

# Recent Progress in the Chemistry of Rhenium Cluster Complexes and Its Relevance to the Prospect of Corresponding Technetium Chemistry

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Metal-metal bonded cluster complexes represent one of the important groups of compounds of group 7 elements, technetium and rhenium. While the chemistry of rhenium-rhenium bonded cluster complexes has developed extensively in these years, corresponding chemistry of technetium remains largely unrevealed. A general rule to classify the metal-metal bonded structural cores in terms of the number of d electrons, is presented, and existing Re-Re bonded cluster complexes are summarized accordingly. Recent progress of hexarhenium cluster complexes has been introduced as a typical example. From these overviews on the Re-Re cluster complexes, it is suggested that the chemistry of Tc-Tc bonded cluster complexes is highly promising.

## 1. Introduction

Technetium and rhenium belong to group 7 elements and their chemistry is expected to be similar to each other in many respects.<sup>1-3</sup> While the chemistry of rhenium coordination compounds developed extensively in these years, corresponding chemistry of technetium still remains largely unrevealed due to difficulty in handling of and in accessibility to this radioactive element. In order to discuss the prospect of still unrevealed technetium chemistry, it is very useful to survey current status of rhenium chemistry.

Rhenium that is located just below technetium in the periodic table, has the most versatile coordination chemistry among transition elements. This is because rhenium, as a member of group 7 elements in the middle of transition metals in the table, shows characteristics of both early and late transition metal complexes. While rhenium tends to form direct metal-metal bond to give various cluster complexes, numerous stable monomeric complexes are also known.<sup>1-3</sup>

Rhenium takes wide range of oxidation states from +1 to +7 under mild conditions. Various air stable complexes are known in the oxidation states of +1, +3, +4, +5, and +7. Thus rhenium takes the widest range of stable oxidation states among the transition elements. For example, with a rather common tripodal ligand, tris(2-pyridylmethyl)amine (tpa), rhenium gives stable complexes in all these oxidation states with the cooperation of appropriate co-ligands. The typical tpa complexes are,  $[\text{Re}^{\text{I}}(\text{CO})_3(\kappa^3\text{-tpa})]^+$ ,<sup>4</sup>  $[\text{Re}^{\text{III}}\text{Cl}_2(\text{tpa})]^+$ ,<sup>5</sup>  $[\text{Re}^{\text{IV}}_2(\mu\text{-O})_2(\text{tpa})_2]^{4+}$ ,<sup>6</sup>  $[\text{Re}^{\text{V}}\text{O}(\text{OCH}_2\text{CH}_2\text{O})(\kappa^3\text{-tpa})]^+$ ,<sup>7</sup> and  $[\text{Re}^{\text{VII}}(\text{O})_3(\kappa^3\text{-tpa})]^+$ .<sup>7</sup> A similar hexadentate polypyridyl-amine ligand, *N,N,N',N'*-tetrakis(2-pyridylmethyl)ethylenediamine (tpen) gives unusual seven-coordinate species,  $[\text{Re}^{\text{IV}}\text{O}(\text{tpen})]^{2+}$  and  $[\text{Re}^{\text{V}}\text{O}(\text{tpen})]^{3+}$ .<sup>8</sup> This ligand takes a unique tridentate mode with  $\text{Re}^{\text{VII}}(\text{O})_3$ .<sup>9,10</sup> These complexes are only limited examples showing the versatility of rhenium coordination compounds. Such structural versatility should be inherently found in technetium chemistry, although the research is limited so far.

Here I will focus on metal-metal bonded cluster compounds, because, while such compounds represent significant part of the rhenium chemistry, corresponding technetium compounds have not been paid much attention so far. A general idea of summarizing the metal-metal bonded cluster complexes will be

given first, and then the current status of the area of rhenium and technetium cluster complexes will be briefly surveyed. Then, as a typical example of the progress of rhenium cluster compounds, octahedral hexarhenium complexes will be reviewed. From these brief summaries, I will try to show how the chemistry of technetium cluster complexes would be versatile and promising area.

## 2. Structures of Rhenium-Rhenium Bonded Cluster Complexes

Rhenium-rhenium bonded cluster complexes are known for the oxidation states from +2 to +6. Core structures of such cluster complexes depend on the number of d electrons and therefore the oxidation states. Since each Re-Re bond is formed by the donation of one d electron each from Re atoms, the maximum number of Re-Re bond formed by each Re atom depends on its d electron number. For a multiple bond, the number may be counted as its bond order; for example, for the Re-Re quadruple bond, the number of Re-Re bonds is counted as four.<sup>11</sup> For the multiply bonded dimers, one  $\sigma$ , one or two  $\pi$ , and one  $\delta$  bonds are possible, energy of the  $\sigma$ ,  $\pi$ , and  $\delta$  bonds decreasing in this order.

