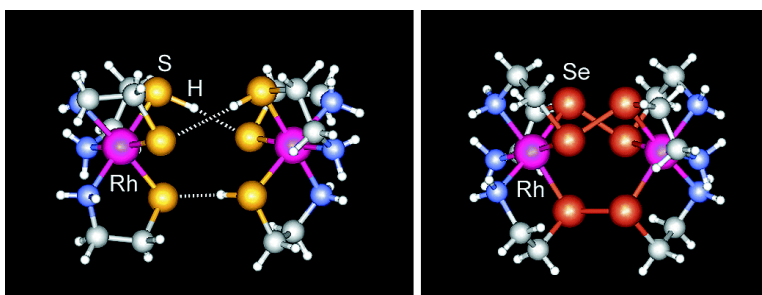Communication

The First Triple Thiol-thiolate Hydrogen Bond versus Triple Diselenide Bond That Bridges Two Metal Centers

Takumi Konno, Kazuyuki Haneishi, Masakazu Hirotsu,
Tadashi Yamaguchi, Tasuku Ito, and Takashi Yoshimura

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 2 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

The First Triple Thiol-thiolate Hydrogen Bond versus Triple Diselenide Bond That Bridges Two Metal Centers

Takumi Konno,*,† Kazuyuki Haneishi,‡ Masakazu Hirotsu,‡ Tadashi Yamaguchi,§ Tasuku Ito,§ and Takashi Yoshimura†

Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan, Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376-8515, Japan, and Department of Chemistry, Graduate School of Science, Tohoku University, Sendai, Miyagi 980-8578, Japan

Received April 15, 2003; E-mail: konno@ch.wani.osaka-u.ac.jp

Hydrogen bonds involving sulfur atoms as both donor and acceptor have currently attracted much interest, because of the potential importance in a variety of systems ranging from inorganic to organic and biological chemistry.[1] While the existence of S−H···S hydrogen bonds was established in the 1960s,[2] well-characterized structures showing these interactions are limited in number.[3] The S−H···S hydrogen bonds are generally very weak, and thus, strong thiol-thiolate hydrogen bonds are extremely rare; the intermolecular thiol-thiolate hydrogen bond found in a pair of $HSCH_2CH_2SCH_2CH_2S^-$ anions is the only example of a very strong S−H···S bond.[3a] For transition metal compounds, strong thiol-thiolate hydrogen bonds have been little recognized, although a relatively strong intermolecular S−H···S hydrogen bond, which is formed between H_2S and thiolate ligands bound to Ru^{II}, has been presented.[4]

In the course of studying the reactivity of coordinated thiolato groups,[5] we noticed that an aqueous suspension of *fac*(*S*)-[M(aet)₃] (M = Co^{III}, Rh^{III}, Ir^{III}; aet = 2-aminoethanethiolate) turns to a clear solution by the addition of acid, despite the sparing solubility in neutral water. This fact suggested that the coordinated thiolato groups in *fac*(*S*)-[M(aet)₃] have an affinity for protons to form some positively charged species, which may possess S−H···S hydrogen bonds. In this communication, we report on the first isolation and characterization of a proton adduct, which is derived from *fac*(*S*)-[Rh(aet)₃] and aqueous HBF₄ under aerobic conditions.[6] It was found that this adduct is a rhodium(III) dimer ([**1**](BF₄)₃) having a strong triple thiol-thiolate S−H···S hydrogen bond. While a triple ol-olate O−H···O hydrogen bond that bridges two metal centers was reported more than 40 years ago,[7] the corresponding thiol-thiolate hydrogen bond has never been discovered. Interestingly, similar treatment of *fac*(*Se*)-[Rh(aes)₃] (aes = 2-aminoethaneselenolate) was found to produce an unique rhodium(III) dinuclear complex with bridging selenocystamine ligands ([**2**](BF₄)₆) (Scheme 1). The formation and characterization of [**2**]⁶⁺, which represents the first example of a triple coordinated diselenide bond, are also communicated.

