2** is almost isostructural with **1**, except that the aet ligand occupies two coordination sites in the equatorial plane in place of the D-Hpen ligand in **1**.

[ReO(Cl)(aet-*N,S*)$_2$] (4). X-ray structural analysis indicated that **4** is a neutral complex consisting of an oxorhenium core, two aet ligands, and a Cl atom. The molecular structure of **4** is shown in Figure 2, and its selected bond distances and angles are listed in Table 3. In **4,** each aet ligand chelates to the oxorhenium core through N and S atoms to form an equatorial N_2S_2 plane. The coordination site trans to the oxo ligand is occupied by Cl atom, which completes a six-coordinate structure in [ReO(Cl)(aet-*N,S*)$_2$]. The arrangement of the donor atoms in the N_2S_2 plane is *cis-S* and *cis-N*, which is consistent with that of the N_2S_2 equatorial planes in **1** and **2**. The coordination environment around the Re atom in **4** is also distorted from a regular octahedron, but the three trans angles (S1−Re−N2 = 161.7(2), S2−Re−N1 = 163.2(2), and Cl−Re−O = 161.4(2)°) are closer to 180° compared with those in **1** and **2**. Furthermore, the displacement of Re atom from the N_2S_2 plane (0.34 Å) is smaller than those in **1** and **2**. Thus, it is seen that the strain around the Re atom in **4** is slightly released by the replacement of the tridentate-*N,O,S* D-pen ligand by the bidentate-*N,S* aet ligand. The Re−S (average 2.296(2) Å), Re−N (average 2.185(6) Å), and Re−O_{oxo} (1.686(4) Å) distances are quite similar to those in **1** (average Re−S = 2.298(3), average Re−N = 2.200(7), and Re−O_{oxo} = 1.687(6) Å) and **2** (average Re−S = 2.291(2), average Re−N = 2.180(7), and Re−O_{oxo} = 1.680(6) Å), while the Re−Cl bond in **4** (2.595(2) Å) is much longer than the Re−$O_{carboxylato}$ bonds in **1** (2.184(6) Å) and **2** (2.177(5) Å), as expected from the difference in covalent radius between Cl and O atoms. It is noteworthy that the distance of 2.595(2) Å is considerably longer than the Re−Cl distances found in [$ReOCl_3(CNCMe_3)_2$] (trans to oxo: 2.436(1); equatorial: 2.363(1) and 2.348(1) Å) and [$ReOCl_2(OPPh_3)(biimH_2)$]$^+$ (2.348(1) and 2.352(1) Å),[12,13] suggesting the relatively weak Re−Cl bond in **4**.

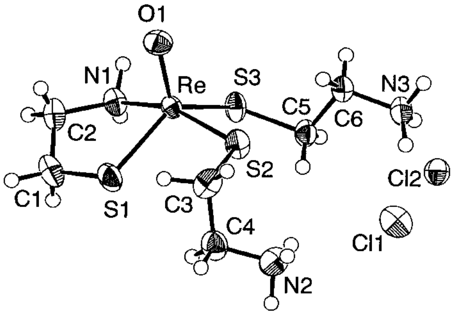

Figure 3. A perspective view of [ReO(aet-*N,S*)(Haet-*S*)$_2$]Cl_2 ([**5**]Cl_2) with the atomic labeling scheme. Ellipsoids represent 50% probability.

Table 4. Selected Bond Distances (Å) and Angles (deg) for [**5**]Cl_2

	Distances		
Re−S1	2.279(1)	Re−O	1.697(3)
Re−S2	2.289(1)	Re−N1	2.153(4)
Re−S3	2.290(1)		
	Angles		
S1−Re−S2	90.40(4)	S2−Re−O	104.9(1)
S1−Re−S3	127.07(4)	S2−Re−N1	158.4(1)
S1−Re−O	116.9(1)	S3−Re−O	114.1(1)
S1−Re−N1	80.7(1)	S3−Re−N1	80.2(1)
S2−Re−S3	89.83(4)	O−Re−N1	96.7(2)

