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A Remarkable 14-Nuclear $\text{Re}_8\text{Ag}_6^{\text{I}}$ Coordination Oligomer Derived from a 2D $(\text{Re}_2\text{Ag}_2^{\text{I}})_n$ Coordination Polymer with D-Penicillamine

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There has been considerable interest in the design and creation of metallo-supramolecular systems that exhibit unique structural and chemical properties.^[1] In many cases, metallo-supramolecular structures have been constructed from organic multidentate ligands and metal ions through self-assembly processes. Our synthetic strategy involves the use of octahedral metal complexes containing relatively simple thiolate ligands, such as 2-aminoethanethiolate (aet), L-cysteinate (L-cys), and D-penicillamine (D-pen; D-H₂pen = D-penicillamine), as building blocks that are aggregated by forming S-bridged structures with metal ions.^[2–5] This method allows the construction of well-organized heterometallic aggregates which have several chiral centers by a systematic variation and combination of metal ions with different coordination geometries. For example, a number of chiral S-bridged aggregates, which include $\text{Co}^{\text{III}}_4\text{Pd}^{\text{II}}_2\text{M}^{\text{I}}_2$ octanuclear metallacycles $[\text{M}^{\text{I}}_2[\text{Pd}^{\text{II}}[\text{Co}^{\text{III}}(\text{aet})_3]_2]^{6+}$ (M = Ag, Au),^[2e] have been prepared just from $[\text{Co}^{\text{III}}(\text{aet})_3]$ and appropriate metal ions.^[2]

While it has been established that thiolato groups coordinated to an M^{II} or M^{III} metal center have the ability to bind to a second metal ion to form S-bridged structures,^[2–6] the coordinating ability of thiolato groups bound to a metal center with a higher oxidation state has not been widely investigated.^[7] In fact, S-bridged heterometallic aggregates based on

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thiolato metal complexes with an oxidation state higher than +5 have never been reported. The higher oxidation state of the metal center may cause the reduction of electron density on the thiolato donor atoms, which prevents the formation of stable S-bridged heterometallic structures with other metal ions. Thus, as part of our recent study on oxorhenium(V) complexes with aminothioloate ligands,^[8c] we investigated the ability of thiolato groups coordinated to a $[\text{Re}^{\text{VO}}]^{3+}$ core to ligate to other metal ions, with the aim of expanding the range of chiral supramolecular architectures based on octahedral metal complexes with thiolate ligands. We found that $[\text{Re}^{\text{VO}}(\text{D-pen-N,S})(\text{D-pen-N,O,S})]^-$ ions which have two coordinated thiolato groups and one free carboxylate group can aggregate with the use of Ag^{I} centers as the bridging metal ions, which leads to the creation of a novel 2D $(\text{Re}^{\text{V}}_2\text{Ag}^{\text{I}}_2)_n$ polymeric structure **1**. Furthermore, the $(\text{Re}^{\text{V}}_2\text{Ag}^{\text{I}}_2)_n$ structure can be converted into an unprecedented 14-nuclear $\text{Re}^{\text{V}}_8\text{Ag}^{\text{I}}_6$ oligomeric structure **2** that exhibits a fascinating metallo-supramolecular stereochemistry (Scheme 1).

Treatment of a purple aqueous solution of $[\text{Re}^{\text{VO}}(\text{D-Hpen-N,S})(\text{D-pen-N,O,S})]^{[8a]}$ with AgNO_3 in a ratio approximately 1:1 gave a dark purple solution, from which dark purple plate crystals of **1** were isolated. The FT-IR spectrum of **1** shows relatively sharp $\tilde{\nu}(\text{C}=\text{O})$ bands at 1675 and 1626 cm^{-1} , which are distinct from a broad $\tilde{\nu}(\text{C}=\text{O})$ band at 1669 cm^{-1} with a shoulder at approximately 1695 cm^{-1} for $[\text{Re}^{\text{VO}}(\text{D-Hpen-N,S})(\text{D-pen-N,O,S})]$. This spectral behavior suggests the absence of COOH groups in **1**.^[9] Moreover, the plasma emission spectral and elemental analyses of **1** are in agreement with the formula for the 1:1 adduct of $[\text{Re}^{\text{VO}}(\text{D-pen})_2]^-$ and Ag^+ ions.

