

# Preparation, Structure, and Properties of Bis( $\mu$ -oxo)dirhenium(III,IV) and -dirhenium(IV) Complexes of Tris(2-pyridylmethyl)amine and Its (6-Methyl-2-pyridyl)methyl Derivatives

Hideki Sugimoto,<sup>†</sup> Masaki Kamei,<sup>†</sup> Keisuke Umakoshi,<sup>†</sup> Yoichi Sasaki,<sup>\*,†</sup> and Masatatsu Suzuki<sup>‡</sup>

Division of Chemistry, Graduate School of Science, Hokkaido University, Kita-ku, Sapporo 060, Japan, and Department of Chemistry, Faculty of Science, Kanazawa University, Kakuma-machi, Kanazawa 920-11, Japan

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A series of bis( $\mu$ -oxo)dirhenium complexes,  $[\text{Re}_2(\mu\text{-O})_2(\text{L})_2](\text{PF}_6)_n$  ( $\text{L} = \text{tris}(2\text{-pyridylmethyl})\text{amine (tpa)}$ ,  $n = 3$  (**1**),  $n = 4$  (**1a**);  $\text{L} = ((6\text{-methyl-2-pyridyl})\text{methyl})\text{bis}(2\text{-pyridylmethyl})\text{amine (Metpa)}$ ,  $n = 3$  (**2**),  $n = 4$  (**2a**);  $\text{bis}((6\text{-methyl-2-pyridyl})\text{methyl})(2\text{-pyridylmethyl})\text{amine (Me}_2\text{tpa)}$ ,  $n = 3$  (**3**),  $n = 4$  (**3a**)), have been prepared and characterized by several physical methods. X-ray crystallographic studies for **2**, **2a**·2CH<sub>3</sub>CN·2H<sub>2</sub>O (**2a'**), and **3a'** ( $\text{ReO}_4^-$  salt), include the first structural determinations of (i) the bis( $\mu$ -oxo)- $\text{Re}^{\text{III}}\text{Re}^{\text{IV}}$  complex (**2**) and (ii) the pair of  $\text{Re}^{\text{III}}\text{Re}^{\text{IV}}$  and  $\text{Re}^{\text{IV}}_2$  complexes (**2** and **2a'**). All the complexes have a centrosymmetric structure, suggesting that the mixed-valence state **2** is of structurally delocalized type. The Re–Re distances for **2**, **2a**·2CH<sub>3</sub>CN·2H<sub>2</sub>O, and **3a'** are 2.426(1), 2.368(1), and 2.383(1) Å, respectively, being consistent with the bond order of 2.5 ( $\sigma^2\pi^2\delta^2\delta^*$ ) for **2** and 3 ( $\sigma^2\pi^2\delta^2$ ) for the others. Methyl substitution on the pyridyl moiety of the ligands has no significant influence to the overall structure. Cyclic voltammetry of **1** shows two reversible redox waves at  $-0.77$  ((III,III)/(III,IV)) and  $0.09$  V ((III,IV)/(IV,IV)) vs Ag/AgCl in acetonitrile. The potentials are slightly more positive for **2** ( $-0.66$  and  $0.14$  V) and **3** ( $-0.64$  and  $0.20$  V). No proton-coupled redox behavior was observed on addition of *p*-toluenesulfonic acid. Complexes, **1a**, **2a**, and **3a** show a strong visible absorption band at 477 nm ( $\epsilon$ , 9200 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>), 482 (11200), and 485 (8700), respectively, which is assigned to the  $\pi$ - $\pi^*$  transition within the  $\text{Re}_2(\mu\text{-O})_2$  core. For the mixed-valence complexes **1**, **2**, and **3**, a strong band is observed in the longer wavelength region (556–572 nm). Crystal data: **2**, monoclinic, space group *C2/c* (No. 15),  $a = 11.799(2)$  Å,  $b = 19.457(3)$  Å,  $c = 21.742(4)$  Å,  $\beta = 98.97(1)^\circ$ ,  $Z = 4$ ; **2a'**, triclinic, space group *P1* (No. 2),  $a = 13.151(3)$  Å,  $b = 13.535(2)$  Å,  $c = 10.243(3)$  Å,  $\alpha = 104.37(2)^\circ$ ,  $\beta = 109.02(2)^\circ$ ,  $\gamma = 106.87(1)^\circ$ ,  $Z = 1$ ; **3a'**, monoclinic, space group *P2<sub>1</sub>/n* (No. 14),  $a = 13.384(3)$  Å,  $b = 14.243(2)$  Å,  $c = 13.215(6)$  Å,  $\beta = 106.88(2)^\circ$ ,  $Z = 2$ .