Treatment of an aqueous suspension of *fac*(*S*)-[Rh(aet)₃] with HBF₄ in air gave an orange-yellow clear solution, from which orange-yellow crystals ([**1**](BF₄)₃) were isolated.[8] The FT-IR spectrum of **1** showed a broad, intense band at ~1050 cm⁻¹ characteristic of the BF₄⁻ stretches, and its elemental analysis was in agreement with the formula for a 2:3 adduct of [Rh(aet)₃] and HBF₄.[8] Single-crystal X-ray analysis of [**1**](BF₄)₃ revealed the presence of two octahedral *fac*(*S*)-[Rh(aet)₃] units and three BF₄⁻ anions.[8] The three S atoms in one Rh^{III} unit faces to those in the other Rh^{III} unit with three short S···S intermolecular distances of
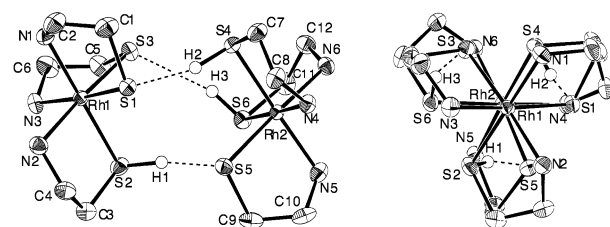
Figure 1. ORTEP drawing of ΔΔ-[**1**]³⁺. Hydrogen atoms attached to carbon and nitrogen atoms are omitted for clarity.

Scheme 1
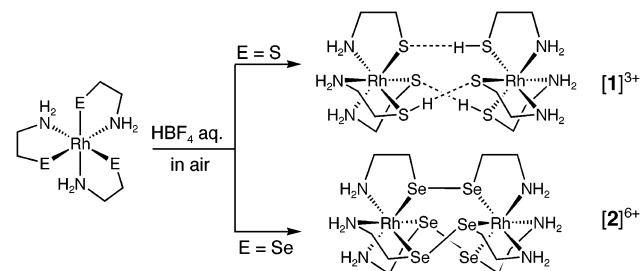
Table 1. S−H···S Hydrogen Bonding Geometry (Å, deg) in ΔΔ-[**1**]³⁺

| S−H···S	S−H	H···S	S···S	S−H···S
S2−H1···S5	1.32(6)	2.21(6)	3.504(1)	166(4)
S4−H2···S1	1.32(4)	2.08(4)	3.378(1)	165(3)
S6−H3···S3	1.17(5)	2.64(5)	3.750(1)	158(4)

3.440(2), 3.579(2), and 3.773(3) Å. This arrangement of the two *fac*(*S*)-[Rh(aet)₃] units in [**1**]³⁺ is reminiscent of the pentanuclear structure of [Ag₃{Rh(aet)₃}₂]³⁺, in which two *fac*(*S*)-[Rh(aet)₃] units are linked by three linear Ag^I ions through sulfur bridges.[9] The bond distances and angles concerning the *fac*(*S*)-[Rh(aet)₃] units in [**1**]³⁺ are very similar to those in [Ag₃{Rh(aet)₃}₂]³⁺. Furthermore, the two *fac*(*S*)-[Rh(aet)₃] units in [**1**]³⁺ have the same chiral configuration to give the *racemic* form (ΔΔ/ΛΛ), like the two units in [Ag₃{Rh(aet)₃}₂]³⁺. Thus, it is assumed that three protons exist between the two trigonal S₃ faces in [**1**]³⁺, in place of the three Ag^I atoms in [Ag₃{Rh(aet)₃}₂]³⁺.

The existence of three H atoms between the two *fac*(*S*)-[Rh(aet)₃] units was established by X-ray analysis for an optically active crystal (ΔΔ-[**1**](BF₄)₃), which was obtained from Δ-*fac*(*S*)-[Rh(aet)₃] and HBF₄.[8] As shown in Figure 1, each H atom unsymmetrically connects two S atoms from the two Δ-*fac*(*S*)-[Rh-(aet)₃] units with one short and the other long S−H distances (Table 1). Thus, the complex cation [**1**]³⁺ is formulated as [{Rh(aet)₂-(Haet)}{Rh(aet)(Haet)₂}]³⁺, rather than [H₃{Rh(aet)₃}₂]³⁺. The short

† Department of Chemistry, Osaka University.
‡ Department of Chemistry, Gunma University.
§ Department of Chemistry, Tohoku University.
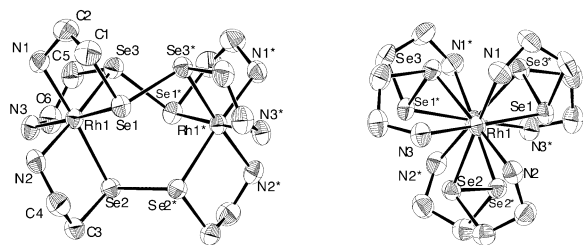
Figure 2. ORTEP drawing of [**2**]$^{6+}$; the ΔΔ isomer is selected. Hydrogen atoms attached to carbon and nitrogen atoms are omitted for clarity.