Single-crystal X-ray analysis of **1** revealed the presence of an asymmetric unit consisting of one $[\text{Re}^{\text{VO}}(\text{D-pen-N,S})(\text{D-pen-N,O,S})]^-$ ion and one Ag^{I} atom, and lattice water molecules.^[10] The overall structure of the $[\text{Re}^{\text{VO}}(\text{D-pen-N,S})(\text{D-pen-N,O,S})]^-$ unit in **1** is very similar to that of the starting mononuclear $[\text{Re}^{\text{VO}}(\text{D-Hpen-N,S})(\text{D-pen-N,O,S})]^{[8b]}$ and have a distorted octahedral geometry with a *cis*(N)-*cis*(S)-*trans*(O) configuration. As shown in Figure 1, the two Re^{V}

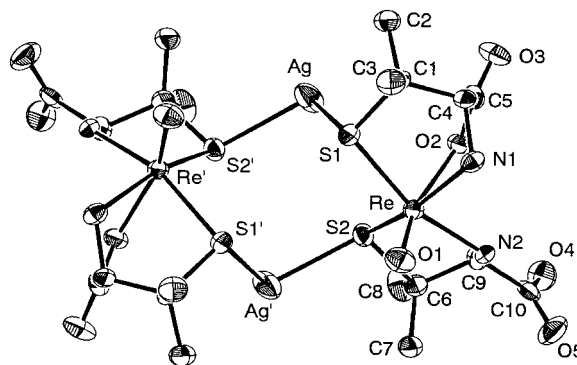
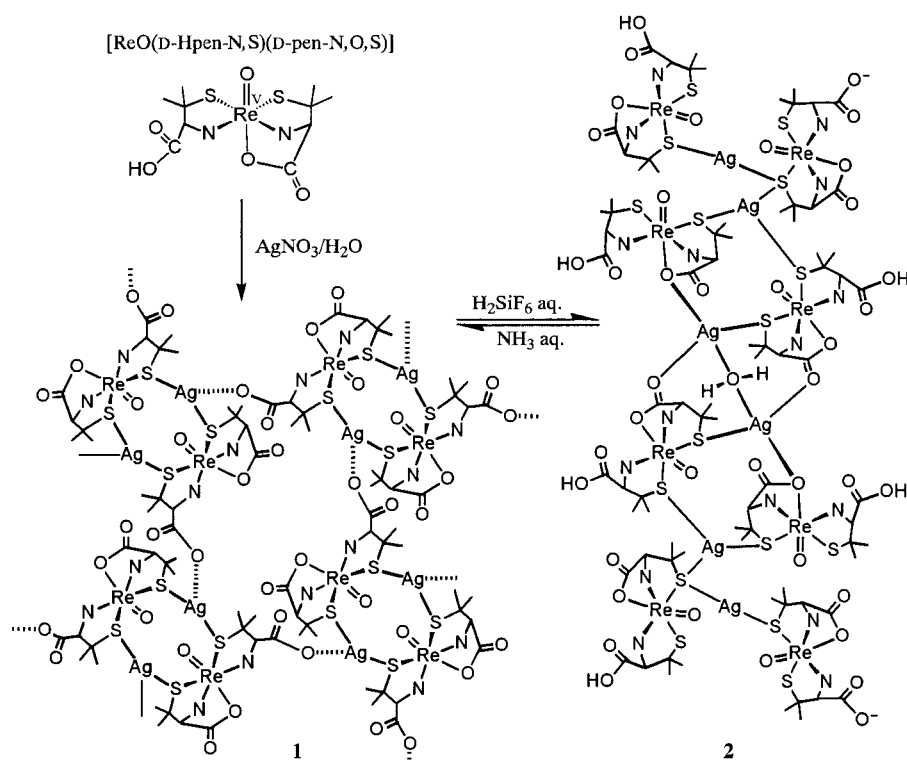