## Introduction

Hydroxide and oxide ions are the most common bridging ligands of di- and polynuclear metal complexes. Important factors in the chemistry of these metal complexes are (i) acid–base properties of the bridging ligands ( $\text{p}K_a$  of the oxide bridge), (ii) redox properties of the metal centers, and (iii) direct or indirect metal–metal interactions. These factors correlate to each other, i.e. redox potentials of the metal centers change significantly upon protonation of the oxide bridge,<sup>1–4</sup> and, where a direct metal–metal bond is formed, the bond order depends on the number of d electrons.<sup>5</sup>

These bridging ligands often give edge-shared bioctahedrons with various metal ions. Dinuclear complexes with bis( $\mu$ -hydroxo) and ( $\mu$ -oxo)( $\mu$ -hydroxo) bridging groups are known for various di- and trivalent metal ions.<sup>6,7</sup> Bis( $\mu$ -oxo) complexes are less common and found for tri- and/or tetravalent ions of

<sup>†</sup> Hokkaido University.

<sup>‡</sup> Kanazawa University.

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group 7 and 8 elements: manganese,<sup>7</sup> technetium,<sup>8,9</sup> rhenium,<sup>10–13</sup> iron,<sup>14,15</sup> ruthenium,<sup>3,16</sup> and osmium.<sup>17</sup> Since these metal ions take more than two stable oxidation states, these complexes should provide important information associated with the various factors mentioned above. Also structural information of the complexes with different oxidation states and different extent of protonation at the bridging ligands would be important. Extensive studies on bis( $\mu$ -oxo)dimanganese complexes with oxidation states (III,III), (III,IV), and (IV,IV) have been carried out in order to understand the structures and functional mechanisms of enzyme dimanganese active sites.<sup>7</sup> X-ray structural information on two neighboring oxidation states with the same ligand system is available. Increasing Mn–Mn distance from (III,IV) to (IV,IV) is explained by electrostatic repulsion of higher oxidation state metal ions.<sup>18–20</sup> In contrast, only two examples of the ( $\mu$ -O)<sub>2</sub> complexes ((III,III) and (III,IV)) have been reported for iron which is also an important element in biological oxo/hydroxo-bridged active centers.<sup>14,15</sup> For the ( $\mu$ -O)<sub>2</sub> complexes of manganese and iron, direct metal–metal bond is presumed to be absent.

Few examples of the ( $\mu$ -O)<sub>2</sub> complexes of technetium,<sup>8,9,21</sup> rhenium,<sup>10–13</sup> ruthenium,<sup>3,16</sup> and osmium<sup>17</sup> feature short metal–metal distances indicative of the direct multiple metal–metal bond. Although extensive studies on the redox chemistry of mononuclear oxo/hydroxo/aqua complexes of these elements have been reported,<sup>22</sup> such studies on dinuclear complexes, in particular on the ( $\mu$ -O)<sub>2</sub> complexes, are still scarce.<sup>16</sup> No example has been found so far for the structural information on the pair of ( $\mu$ -O)<sub>2</sub> complexes of neighboring oxidation states with the same ligand system. Such studies on single oxo-bridged complexes including linear ( $\mu$ -O) and bent ( $\mu$ -O)( $\mu$ -carboxylato)<sub>2</sub> systems are available, but they do not have a direct metal–metal bond.<sup>1,23,24</sup>

With rhenium, examples of the structurally characterized ( $\mu$ -O)<sub>2</sub> complexes are as follows: [Re<sup>IV</sup><sub>2</sub>( $\mu$ -O)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]<sup>4-</sup>,<sup>10</sup> [Re<sup>IV</sup><sub>2</sub>( $\mu$ -O)<sub>2</sub>Cl<sub>2</sub>(tacn)<sub>2</sub>]<sup>2+</sup>,<sup>11</sup> [Re<sup>IV</sup><sub>2</sub>( $\mu$ -O)<sub>2</sub>I<sub>2</sub>(tacn)<sub>2</sub>]<sup>2+</sup> (tacn = 1,4,7-triazacyclononane)<sup>12</sup> and [Re<sup>IV</sup><sub>2</sub>( $\mu$ -O)<sub>2</sub>(edta)<sub>2</sub>]<sup>4-</sup> (edta = ethylenediamine-*N,N,N',N'*-tetraacetate(4-)).<sup>13</sup> All of them are in the

Re<sup>IV</sup><sub>2</sub> oxidation state. The Re–Re distances in these complexes are in the range 2.362–2.381 Å and are considerably longer than those of metal–metal triple-bonded complexes of other structural type.<sup>25</sup> There have been discussions on the electronic configuration of d<sup>3</sup>–d<sup>3</sup> M–M bond in edge-shared bioctahedral complexes, i.e.  $\sigma^2\pi^2\delta^2$  or  $\sigma^2\pi^2\delta^*$ .<sup>8</sup>