S···S distances, together with the roughly linear S−H···S angles, is suggestive of relatively strong S−H···S hydrogen bonds. In particular, the S4−H2···S1 hydrogen bond with S···S distance of 3.378(1) Å and S−H···S angle of 165(3)°, which is comparable to a very strong S−H···S hydrogen bond found in a pair of HSCH$_2$CH$_2$SCH$_2$CH$_2$S$^-$ anions (S···S = 3.454(2) Å, S−H···S = 176(2)°),[3a] would be considerably strong. It is interesting to note that in ΔΔ-[**1**]$^{3+}$ the protonated Haet chelate rings uniformly adopt the δ conformation, while the deprotonated aet chelate rings have the λ conformation. In addition, note that the shorter S1···S4 and S2···S5 linkages involve the longer S−H bonds, compared with the S−H bond in the longer S6···S3 linkage (Table 1). This observation evidences that a stronger S−H···S hydrogen bond requires a bridging H atom to be more equally shared between two S atoms.[2c]

Similar treatment of an aqueous suspension of *fac*(*Se*)-[Rh(aes)$_3$] with HBF$_4$ in air produced an orange-red reaction solution, from which orange crystals ([**2**](BF$_4$)$_6$) were isolated.[8] The FT-IR spectrum of [**2**](BF$_4$)$_6$ showed a broad, intense band at ∼1050 cm^{-1}, indicative of the presence of BF$_4^-$ anions. However, its elemental analysis was not consistent with the 2:3 stoichiometry of [Rh(aes)$_3$] and HBF$_4$, but with the 2:6 one.[8] Furthermore, [**2**](BF$_4$)$_6$ was soluble in water, which is in contrast to the fact that dissolution of [**1**]-(BF$_4$)$_3$ in water immediately caused the precipitation of *fac*(*S*)-[Rh-(aet)$_3$] because of the rapid uptake of the bridging protons.[10] X-ray analysis of [**2**](BF$_4$)$_6$ indicated the presence of an asymmetric unit consisting of one octahedral *fac*(*Se*)-[Rh(aes)$_3$] unit and three BF$_4^-$ anions.[8] As illustrated in Figure 2, the symmetry operation revealed a dinuclear rhodium(III) structure of [Rh$_2$(selenocystamine)$_3$]$^{6+}$, in which two Rh^{III} octahedra are joined by a triple diselenide bond (av 2.387(2) Å). While several mono(diselenide)-bridged dinuclear complexes have been structurally characterized,[11] as far as we know, [**2**]$^{6+}$ is the first example of a tris(diselenide)-bridged structure, which was created by autoxidation of coordinated selenolato groups by air. It should be noted that in [**2**]$^{6+}$ the chirality at Co and Se centers, as well as the conformation of *N,Se*-chelate rings, is unified to give a pair of enantiomers, (Δ)$_2$(δ)$_6$(*R*)$_6$ and (Λ)$_2$(λ)$_6$(*S*)$_6$; the former isomer is selected in Figure 2. Consistent with this, the ^{13}C NMR spectrum in CD$_3$CN gives only two sharp signals (δ 45.08 for CH$_2$Se and δ 51.36 for CH$_2$N) for 12 carbon atoms in the complex. The cyclic voltammogram (CV) of [**2**](BF$_4$)$_6$ in aqueous 0.1 M NaBF$_4$ displayed a broad 2e reduction wave at +0.28 V (vs Ag/AgCl), while its coupled 2e oxidation wave was observed at +0.73 V. This result implies that the electrochemical interconversion between [Rh$_2$(diselenide)$_3$]$^{6+}$ and [Rh$_2$(diselenide)$_2$(selenolato)$_2$]$^{4+}$ species occurs in solution.

In summary, thiolato and selenolato groups bound to a Rh^{III} center showed dramatically distinct reactivity toward aqueous HBF$_4$, leading to a dimeric structure in [**1**]$^{3+}$ aggregated by a triple S−H···S hydrogen bond and a dinuclear structure in [**2**]$^{6+}$ connected by a triple Se−Se diselenide bond, respectively. The CV of *fac*(*Se*)-[Rh(aes)$_3$] dissolved in aqueous 10% HBF$_4$/0.1 M NaBF$_4$ showed a reversible 1e redox couple at +0.68 V (vs Ag/AgCl, E_{pa} = +0.71 V, E_{pc} = +0.65 V), which is assignable to a Rh^{III}/Rh^{IV} redox process. On the other hand, an irreversible 2e oxidation wave, presumably due to the oxidation at sulfur, was observed at +0.94 V for *fac*(*S*)-[Rh(aet)$_3$] under the same conditions. Thus, in acidic media the Rh^{III} center in *fac*(*Se*)-[Rh(aes)$_3$] is more easily oxidized to Rh^{IV}, which is responsible for the facile formation of a coordinated diselenide bond. Finally, the present results should contribute significantly to our understanding of the nature of thiolato and selenolato groups, which have received considerable attention in connection with the important roles of cysteine and selenocysteine residues in biological systems.[12]