Figure 1. An ORTEP drawing of the $\text{Re}^{\text{V}}_2\text{Ag}^{\text{I}}_2$ unit of **1**, (thermal ellipsoids set to 50% probability).

octahedra are linked by two Ag^{I} atoms through sulfur bridges to form a $\text{Re}^{\text{V}}_2\text{Ag}^{\text{I}}_2$ tetranuclear structure $[\text{Ag}_2\{\text{Re}^{\text{VO}}(\text{D-pen-N,S})(\text{D-pen-N,O,S})\}_2]$ (average $\text{Re}-\text{S}$ 2.324(3) Å, $\text{Ag}-\text{S}$ 2.477(3) Å). This S-bridged tetranuclear structure is to be expected, however, the S-Ag-S angle (109.29(9)°) deviates significantly from linearity. An inspection of the extended structure of **1** (Figure 2) reveals that each Ag^{I} atom in the $\text{Re}^{\text{V}}_2\text{Ag}^{\text{I}}_2$ tetranuclear unit is bound

by a D-pen-N,S COO⁻ group from a neighboring tetranuclear unit ($\text{Ag}-\text{O4}'$ 2.351(10) Å), so as to adopt a trigonal-planar geometry. Thus, in **1** the S-bridged $\text{Re}^{\text{V}}_2\text{Ag}^{\text{I}}_2$ tetranuclear units are connected with one another through Ag-O bonds, which completes a 2D sheetlike structure made up by the cyclic $\text{Re}^{\text{V}}_4\text{Ag}^{\text{I}}_4$ network unit.

Compound **1** is sparingly soluble in water, consistent with its polymeric structure. However, treatment of an aqueous suspension of **1** with H_2SiF_6 gave a clear purple solution (pH < 1), from which a brown-purple compound **2** was isolated. It was anticipated that a discrete $\text{Re}^{\text{V}}_2\text{Ag}^{\text{I}}_2$ tetranuclear complex, $[\text{Ag}_2\{\text{Re}^{\text{VO}}(\text{D-Hpen-N,S})(\text{D-pen-N,O,S})\}_2]^{2+}$, was produced by the protonation at D-pen-N,S COO⁻ groups, which results in the cleavage of Ag-O bonds in **1**. Indeed, the IR spectrum of **2** exhibits a $\tilde{\nu}(\text{C}=\text{O})$ band at 1722 cm^{-1} indicative of the presence of a COOH



Scheme 1. Synthesis of **1** and **2**.

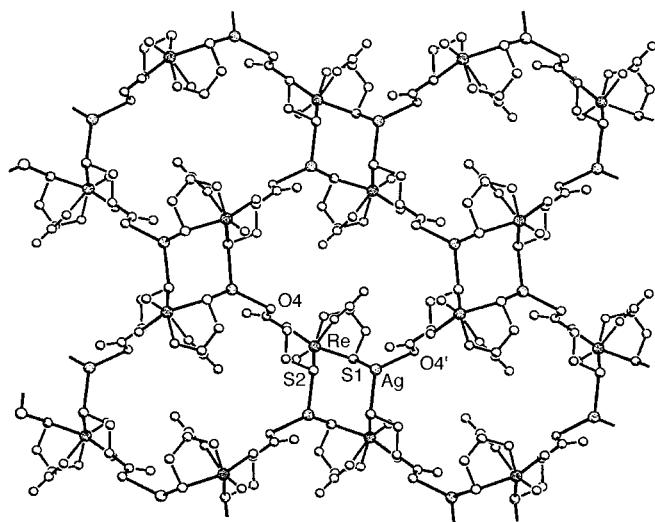


Figure 2. The 2D sheetlike structure of **1**. Methyl groups of each d-pen ligand and hydrogen atoms, as well as the lattice water molecules, are omitted for clarity.

group,^[9] in addition to $\tilde{\nu}(\text{C}=\text{O})$ bands at 1655 and 1602 cm^{-1} arising from COO^- groups. However, the plasma emission spectral analysis indicates a 3:4 ratio of Ag:Re atoms in **2**, and the elemental analysis agrees with the 3:4 stoichiometry $[\text{Ag}_3[\text{ReO}(\text{d-pen})(\text{d-pen})]_3\text{-}[\text{ReO}(\text{d-pen})_2]](\text{SiF}_6) \cdot n\text{H}_2\text{O}$, rather than the expected 2:2 stoichiometry.