Crystal Structure of [ReO(aet-*N,S*)(Haet-*S*)$_2$]Cl_2 ([5]Cl_2). X-ray analysis for [**5**]Cl_2 revealed the presence of a complex cation and two Cl^- anions in the asymmetric unit. The number of Cl^- anions implies that the complex cation is divalent. The structure of the complex cation is depicted in Figure 3, and its selected bond distances and angles are summarized in Table 4. The complex cation [**5**]$^{2+}$ consists of an oxorhenium core and three aet ligands. Of the three aet ligands, one is bound to the oxorhenium core through S and N atoms and the others through only a S atom, giving a five-coordinate structure in [ReO(aet-*N,S*)(Haet-*S*)]$^{2+}$. Each noncoordinated amine group of the two monodentate aet ligands is protonated, which is compatible with the formal charge 2+ of the complex cation. The coordination geometry about the Re atom can be described as an intermediate between the trigonal bipyramid and square pyramid. In [**5**]$^{2+}$, the two largest bond angles around the Re atom defined by four of five donor atoms are α = S1−Re−S3 = 127.07(4)° and β = S2−Re−N1 = 158.4(1)°, from which the angular structural index parameter $\tau = (\beta - \alpha)/60$ is calculated to be 0.52 ($\beta > \alpha$; $\tau = 0$ for an ideal square pyramid and $\tau = 1$ for an ideal trigonal bipyramid).[14] From this τ value it is evaluated that the structure of [**5**]$^{2+}$ is just between the trigonal bipyramid and square pyramid. We have recently proposed the improved structural index parameter $\chi = (\beta + \delta + \gamma - 2\alpha)/180$ for the five-coordinate geometry based on the four largest angles, modifying the τ parameter so as to take into account all five donor atoms ($\beta > \alpha > \delta$ or γ; $\chi = 0$ for an ideal square pyramid and $\chi = 1$ for an ideal trigonal bipyramid).[15] The χ value for [**5**]$^{2+}$ becomes 0.75 (δ = S1−Re−O1 =116.9(1) and γ = S3−Re−O1 = 114.1(1)°), which indicates that the coordination geometry of [**5**]$^{2+}$ is a distorted trigonal bipyramid with the basal S1S3O1 trigonal plane, rather than a trigonally distorted square pyramid. Quite recently, closely related five-coordinated ox-

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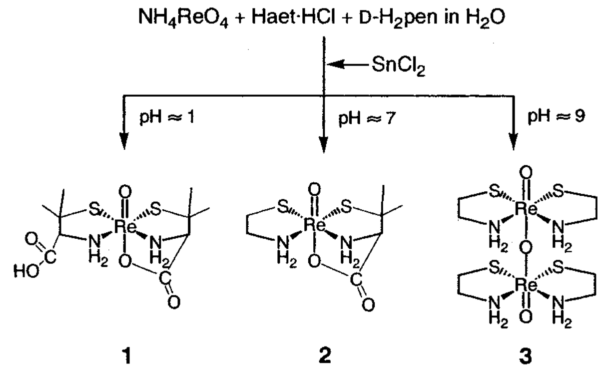
(12) Bryan, J. C.; Stenkamp, R. E.; Tulip, T. H.; Mayer, J. M. *Inorg. Chem.* **1987**, *26*, 2283−2288.

(13) Fortin, S.; Beauchamp, A. L. *Inorg. Chem.* **2000**, *39*, 4886−4893.

(14) Addison, A. W.; Rao, T. N.; Reedijk, J.; Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356.

(15) Konno, T.; Tokuda, K.; Sakurai, J.; Okamoto K. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2767−2773.

Scheme 1



orhenium(V) complexes having a $N_1O_1S_3$ donor set, $[ReO\{[(CH_3)_2CH]_2NCH_2CH_2NHCH_2CH_2S\text{-}N,S\}(XS)_2]$ (X = phenyl, *p*-methyphenyl), have been reported.[5b] The χ values for these complexes become 0.69 and 0.71. Thus, the distortion from the trigonal bipyramid to square pyramid for these complexes is slightly greater than that for $[\mathbf{5}]^{2+}$. The three Re−S bond distances in $[\mathbf{5}]^{2+}$, which are within the range normally observed for the thiolato oxorhenium(V) complexes,[2−9] resemble each other. However, it is noticed that the Re−S1 distance (2.279(1) Å) is somewhat shorter than the Re−S2 and Re−S3 distances (2.289(1), 2.290 (1) Å). This can be attributed to the chelate effect, which allows the bidentate-*N,S* aet ligand to bind with the Re^V center more tightly than do the monodentate-*S* Haet ligands. The Re−S1 (2.279(1) Å) and Re−N1 (2.153(4) Å) distances in $[\mathbf{5}]^{2+}$ are shorter than the corresponding $Re-S_{aet}$ and $Re-N_{aet}$ distances in **2** and **4** (Re−S = 2.291(2) and Re−N = 2.171(7) Å for **2**; average Re−S = 2.296(2) and Re−N = 2.185(6) Å for **4**), which reflects the difference between the five-coordinate structure in $[\mathbf{5}]^{2+}$ and the six-coordinate structures in **2** and **4**.