Supporting Information Available: Synthetic procedures and summary of X-ray crystallographic data (PDF). X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: New York, 1999; pp. 258−263. (b) Karty, J. M.; Wu, Y.; Brauman, J. I. *J. Am. Chem. Soc.* **2001**, *123*, 9800−9805. (c) Aullón, G.; Capdevila, M.; Clegg, W.; González-Duarte, P.; Lledós, A.; Mas-Ballesté, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2776−2778.

(2) (a) McDaniel, D. H.; Evans W. G. *Inorg. Chem.* **1966**, *5*, 2180−2182. (b) Marcus, S. H.; Miller, S. I. *J. Am. Chem. Soc.* **1966**, *88*, 3719−3724. (c) Sabin, J. R. *J. Chem. Phys.* **1971**, *54*, 4675−4680.

(3) (a) Boorman, P. M.; Gao, X.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1992**, 1656−1658. (b) Görbitz, C. H.; Dalhus, B. *Acta Crystallogr., Sect. C* **1996**, *52*, 1756−1759. (c) Mallinson, P. R.; MacNicol, D. D.; McCormack, K. L.; Yufit, D. Y.; Gall, J. H.; Henderson, R. K. *Acta Crystallogr., Sect. C* **1997**, *53*, 90−92. (d) Steiner, T. *Acta Crystallogr., Sect. C* **2000**, *56*, 876−877.

(4) Sellmann, D.; Lecher, P.; Knoch, F.; Moll, M. *J. Am. Chem. Soc.* **1992**, *114*, 922−930.

(5) Konno, T.; Shimazaki, Y.; Yamaguchi, T.; Ito, T.; Hirotsu, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 4711−4715 and references therein.

(6) Attempts to obtain proton adducts for *fac*(*S*)-[Co(aet)$_3$] and *fac*(*S*)-[Ir-(aet)$_3$] were unsuccessful, because of the cleavage of Co−S bonds to form [Co{Co(aet)$_3$}$_2$]$^{3+}$ and because of the autoxidation of one of three thiolato donors to form [Ir$_2$(aet)$_4$(cystamine)]$^{2+}$, respectively. Konno, T.; Miyashita, Y.; Okamoto, K. *Chem. Lett.* **1997**, 85−86.

(7) (a) Yoneda, H.; Kida, S. *J. Am. Chem. Soc.* **1960**, *82*, 2139−2141. (b) Bertrand, J. A.; Eller, P. G.; Fujita, E.; Lively, M. O.; Vanderveer, D. G. *Inorg. Chem.* **1979**, *18*, 2419−2423.

(8) See Supporting Information.

(9) Konno, T.; Okamoto, K. *Inorg. Chem.* **1997**, *36*, 1403−1406.

(10) [**1**](BF$_4$)$_3$ is reasonably soluble in CH$_3$CN to give a yellow solution, the absorption spectrum of which is very similar to that of *fac*(*S*)-[Rh(aet)$_3$] dissolved in 20% HBF$_4$.

(11) (a) Mittal, P. K.; Orrell, K. G.; Sik, V.; Cameron, T. S. *J. Chem. Soc., Chem. Commun.* **1984**, 1312−1313. (b) Abel, E. W.; Mittal, P. K.; Orrell, K. G.; Dawes, H.; Hursthouse, M. B. *Polyhedron* **1987**, *6*, 2073−2075. (c) Baratta, W.; Pregosin, P. S.; Bacchi, A.; Pelizzi, G. *Inorg. Chem.* **1994**, *33*, 4494−4501. (d) Mckarns, P. J.; Lewkebandara, T. S.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A. L.; Winter, C. H. *Inorg. Chem.* **1998**, *37*, 418−424.

(12) (a) Nordstrand, K.; Aslund, F.; Meunier, S.; Holmgren, A.; Otting, G.; Berndt, K. D. *FEBS Lett.* **1999**, *449*, 196−200. (b) Becker, K.; Gromer, S.; Schirmer, R. H.; Muller, S. *Eur. J. Biochem.* **2000**, *267*, 6118−6125.

JA0302331