The molecular structure of **2** was established by a single-crystal X-ray analysis.^[10] The complex cation of **2** is an unprecedented 14-nuclear coordination oligomer consisting of eight *cis*(N)·*cis*(S)·*trans*(O) configuration Re^{V} octahedral units and six Ag^{I} atoms. The presence of two SiF_6^{2-} ions implies that the entire complex cation of **2** has an overall charge of 4+. Six of the eight Re^{V} units adopt a protonated form $[\text{ReO}(\text{d-pen-N,S})(\text{d-pen-N,O,S})]$, while the remaining two units have a deprotonated form $[\text{ReO}(\text{d-pen-N,S})(\text{d-pen-N,O,S})]^-$. In the complex cation of **2**, the eight Re^{V} units are zigzag linked by three types of Ag^{I} atoms with different coordination geometries (Figure 3): a) Ag^{I} atoms coordinated by two S atoms from two Re^{V} units (Ag1 and Ag6; average Ag-S 2.473(4) Å), b) a trigonal-planar environment for Ag^{I} atoms coordinated by three S atoms from three Re^{V} units (Ag2 and Ag5; average Ag-S 2.513(4) Å), and c) Ag^{I} atoms in a tetrahedral geometry coordinated by one S and two O atoms from three Re^{V} units, as well as a water O atom (O41) located at the center of the 14-nuclear structure (Ag3 and Ag4; average Ag-S 2.500(4) Å, Ag-O 2.438(12) Å). Although the entire complex cation has no crystallographically imposed symmetry, a quasi C_2 axis passes through the central water oxygen atom. Interestingly, three types of thiolato S atoms are found in the complex cation of **2**: a) non-bridging S atoms (S2, S4, S6, S12, S14, and S16; average Re-S 2.282(4) Å), b) μ_2 -S atoms bridging Ag^{I} and Re^{V} centers (S1, S5, S7, S8, S9, S10, S11, and S15; average Re-S 2.331(4) Å, Ag-S 2.489(4) Å), and c) μ_3 -S atoms bridg-

ing two Ag^{I} and a Re^{V} centers (S3 and S13; average Re-S 2.373(4) Å, Ag-S 2.514(4) Å). In addition, there exist four types of Re^{V} units with different coordination modes: a) a monodentate S coordination with a μ_2 -S bridge (Re1 and Re8), b) a monodentate S coordination with a μ_3 -S bridge (Re2 and Re7), c) a bidentate O,S coordination with μ_2 -O and μ_2 -S bridges (Re3 and Re6), and d) a tridentate O,S,S coordination with a terminal O atom and two μ_2 -S bridges (Re4 and Re5). Thus, the 14-nuclear Re_8Ag_6 oligomeric structure in **2** is constructed by the ingenious organization of three types of coordination geometries around the Ag^{I} atoms and four types of coordination modes of Re^{V} octahedral units, as well as three types of bridging modes of thiolato S atoms (Scheme 2). This situation is in contrast with the 2D extended structure of **1** (compare Figure 2 with Figure 4), in which the Ag^{I} atoms have only one kind of coordination environment and the Re^{V} units have only one type of coordination mode. It is noteworthy that each Re_8Ag_6 molecule of **2** is bound to four neighboring Re_8Ag_6 molecules through $\text{COOH}\cdots\text{OOC}$