Figure 1 shows the core structures of some typical metal-metal bonded cluster complexes associated with d electron numbers. Although the correlation in Figure 1 only provides a simplified view, it would help to summarize systematically various types of metal-metal bonded cluster core structures. For a series of metal-metal single bonded clusters, metal ions with  $d^2$ ,  $d^3$ , and  $d^4$  electron numbers form the metal-metal bonded core structures with triangle, tetrahedral, and octahedral shapes, respectively.<sup>11</sup> Figure 2 shows the existing exam-

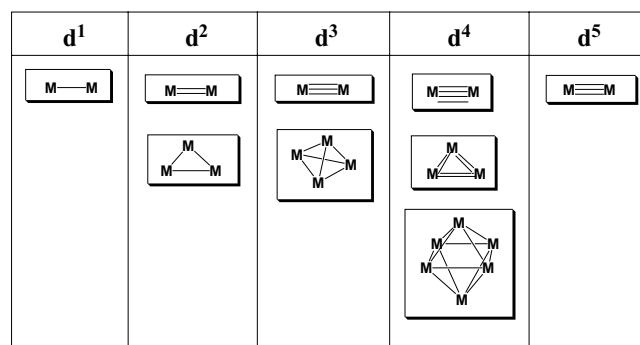
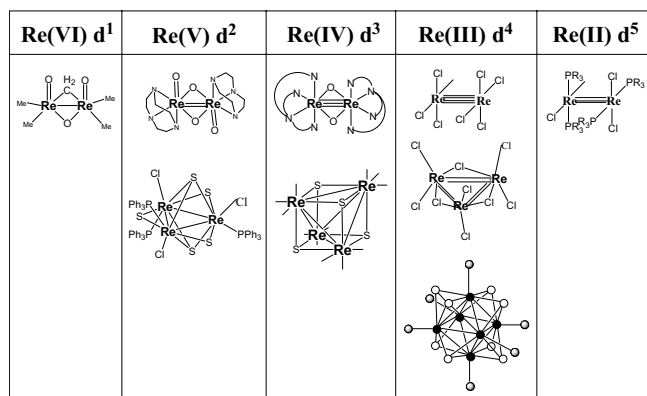


Figure 1. Correlation between d-electron number and typical M-M bonded cluster core structures.

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**Figure 2.** Correlation between d-electron number and the structure of some typical Re-Re bonded cluster complexes.

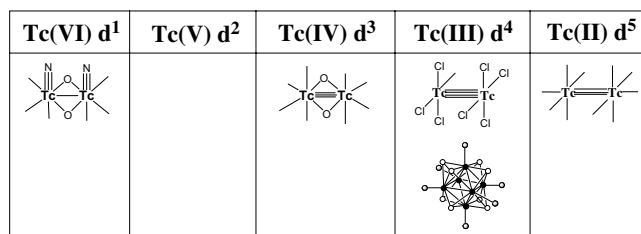
ples of Re cluster complexes. It is seen that the general view of the basic structural cores is successfully applied to Re chemistry. For example, a trivalent Re ion has four d electrons and can form dimers with a quadruple bond, or octahedral hexarhenium clusters where each Re ion forms four Re-Re single bonds with four neighboring Re atoms. Other type of clusters like triangular trimers with three Re-Re double bonds is also known. Tetravalent Re with d<sup>3</sup> electronic configuration may form Re-Re triple bonded dimer or tetrahedral tetramer with six Re-Re single bonds. It should be noted that the bond order of edge-shared dimers of a d<sup>3</sup> metal is complicated as the order of  $\delta$  and  $\delta^*$  orbitals are often in the reverse order ( $\delta > \delta^*$ ) depending on the interaction with the bridging ligands.<sup>6, 12</sup> Pentavalent Re with d<sup>2</sup> electronic configuration prefers to take monomeric oxo complexes, but Re-Re double bonded dimer is also known.<sup>13</sup> Triangular trinuclear complex with two Re-Re single bonds is another choice of cluster structure. The Re-Re single bonded dimer is the only structure for d<sup>1</sup> Re(VI).<sup>14</sup> An example of the dimer given in Figure 2 adopted the extreme expression that assumes highly basic ligand CH<sub>2</sub><sup>2-</sup> coordinates to Re(VI). The alternative way of considering covalent bond between Re and CH<sub>2</sub> is of course possible.

For the metal ions with the number of d electrons larger than 4, dimers of reduced bond order may be formed, since additional d electrons would occupy anti-bonding orbitals of metal-metal bonds.