Synthesis and Characterization. Treatment of NH_4ReO_4 with a 1:1 mixture of Haet•HCl and D-H_2pen in the presence of reductant of $SnCl_2{\bullet}2H_2O$ in water gave a dark purple reaction solution, from which a red−brown powder (**3**) was first precipitated on adjusting the pH to ca. 9 (Scheme 1). After removal of **3** by filtration, an oxorhenium(V) complex with mixed bidentate-*N,S* aet and tridentate-*N,O,S* D-pen ligands, [ReO(aet-*N,S*)(D-pen-*N,O,S*)] (**2**), was isolated by the neutralization of the filtrate, followed by concentration. The remaining solution was found to contain the known oxorhenium(V) complex, $[ReO(\text{D-pen-}N,S)(\text{D-pen-}N,O,S)]^-$,[7] which was precipitated as [ReO(D-Hpen-*N,S*)(D-pen-*N,O,S*)] (**1**) by the addition of HCl. Although **2** is a neutral complex molecule, as evidenced by the molar conductivity of 7.6 Ω^{-1} cm^2 mol^{-1} in water, **2** is considerably soluble in water. On the other hand, its solubility in methanol is quite low, which enabled the isolation of **2** in a higher yield from the corresponding reaction in methanol.

Figure 4 illustrates the electronic absorption and CD spectra of **1** and **2**; their data are summarized in Table 5. The absorption spectrum of **2** is characterized by a visible band at 20.16 × 10^3 cm^{-1}, with a shoulder at the lower energy side, and an intense near-UV band at 29.04 × 10^3 cm^{-1}, with a shoulder at the higher energy side. The former visible band can be assigned as arising from a d−d transition and the latter intense band from a sulfur−to−metal CT transition, considering their extinction coefficients. The absorption spectral behavior of **2** is in good agreement with that of **1** over the whole region. This is compatible with the X-ray analytical results, which demonstrated that the Re^V atom in **2** is situated in a coordination environment quite similar to that in **1**. In the CD spectrum, **2** exhibits a major negative and a positive CD band from lower energy. This CD pattern is the same as that observed for **1**, although a slight difference in intensity of each band is noticed between **1** and **2**. This clearly indicates that the chirality due to the asymmetric carbon atom of the bidentate-*N,S* D-Hpen ligand in **1** affects the overall CD spectral pattern little. The ^1H NMR spectrum of **2** in D_2O exhibits three singlet signals at δ 1.64, 1.81, and 4.01 for the D-pen ligand and four multiplet signals centered at δ 3.03, 3.09, 3.21, and 3.29 for the aet ligand, while six singlet signals are observed for **1** at δ 1.32, 1.64, 1.81, 2.08, 3.30, and 4.06. Comparing their ^1H NMR spectra, it is obvious that for **1** the three signals at δ 1.64, 1.81, and 4.06 are due to the tridentate D-pen ligand and those at δ 1.32, 2.08, and 3.30 are due to the bidentate D-Hpen ligand, which is consistent with the assignment made by Hansen et al.[7b]