We have recently reported the crystal structure of a bis( $\mu$ -oxo) dimer, [Re<sup>IV</sup><sub>2</sub>( $\mu$ -O)<sub>2</sub>(tpa)<sub>2</sub>]<sup>4+</sup> (tpa = tris(2-pyridylmethyl)amine) (Re–Re, 2.364(1) Å).<sup>26</sup> The complex was obtained as a minor byproduct of a single-oxo-bridged Re(III) dimer, [Re<sup>III</sup><sub>2</sub>( $\mu$ -O)Cl<sub>2</sub>(tpa)<sub>2</sub>]<sup>2+</sup>.<sup>27</sup> At the time of the report we were unable to prepare a sufficient amount of the bis( $\mu$ -oxo) compound to study its redox properties. Subsequently we found a better preparative route to the bis( $\mu$ -oxo) complexes both in the mixed-valent Re<sup>III</sup>Re<sup>IV</sup> and the Re<sup>IV</sup><sub>2</sub> oxidation states. The study has been extended to analogous complexes containing relevant ligands, bis(2-pyridylmethyl)((6-methyl-2-pyridyl)methyl)amine (Metpa) and bis((6-methyl-2-pyridyl)methyl)(2-pyridylmethyl)amine (Me<sub>2</sub>tpa). We report herein the structures and properties of the bis( $\mu$ -oxo)dirhenium(III,IV) and -dirhenium(IV) complexes of the three ligands. Comparative X-ray structural data of the (III,IV) and (IV,IV) pair provide an answer to the question of the Re<sup>IV</sup>–Re<sup>IV</sup> bond order.

## Experimental Section

**1. Materials.** The ligands tris(2-pyridylmethyl)amine (tpa),<sup>28</sup> ((6-methyl-2-pyridyl)methyl)bis(2-pyridylmethyl)amine (Metpa),<sup>29</sup> and bis((6-methyl-2-pyridyl)methyl)(2-pyridylmethyl)amine (Me<sub>2</sub>tpa)<sup>30</sup> and the complex ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub><sup>31</sup> were prepared as described in the literatures. Acetonitrile was dried over calcium hydride and distilled under argon atmosphere. Tetrabutylammonium hexafluorophosphate (TBAP) was recrystallized twice from ethanol. All other commercially available reagents were used as purchased.

**2. Preparation of the Complexes. [Re<sup>III</sup>Re<sup>IV</sup>( $\mu$ -O)<sub>2</sub>(tpa)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub> (1). a. Method A.** A suspension of [Re<sup>III</sup>Cl<sub>2</sub>(tpa)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub><sup>32</sup> (0.07 g, 0.1 mmol) and CH<sub>3</sub>COONa (0.31 g, 2.3 mmol) in 6 mL of H<sub>2</sub>O was refluxed under argon atmosphere. After 3 h, the suspension changed gradually to a red-purple solution. An aqueous solution (5 mL) of NH<sub>4</sub>PF<sub>6</sub> (0.20 g, 1.2 mmol) was added to the solution. A red purple microcrystalline powder was formed, which was filtered, washed with cold ethanol, and air dried; yield 0.03 g (55%).

**b. Method B.** A mixture of tpa (0.105 g, 0.360 mmol) and Re<sup>VO</sup>Cl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.200 g, 0.240 mmol) in 21 mL of methanol containing ca. 0.05 M CH<sub>3</sub>COOH–CH<sub>3</sub>COONa (in the ratio of the pH 4 aqueous buffer), was refluxed under argon atmosphere for 1 h, during which time the color of the suspension changed from yellow to greenish yellow. Water (2 mL) was added to the suspension and the reflux was continued further 7 h to obtain a reddish-purple solution. Ammonium hexafluorophosphate, NH<sub>4</sub>PF<sub>6</sub> (0.392 g (2.40 mmol)), was added to the solution to obtain a purple precipitate. The solid was filtered after a day and washed with diethyl ether; yield 0.01 g (ca. 6%). Anal. Calcd for C<sub>36</sub>H<sub>36</sub>N<sub>8</sub>F<sub>18</sub>O<sub>3</sub>P<sub>3</sub>Re<sub>2</sub> (MW 1420.04): C, 30.45; H, 2.56; N, 7.89. Found: C, 30.75; H, 2.70; N, 7.82. FAB MS: *m/z* = 1274 ([Re<sub>2</sub>( $\mu$ -O)<sub>2</sub>(tpa)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub>]<sup>+</sup>). IR (KBr/cm<sup>-1</sup>): 693 ( $\nu$ (Re–O–Re)).