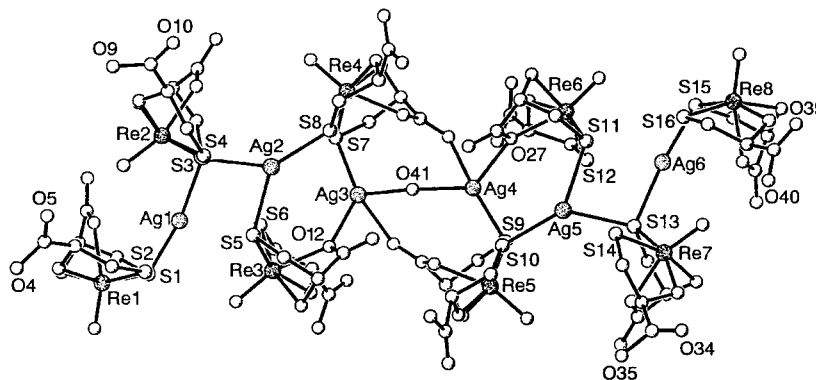
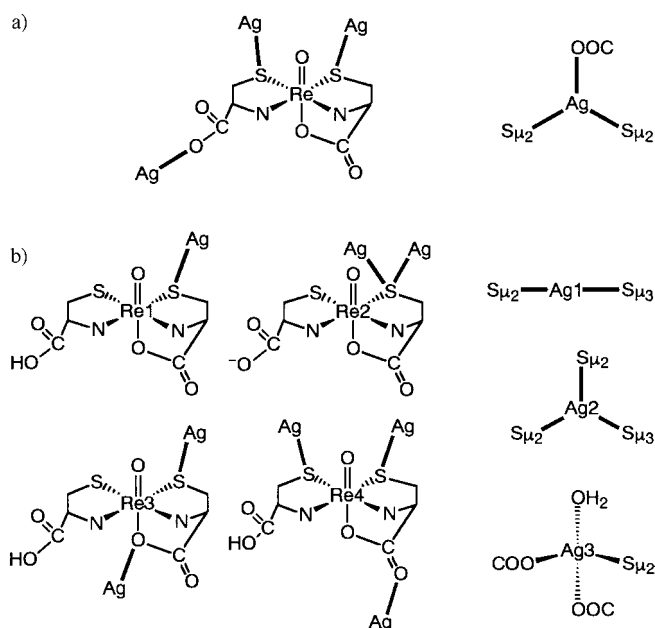


Figure 3. A perspective view of the Re_8Ag_6 oligomeric cation of **2**. Methyl groups of each d-pen ligand and hydrogen atoms are omitted for clarity.



Scheme 2. Coordination modes of Re^{V} units and coordination geometries of Ag^{I} atoms in **1** (a) and **2** (b).

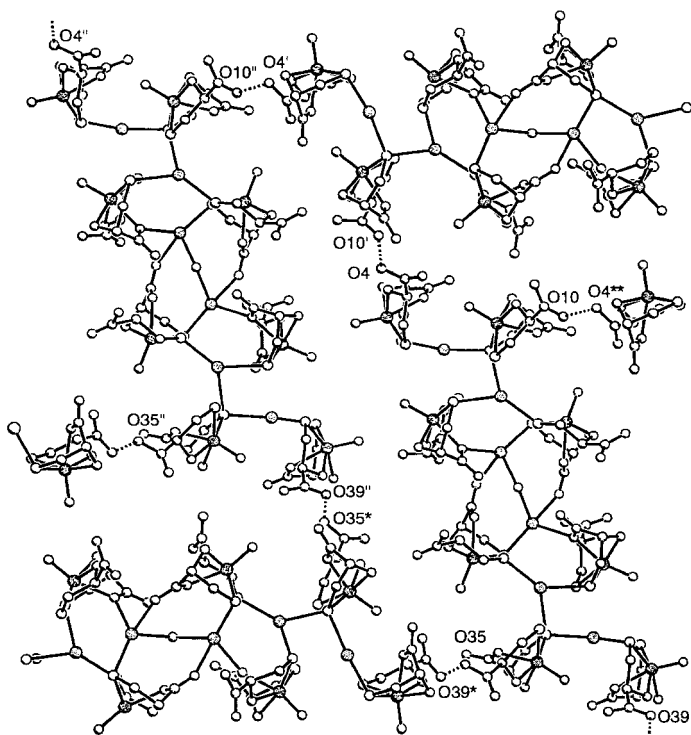


Figure 4. The 2D sheetlike structure of **2**. Methyl groups of each *D*-pen ligand and hydrogen atoms, as well as SiF_6^{2-} ions and lattice water molecules, are omitted for clarity.