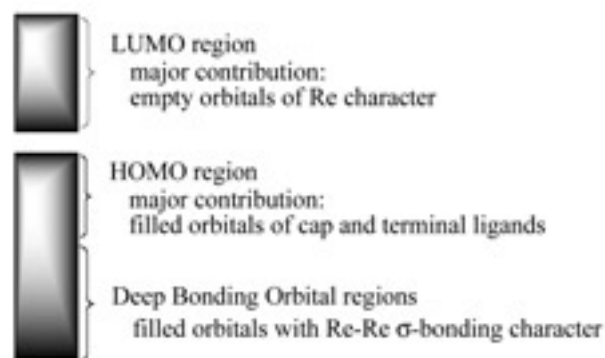
It should be noted that overall structure is completed by the cooperation of appropriate ligands that stabilized the given oxidation state. For the higher oxidation states, highly basic ligands such as O<sup>2-</sup> and N<sup>3-</sup> should be required. Chemistry of tri-, tetra-, and hexanuclear calcogenido-bridged clusters with Re-Re single bonds have developed considerably in the last decade.<sup>15-17</sup> Mixed valent cluster complexes are often found where the bond-order as summarized above have to be modified adequately.

### 3. Structures of Technetium-Technetium Bonded Cluster Complexes

Figure 3 shows some technetium cluster complexes which are summarized based on the general scheme given in Figure 1. It is obvious that Tc-Tc bonded cluster chemistry is so far dominated by only dimeric complexes. Thus, Tc-Tc dimers with single to quadruple bonds are known. The bond-order depends on the number of d electrons. The hexavalent Tc forms Tc-Tc single bonded dimers that are stabilized by the cooperation of highly negative nitride ligands (Tc  $\equiv$  N).<sup>18</sup> So far, tri-, tetra- and hexamers with metal-metal single bonds are not very common for Tc.<sup>19</sup> This is unlikely to be the reflection of intrinsic nature of technetium, but rather such compounds have not yet been the targets of extensive study. Namely, sulfur bridged cluster complexes that characterize the tri-, tetra-



**Figure 3.** Correlation between d-electron number and the structure of some Tc-Tc bonded cluster complexes.



**Figure 4.** Simplified MO characteristics of hexarhenium(III) core.

and hexarhenium cluster chemistry, have not yet been studied extensively for technetium.

### 4. Some Recent Developments in Octahedral Rhenium Cluster Complexes

Among various Re cluster complexes, hexarhenium(III) complexes have been studied most extensively in these years.<sup>17</sup> The complexes with an octahedral Re<sub>6</sub>( $\mu_3$ -E)<sub>8</sub> (E = S, Se, Te) core show various interesting properties which would likely be observed for yet unexplored analogous hexatechnetium complexes. The structure of the hexarhenium core is seen in the d<sup>4</sup> part of Figure 2, in which six ligands oriented outward are called as terminal ones, and the eight  $\mu_3$ -ligands occupy capping sites. Since various characteristic properties of hexarhenium complexes described herein are a reflection of the electronic structure of the hexameric structural core, simplified views of the molecular orbital studies as illustrated in Figure 4 are considered first.<sup>20-23</sup> Octa(calcogenido)hexarhenium(III) core is featured by strong bonding orbitals of the Re-Re  $\sigma$  bond which are in deep bonding orbital level. The HOMO region is mainly composed of capping and terminal ligand filled orbitals. Orbitals in the LUMO region are mainly composed of empty metal orbitals which are basically of  $\pi$  character with regard to the metal-metal bond. Therefore the hexarhenium core is considered as a poor  $\pi$ -donating and rather good  $\pi$ -accepting moiety.

The hexarhenium(III) complexes may be regarded as a giant octahedron, by considering the Re<sub>6</sub>( $\mu_3$ -E)<sub>8</sub> core as a metal ion and each terminal site (gray circles in the Figure) as a ligand of simple mononuclear metal complexes. By referring various aspects of mononuclear metal complexes, some new approaches to the hexarhenium cluster chemistry have been made. The hexarhenium core is extremely stable. The ligand substitution reactions of the terminal sites are very slow and require higher temperature (> 100 °C) to cause the substitution efficiently. Terminal sites can be substituted in a stepwise manner by various ligands such as halide ions, CN<sup>-</sup>, NCS<sup>-</sup>, pyridyl ligands, phosphine ligands, CH<sub>3</sub>CH, DMSO, and so on. A series of the mixed terminal ligand complexes such as [Re<sub>6</sub>( $\mu_3$ -E)<sub>8</sub>(X)<sub>6-n</sub>(L)<sub>n</sub>]<sup>(4-n)-</sup> (L = P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, E = S, n = 2-6; E = Se, n = 3-6;<sup>24, 25</sup> L = pyridine (py) and some pyridine deriva-