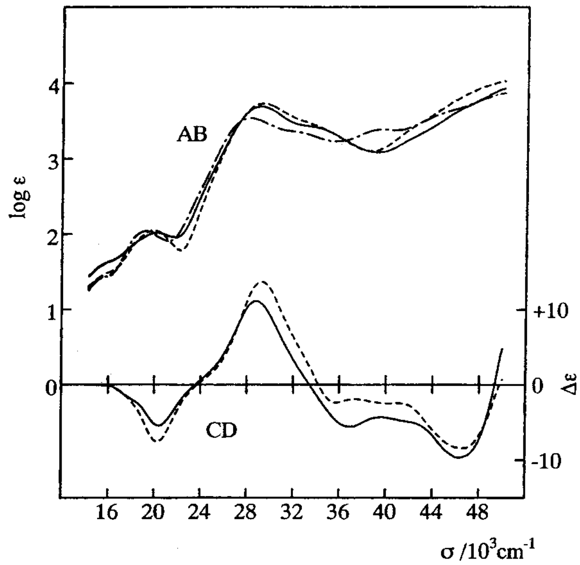


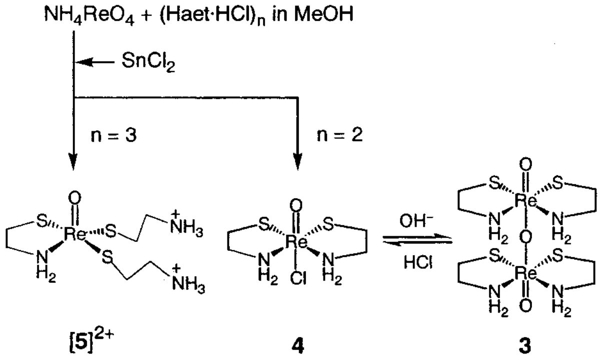
Figure 4. Electronic absorption and CD spectra of **1** (- - -) and **2** (—) in water, and an absorption spectrum of **3** (-•-) in 0.1 mol dm^{-3} aqueous $HClO_4$.

Table 5. Absorption and CD Spectral Data in H_2O (**1**, **2**) or in 0.1 mol dm^{-3} Aqueous $HClO_4$ (**4**, [**5**]Cl_2)

abs max: $\sigma/10^3$ cm^{-1}	($\log \epsilon/mol^{-1}$ dm^3 cm^{-1})	CD extrema: $\sigma/10^3$ cm^{-1}	($\Delta\epsilon/mol^{-1}$ dm^3 cm^{-1})
[ReO(D-Hpen-*N,S*)(D-pen-*N,O,S*)] (**1**)			
16.47	(1.53)[a]	20.28	(−7.57)
19.81	(2.05)	29.24	(+13.67)
29.27	(3.73)	35.29	(−2.25)
31.75	(3.56)[a]	46.64	(−8.44)
[ReO(aet-*N,S*)(D-pen-*N,O,S*)] (**2**)			
16.49	(1.66)[a]	20.41	(−5.45)
20.16	(2.02)	28.77	(+11.11)
29.04	(3.69)	36.87	(−5.60)
32.24	(3.46)[a]	46.25	(−9.70)
$[ReO(Cl)(aet\text{-}N,S)_2]$ (**4**)			
16.09	(1.54)[a]		
19.39	(2.07)		
28.16	(3.55)		
31.33	(3.38)[a]		
40.00	(3.34)		
$[ReO(aet\text{-}N,S)(Haet\text{-}S)_2]Cl_2$ ([**5**]Cl_2)			
18.35	(1.88)		
28.38	(3.40)		
39.52	(3.77)		
45.91	(3.89)[a]		

[a] Denotes a shoulder.

Scheme 2



Complex **3** is sparingly soluble in water, but soluble in an acidic solution. As shown in Figure 4, the absorption spectrum of **3** dissolved in 0.1 mol dm^{-3} aqueous $HClO_4$ is quite similar to those of **1** and **2** over the whole region, although each band for **3** is located at somewhat lower energy than the corresponding bands for **1** and **2**. This suggests that in acidic solution **3** adopts a coordination environment quite similar to those of **1** and **2**. In the IR spectrum **3** exhibits a sharp intense band at 915 cm^{-1}, which is assignable to the Re═O stretching vibration. This value is much lower in energy than those of the Re═O stretching bands for **1** (973 cm^{-1}) and **2** (965 cm^{-1}), suggesting the weaker Re═O bond in **3** owing to the stronger donor group on the coordination site trans to the oxo ligand. Besides this Re═O stretching band, **3** shows a broad intense band at 675 cm^{-1}. This band corresponds well with the Re−O−Re asymmetric stretching band commonly found in the oxo-bridged Re^V dimers.[13,16] Considering these spectral features and the elemental analysis, it is assigned that **3** has an oxo-bridged dimeric structure in [{ReO(aet-*N,S*)$_2$}$_2$O], which is readily converted to the monomeric structure in [ReO(aet-*N,S*)$_2$(H_2O)]$^+$ having a *cis-N cis-S trans-O* configuration in aqueous acidic solution. This assignment is supported by its electrospray-ionization (ESI) mass spectrum in 0.1% aqueous CH_3COOH, which gives two major peaks at *m*/*z* 353.1 and 355.1 corresponding to [^{185}ReO(aet)$_2$]$^+$ and [^{187}ReO(aet)$_2$]$^+$. As is expected from this assignment, **3** was obtained in a high yield on treating NH_4ReO_4 only with Haet·HCl in the presence of $SnCl_2·2H_2O$, followed by adjusting the pH of the reaction solution to ca. 9.