hydrogen bonds ($\text{O4}\cdots\text{O10}'$ 2.64(2) Å, $\text{O35}\cdots\text{O39}^*$ 2.48(2) Å), which creates a 2D sheetlike structure made up of huge cyclic- $\text{Re}^{\text{V}}_{14}\text{Ag}^{\text{I}}_{10}$ -network units. The existence of two deprotonated $[\text{ReO}(\text{D-pen-N,S})(\text{D-pen-N,O,S})]^-$ units,^[11] together with the protonated $[\text{ReO}(\text{D-Hpen-N,S})(\text{D-pen-N,O,S})]$ units, is essential for this hydrogen bonding, which would in turn contribute significantly to the stabilization of the 14-nuclear oligomeric structure of **2**. Thermogravimetric (TGA) analysis showed that the structure of **2** collapses above approximately 210 °C, while the collapsing temperature for **1** was approximately 240 °C. These results show that **2** is thermally less stable than **1**, partly because the $\text{COOH}\cdots\text{OOC}$ hydrogen bonds in **2** are expected to be weaker than the $\text{Ag}-\text{O}$ coordination bonds in **1**.^[12]

When an aqueous solution of **2** was treated with aqueous ammonia to adjust the pH to approximately 5, purple microcrystals of **1** were formed. This result implies that **2** reverts back to the polymeric structure of **1** on changing the pH of the solution, despite the different stoichiometries found in **1** ($\text{Ag}:\text{Re} = 1:1$) and **2** ($\text{Ag}:\text{Re} = 3:4$; Scheme 1). The electronic absorption and circular dichroism (CD) spectra of **1** and **2** in water, which were only qualitatively measured because of the poor solubility of the compounds, are essentially the same as the spectra of the starting material $[\text{Re}^{\text{V}}\text{O}(\text{D-Hpen-N,S})(\text{D-pen-N,O,S})]$,^[8] which shows a characteristic near-UV absorption band at approximately 340 nm with a shoulder at the shorter wavelength side and a major positive CD band also in this region. Furthermore, in the ^1H NMR spectrum in D_2O , **1** and **2** give only a single set of resonance signals arising from four methyl and two methine groups at nearly the same positions as the resonance signals observed for $[\text{Re}^{\text{V}}\text{O}-$

$(\text{D-Hpen-N,S})(\text{D-pen-N,O,S})]$. Thus, the rapid exchange of the Re^{V} octahedral units occurs in solution with retention of the *cis*(N)-*cis*(S)-*trans*(O) geometry, which is responsible for the pH dependent interconversion between **1** and **2**.^[13]

In summary, the chiral mononuclear compound $[\text{Re}^{\text{V}}\text{O}-(\text{D-Hpen-N,S})(\text{D-pen-N,O,S})]$ readily reacts with Ag^+ ions to afford the 2D sheetlike coordination polymer **1**. This result shows that thiolato groups coordinated to a $[\text{Re}^{\text{V}}\text{O}]^{3+}$ core have an ability to bind with metal ions to form an S-bridged heterometallic polynuclear structure. In addition, the polymeric structure in **1** was successfully converted into **2** by treatment with aqueous H_2SiF_6 while retaining the coordination environment around the Re^{V} center. To our surprise, **2** was found to be a remarkable coordination oligomer composed of eight Re^{V} octahedra and six Ag^{I} ions. Although a large number of coordination polymers have been prepared from organic ligands and Ag^{I} ions, coordination oligomers containing Ag^{I} ions are quite rare.^[14] Furthermore, **2** is the first example of a highly organized chiral molecular architecture involving three different coordination geometries of Ag^{I} , four different coordination modes of Re^{V} units, and three different bridging modes of thiolato donors, all existing in one quasi C_2 symmetrical molecule. Note that **2** constructs a 2D sheetlike structure, which results from the self-assembly of the 14-nuclear $\text{Re}^{\text{V}}_8\text{Ag}^{\text{I}}_6$ molecules through $\text{COOH}\cdots\text{OOC}$ hydrogen bonds, while the structure of **1** is the result of the self-assembly of tetranuclear $\text{Re}^{\text{V}}_2\text{Ag}^{\text{I}}_2$ molecules through $\text{Ag}-\text{O}$ coordination bonds. Accordingly, the present results should provide an insight into the design and construction of second-generation metallo-supramolecular systems,^[14b] which are generated by self-assembly processes of discrete metallo-supramolecules consisting of metal polyhedra, and should also contribute to the development of thiolatooxorhenium(v) chemistry which is currently drawing much attention for potential therapeutic applications in nuclear medicine.