tives,  $E = S, n = 2-4$ )<sup>26,27</sup> were prepared. Geometrical isomers were also isolated for the complexes with  $n = 2-4$ . By using a long chain chelating ligand  $(C_6H_5)_2P(CH_2)_6P(C_6H_5)_2$  (dpph), the formation of a novel giant chelate ring was found in a series of the complexes,  $[Re_6(\mu_3-Se)_8I_{6-2n}(\mu-dpph)_n]^{(2n-4)+}$  ( $n = 2-4$ ).<sup>28</sup> A bulky porphyrin ligand 5-(4-pyridyl)-10,15,20-tritolylporphyrin can be successfully introduced into all of the six terminal sites of the hexarhenium(III) core.<sup>29</sup> A kinetic study of ligand exchange reactions of the mixed ligand system, *cis*- and *trans*- $[Re_6(\mu_3-S)_8Cl_4(py)_2]^{2-}$ , with  $py-d^5$ , showed selective substitution of *py* ligands but not  $Cl^-$ .<sup>30</sup> The results are in sharp contrast to some mononuclear complexes with  $d\pi$  rich metal ions like Co(III) where less basic  $Cl^-$  should be the ligands that are preferentially substituted. The poor  $\pi$ -donating and rather good  $\pi$ -accepting character of the hexarhenium(III) core makes stronger coordination with  $Cl^-$  as compared with *py*.

The hexarhenium(III) clusters undergo one-electron oxidation to the  $Re_6(III,III,III,III,III,IV)$  oxidation state where the half-filled orbital is considered to be delocalized over the entire hexarhenium core. X-ray structural analyses of one-electron oxidized species have revealed Jahn-Teller distortion of the hexarhenium core.<sup>31</sup> The one-electron oxidation potentials shift to positive direction with an increase in the number of pyridine ligands; the redox potentials of  $[Re_6(\mu_3-S)_8Cl_6]^{4-}$ ,  $[Re_6(\mu_3-S)_8Cl_4(py)_2]^{2-}$  (both *cis* and *trans*), and *mer*- $[Re_6(\mu_3-S)_8Cl_3(py)_3]^-$ , being +0.31, +0.77, and +0.97 V vs Ag/AgCl, respectively.<sup>26</sup> Thus the coordination of pyridine makes the hexarhenium clusters more difficult to oxidize. This fact may be explained by considering that pyridine is a less effective  $\pi$ -donating ligand than  $Cl^-$  is and reduce the electron density of the core. Another interesting feature is the splitting of the ligand reduction waves of  $[Re_6(\mu_3-S)_8Cl_4(L)_2]^{2-}$  (both *cis* and *trans*) ( $L =$  pyrazine, 4-cyanopyridine). The splitting indicates the ligand-ligand electronic interaction through the giant hexarhenium(III) core. This is remarkable since simple mononuclear metal center is not as effective as in this case for the splitting of ligand redox waves.<sup>23</sup> When six redox active ligands are introduced into the six terminal sites of the hexarhenium(III), the ligand redox waves split into six in some cases. The ligand-ligand electronic interaction may be mediated through  $\pi$ -type LUMO of the hexarhenium(III) core.

The most significant aspect of the hexarhenium(III) complexes is their strong luminescence with relatively long lifetime (in the order of  $\mu s$ ).<sup>32</sup> The emissive properties are reserved by changing the terminal and capping ligands. Emissions are observed also for other  $d^4$  octahedral complexes such as Mo(II) and W(II).<sup>33</sup> This fact indicates that corresponding hexanuclear Tc(III) clusters would also be strongly luminescent.

All the interesting features of the hexarhenium cluster complexes mentioned here could be inherently observed for analogous hexatechnetium complexes in somewhat modified way, and indicate potential versatility of technetium cluster chemistry. It should be noted that the MO characteristics (poor  $\pi$ -donor and good  $\pi$ -acceptor) as mentioned above could be a common feature of metal cluster complexes particularly those with metal-metal single bonded ones. Therefore the knowledge of various characteristic properties of hexarhenium complexes is useful for the understanding of the properties of other type of cluster complexes.

## 5. Similarity and Differences between Rhenium and Technetium Complexes

In general, second transition metals and their congener of third transition series give structurally similar complexes, and the basic structures found in rhenium are very likely seen also in technetium. The most significant difference in the structurally analogous rhenium and technetium complexes would be found in their redox potentials. From the general trends found

in the pairs of complexes in other groups such as Mo-W, Ru-Os, and Rh-Ir, it is expected that a technetium complex would show redox potentials more positive by ca. 0.5 V than its rhenium analogue. Thus lower oxidation state is more stabilized in technetium. Ligand substitution lability would be expected to be somewhat higher in Tc than corresponding Re compounds.

In summary, rhenium cluster chemistry is now expanding significantly and its versatility and significance have increasingly verified. There should be a wide variety of technetium cluster chemistry to be explored, significantly contributing not only to basic transition metal chemistry, but also to wider potential applications. Technetium cluster chemistry should certainly be a highly promising area.

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