The monomeric bis-aet species was successfully isolated as the neutral [ReO(Cl)(aet-*N,S*)$_2$] (**4**) by treatment of **3** with aqueous HCl in ethanol. Since **3** and **4** exhibit absorption spectra identical with each other in 0.1 mol dm^{-3} aqueous $HClO_4$, it is assumed that the Cl^- donor in **4** is replaced by a water molecule to form [ReO(aet-*N,S*)$_2$(H_2O)]$^+$ in aqueous solution. This is consistent with the X-ray analytical result of **4**, which revealed the elongated Re−Cl bond. Complex **4** is almost quantitatively reverted back to **3** in a few minutes by treatment with aqueous ammonia in water, indicating the rapid dimerization of [ReO(aet-*N,S*)$_2$(H_2O)]$^+$ to [{ReO(aet-*N,S*)$_2$}$_2$O] with retention of the *cis-N cis-S trans-O* configuration. Complex **4** was also prepared directly by the 1:2 reaction of NH_4ReO_4 with Haet·HCl in the presence of $SnCl_2·2H_2O$ in methanol (Scheme 2). However, the corresponding 1:3 reaction resulted in the isolation of [**5**]Cl_2, which was determined to have a five-coordinate oxorhenium(V) structure in [ReO(aet-*N,S*)(Haet-*S*)$_2$]Cl_2. As shown in Figure 5, the electronic absorption spectrum of [**5**]Cl_2 in 0.1 mol dm^{-3} aqueous $HClO_4$ resembles that of **4**, especially in the energy region of 24×10^3−36×10^3 cm^{-1}, giving an intense CT band at nearly the same position (28.38×10^3 cm^{-1}) as that of **4**. From this spectral behavior, one may assume that [**5**]$^{2+}$ is converted to the six-coordinate structure in solution. However, the d−d band for [**5**]Cl_2 (18.35×10^3 cm^{-1}) has no distinct shoulder and is located at lower energy with a lower intensity, compared with that of **4**. Furthermore, the solid-state spectrum of [**5**]Cl_2 (Nujol mull) is essentially the same as its spectrum in 0.1 mol dm^{-3} aqueous $HClO_4$. Accordingly, it is reasonable to assume that the five-coordinate structure of [**5**]$^{2+}$ observed in crystal is retained in solution.

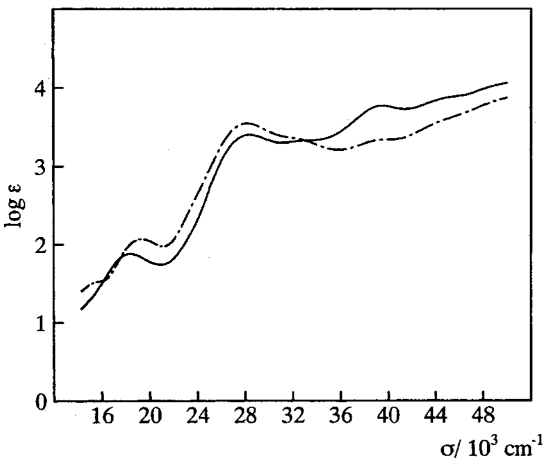


Figure 5. Electronic absorption spectra of **4** (-·-) and [**5**]Cl_2 (—) in 0.1 mol dm^{-3} aqueous $HClO_4$.