Experimental Section

1: A solution of AgNO_3 (0.07 g, 0.41 mmol) in water (15 mL) was added to a stirred solution of $[\text{ReO}(\text{D-Hpen-N,S})(\text{D-pen-N,O,S})]$ ^[8a] (0.20 g, 0.40 mmol) in water (120 mL). The mixture was allowed to stand at RT for 3 days, and the resulting purple microcrystals were collected by filtration. Yield: 0.22 g (73%); elemental analysis calcd (%) for $[\text{Ag}(\text{ReO}(\text{D-pen}))_2]\cdot 8\text{H}_2\text{O}$: $\text{C}_{10}\text{H}_{34}\text{AgN}_2\text{O}_{13}\text{ReS}_2$: C 16.04, H 4.58, N 3.73; found: C 16.08, H 4.51, N 3.67; ^1H NMR (D_2O): $\delta = 1.29, 1.65, 1.82, 2.06$ (CH_3), 3.14, 4.08 (CH). Dark purple plate crystals suitable for X-ray analysis were obtained as follows: a solution of AgNO_3 (0.07 g) in water (2 mL) was added to a stirred solution of $[\text{ReO}(\text{D-Hpen-N,S})(\text{D-pen-N,O,S})]$ (0.20 g) in water (400 mL). The mixture was allowed to stand at RT for 3 days.

2: A 40% solution of H_2SiF_6 (0.3 mL) was added dropwise to a stirred suspension of **1** (0.075 g, 0.05 mmol) in water (30 mL), which gave a clear purple solution. The solution was allowed to stand at RT for 3 days, and the resulting brown-purple crystalline solid was collected by filtration. Yield: 0.044 g (69%); elemental analysis calcd (%) for $[\text{Ag}_6(\text{ReO}(\text{D-Hpen})(\text{D-pen}))_6(\text{ReO}(\text{D-pen}))_2(\text{H}_2\text{O})](\text{SiF}_6)_2\cdot 10\text{H}_2\text{O}$: $\text{C}_{80}\text{H}_{172}\text{Ag}_6\text{F}_{12}\text{N}_{16}\text{O}_{31}\text{Re}_8\text{S}_{16}\text{Si}_2$: C 18.81, H 3.39, N 4.39; found: C 18.47, H 3.35, N 4.34; ^1H NMR (D_2O): $\delta = 1.34, 1.66, 1.84, 2.08$ (CH_3), 3.27, 4.13 (CH). Brown-purple plate crystals suitable for X-ray analysis were obtained as follows: several drops of 5% aqueous H_2SiF_6 were added to a purple solution of **1** (0.03 g) dissolved in 0.4% aqueous HBF_4 (10 mL), and the resulting solution was allowed to stand at RT for 2 weeks.

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- [10] Crystal structure analysis for **1**: Rigaku AFC7S diffractometer, *T* = 23 °C, MoK α radiation (λ = 0.71069 Å). The structure was solved by direct method (SIR92) and refined with full-matrix least-squares analysis on *F*² using SHELXL-93. Hydrogen atoms except those of water molecules were placed at calculated positions but were not refined. C₁₀H₃₄AgN₂O₁₃ReS₂, crystal size 0.07 × 0.20 × 0.22 mm, orthorhombic, space group *C*22₂₁, *a* = 13.636(3), *b* = 22.586(4), *c* = 15.486(3) Å, *V* = 4769(1) Å³, *Z* = 8, ρ_{calcd} = 2.085 g cm⁻³, μ = 61.26 cm⁻¹, ω –2 θ scan mode, $2\theta_{\text{max}}$ = 55.0, 3039 reflections collected, 3030 independent reflections, 2614 observed reflections (*F* > 4 σ (*F*)), 264 parameters, empirical absorption corrections based on ψ scans, max/min transmission 0.999/0.550, *R* (*F* > 4 σ (*F*)) = 0.034, *wR*₂ (all data) = 0.107, Flack parameter –0.01(1), residual electron density 1.19/–1.27 e Å⁻³. Crystal structure analysis for **2**: Bruker CCD area detector, *T* = –70 °C, MoK α radiation (λ = 0.71069 Å). The structure was solved by direct methods (SHELXS-97) and refined with full-matrix least-squares analysis on *F*² using SHELXL-97. Hydrogen atoms were not included in the calculations. C₈₀H₁₇₂Ag₆F₁₂N₁₆O₅₁–Re₈S₁₆Si₂, crystal size 0.11 × 0.11 × 0.45 mm, monoclinic, space group *P*2₁, *a* = 11.816(2), *b* = 20.295(3), *c* = 31.156(5) Å, β = 90.049(3)°, *V* = 7472(2) Å³, *Z* = 2, ρ_{calcd} = 2.271 g cm⁻³, μ = 75.51 cm⁻¹, ω scan mode, $2\theta_{\text{max}}$ = 55.1, 52277 reflections collected, 28443 independent reflections, 26902 observed reflections (*F* > 4 σ (*F*)), 1721 parameters, empirical absorption corrections with SADABS, max/min transmission 0.549/0.186, *R*₁ (*F* > 4 σ (*F*)) = 0.038, *wR*₂ (all data) = 0.083, Flack parameter –0.006(5), residual electron density 1.84/–1.61 e Å⁻³ (the peaks larger than 1.0 e Å⁻³ were found in the vicinity of heavy atoms). CCDC-189338 (**1**) and CCDC-189339 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
- [11] Based on the comparison of the C–O bond lengths (C6–O4 1.34(2), C16–O10 1.24(2), C66–O35 1.33(3), C76–O39 1.23(2) Å), the Re2 unit containing O10 and the Re8 unit containing O39 are assigned to have a deprotonated form (see Figure 3).
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- [13] As indicated by the referees, the solid-state structures of **1** and **2** would not be retained in solution. The electrospray-ionization (ESI) mass spectrum of **2** in water mainly showed four clusters of peaks centered at *m/z* 605.1 (relative intensity: 100%), 623.2 (19%), 1103.1 (83%), and 1209.0 (21%). The calculated molecular mass and the isotopic distribution of these clusters of peaks match very well with those for [Ag{ReO(*p*-Hpen)(*p*-pen)}]⁺, [Ag{ReO(*p*-Hpen)(*p*-pen)}(H₂O)]⁺, [Ag{ReO(*p*-Hpen)(*p*-pen)}₂]⁺, and [Ag₂{ReO(*p*-Hpen)(*p*-pen)}–{ReO(*p*-pen)}₂]⁺ ions, respectively. This result suggests that in water the Re^V₈Ag^I₆ 14-nuclear structure in **2** breaks down to Re^V₂Ag^I₁ trinuclear and Re^V₂Ag^I₂ tetranuclear species, followed by the dissociation of Re^V₂Ag^I₂ tetranuclear species into Re^VAg^I dinuclear species. Attempts to measure the ESI mass spectrum of **1** were unsuccessful, because of its extremely poor solubility in water.
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Using Mass Spectrometry to Characterize Self-Assembled Monolayers Presenting Peptides, Proteins, and Carbohydrates**

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Mass spectrometry (MS) is an important technique for characterizing the structures of surfaces and has several characteristics that are especially valuable in bioanalytical applications. In biochip applications, for example, MS offers the significant advantage that it does not require analytes to be labeled—either by direct attachment of fluorescent and radioactive labels or by binding of antibodies—and therefore offers greater flexibility in experiments.^[1–4] Further, the use of immobilized ligands to isolate active proteins from the

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