Concluding Remarks

In the present study, it was found that the reaction of NH_4ReO_4 with a 1:1 mixture of Haet·HCl and D-H_2pen in the presence of $SnCl_2·2H_2O$ in water produces a dark red−purple solution containing the mono-aet oxorhenium(V) complex [ReO(aet-*N,S*)(D-pen-*N,O,S*)] (**2**), besides [ReO(D-pen-*N,S*)(D-pen-*N,O,S*)]$^-$ and [ReO(aet-*N,S*)$_2$(H_2O)]$^+$. This result clearly indicates that the simple bidentate-*N,S* ligand aet possesses a sufficient coordinating ability toward the oxorhenium(V) center. From the reaction mixture, [{ReO(aet-*N,S*)$_2$}$_2$O] (**3**), [ReO(aet-*N,S*)(D-pen-*N,O,S*)] (**2**), and [ReO(D-Hpen-*N,S*)(D-pen-*N,O,S*)] (**1**) were fractionally precipitated by adjusting the pH of the solution so as to form the neutral species (Scheme 1). Complex **3**, having an oxo-bridged dimeric structure, was also prepared from the 1:2 reaction of NH_4ReO_4 with Haet·HCl in the presence of $SnCl_2·2H_2O$ in water, followed by the addition of base. Isolation of the monomeric bis-aet complex, [ReO(Cl)(aet-*N,S*)$_2$] (**4**), which is interconvertible with **3**, was achieved by the corresponding 1:2 reaction in methanol (Scheme 2). On the other hand, the 1:3 reaction of NH_4ReO_4 with Haet·HCl in methanol was found to lead to the isolation of the tris-aet complex, [ReO(aet-*N,S*)(Haet-*S*)$_2$]Cl_2 ([**5**]Cl_2). Thus, the oxorhenium(V) complexes with one, two, or three aet ligands are systematically prepared by the control of pH, reaction stoichiometry,and the choice of solvent.

X-ray analysis established that the Re^V ion in **2** is situated in a distorted octahedral structure, having a N_2S_2 equatorial plane perpendicular to an O−Re−O axis, like the Re^V ion in **1**.[8] Since a quite similar octahedral structure with an O−Re−Cl axis was found in **4**, it is seen that bis(amine)-bis(thiolato)-type oxorhenium complexes favor a six-coordination with a N_2S_2 plane,

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(16) (a) Backes-Dahmann G.; Enemark, J. H. *Inorg. Chem.* **1987**, *26*, 3960−3962. (b) West, B. O. *Polyhedron* **1989**, *8*, 219−274. (c) Hahn, F. E.; Imhof, L.; Lügger, T. *Inorg. Chim. Acta* **1998**, *269*, 347−349. (d) Alessio, E.; Zangrando, E.; Iengo, E.; Macchi, M.; Marzilli, P. A.; Marzilli, L. G. *Inorg. Chem.* **2000**, *39*, 294−303.

accommodating the sixth donor group trans to the oxo ligand. Here it should be noted that **1**, **2**, and **4** with two thiolato groups commonly provide a *cis-N cis-S* configurational equatorial plane. This may be ascribed to a mutual trans influence due to thiolato donors exerted in a *trans-S* arrangement,[17] which could weaken the Re−S bonds. Contrary to the cases of **1**, **2**, and **4**, the Re^V ion in [**5**]$^{2+}$ with three thiolato groups was found to be in a five-coordinate structure having a distorted trigonal-bipyramidal geometry with a basal S_2O_1 trigonal plane perpendicular to an angular S−Re−N axis. Given that [**5**]$^{2+}$ accepts the sixth coordination trans to the oxo ligand to form an octahedral geometry (or adopts a regular square-pyramidal geometry), one of two thiolato groups from the monodentate Haet ligands is forced to occupy the trans position to the thiolato group of the bidentate aet ligand. Accordingly, it is concluded that aliphatic aminothiolate ligands tend to bind with an oxorhenium(V) core so as to avoid formation of the *trans-S* arrangement, taking account of the distorted trigonal-bipyramidal geometry in [**5**]$^{2+}$ in addition to the regulated *cis-N cis-S* configuration found in the octahedral **1**, **2**, and **4**.

Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determination of **2**, **4**, and [**5**]Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) (a) Stein, C.; Bouma, S.; Carlson, J.; Cornelius, C.; Maeda, J.; Weschler, C.; Deutsch, E.; Hodgson, K. O. *Inorg. Chem.* **1976**, *15*, 1183−1186. (b) Konno, T.; Gotoh, Y.; Okamoto, K. *Inorg. Chem.* **1997**, *36*, 4992−4997. (c) Yonemura, T.; Bai, Z.-P.; Okamoto, K.; Ama, T.; Kawaguchi, H.; Yasui, T.; Hidaka, J. *J. Chem. Soc., Dalton Trans.* **1999**, 2151−2157.