**[Re<sup>IV</sup><sub>2</sub>( $\mu$ -O)<sub>2</sub>(tpa)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub>·2C<sub>2</sub>H<sub>5</sub>OH (1a).** A few drops of H<sub>2</sub>O<sub>2</sub> (30%) were added to 10 mL of the acetonitrile solution containing 0.05

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**Table 1.** Crystallographic Data for **2**, **2a'**, and **3a'**

	<b>2</b>	<b>2a'</b>	<b>3a'</b>
formula	C <sub>38</sub> H <sub>40</sub> N <sub>8</sub> O <sub>2</sub> F <sub>18</sub> P <sub>3</sub> Re <sub>2</sub>	C <sub>42</sub> H <sub>50</sub> N <sub>8</sub> O <sub>4</sub> F <sub>24</sub> P <sub>4</sub> Re <sub>2</sub>	C <sub>40</sub> H <sub>44</sub> N <sub>8</sub> O <sub>18</sub> Re <sub>6</sub>
fw	1448.09	1683.18	2042.07
space group	C2/c (No. 15)	P1 (No. 2)	P2 <sub>1</sub> /n (No. 14)
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73
T, °C	20	20	20
a, Å	11.799(2)	13.151(3)	13.384(3)
b, Å	19.457(3)	13.535(2)	14.243(2)
c, Å	21.742(4)	10.243(3)	13.215(6)
α, deg		104.37(2)	
β, deg	98.97(1)	109.02(2)	106.88(2)
γ, deg		106.87(1)	
V, Å <sup>3</sup>	4930.5(14)	1526.6(7)	2410.5(11)
Z	4	1	2
d <sub>calc</sub> , g/cm <sup>3</sup>	1.95	1.86	2.81
cryst size, mm	0.30 × 0.26 × 0.10	0.28 × 0.22 × 0.12	0.24 × 0.23 × 0.02
scan range, deg	1.8 + 0.4 tan θ	1.9 + 0.5 tan θ	1.2 + 0.4 tan θ
scan mode	ω-2θ	ω-2θ	ω-2θ
scan speed, deg	6	6	6
2θ <sub>max</sub> , deg	55	55	55
μ(Mo Kα), cm <sup>-1</sup>	51.79	42.41	152.99
no. of unique reflns	5668	7550	5666
no. of obsd reflns	2768, F <sub>o</sub> > 6σ(F <sub>o</sub> )	4493, F <sub>o</sub> > 6σ(F <sub>o</sub> )	3723, F <sub>o</sub> > 3σ(F <sub>o</sub> )
R <sup>a</sup> (%)	7.42	5.00	5.20
R <sub>w</sub> <sup>a</sup> (%)	7.92	5.88	5.00

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

g (0.03 mmol) of **1**. The solution changed its color from red-purple to gray in a day. Gray microcrystals deposited after standing for a few days, which were filtered off, washed with diethyl ether, and air dried. Recrystallization from acetonitrile-ethanol gave gray crystals. Yield: 0.03 g (65%). Anal. Calcd for C<sub>40</sub>H<sub>48</sub>N<sub>8</sub>F<sub>24</sub>O<sub>4</sub>P<sub>4</sub>Re<sub>2</sub> (MW 1657.14): C, 29.39; H, 3.06; N, 6.90. Found: C, 28.99; H, 2.92; N, 6.76. IR (KBr/cm<sup>-1</sup>): 718 (ν(Re-O-Re)).

**[Re<sup>III</sup>Re<sup>IV</sup>(μ-O)<sub>2</sub>(Metpa)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub>·2H<sub>2</sub>O (**2**). a. Method A.** This complex was prepared by a method analogous to method A of complex **1** except that [Re<sup>III</sup>Cl<sub>2</sub>(Metpa)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> was used instead of [Re<sup>III</sup>Cl<sub>2</sub>(tpa)](CF<sub>3</sub>SO<sub>3</sub>); yield 0.04 g (60%).

**b. Method B.** A suspension of Re<sup>V</sup>OCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.33 g, 0.4 mmol) and Metpa (0.12 g, 0.4 mmol) in a 1:1 mixture of ethanol-H<sub>2</sub>O (20 mL) was refluxed under argon atmosphere. The suspension changed to a red-purple solution after 6 h, to which NH<sub>4</sub>PF<sub>6</sub> (0.16 g, 1.0 mmol) in 5 mL of ethanol was added to obtain a microcrystalline powder. This was filtered, washed with diethyl ether, and air dried. Recrystallization from acetonitrile-2-propanol gave purple crystals, which were suitable for X-ray structural determination. Yield: 0.09 g (30%). Anal. Calcd for C<sub>38</sub>H<sub>44</sub>N<sub>8</sub>F<sub>18</sub>O<sub>4</sub>P<sub>3</sub>Re<sub>2</sub> (MW 1484.13): C, 30.75; H, 2.99; N, 7.55. Found: C, 30.66; H, 3.01; N, 7.58. IR (KBr/cm<sup>-1</sup>): 682 (ν(Re-O-Re)).

**[Re<sup>IV</sup><sub>2</sub>(μ-O)<sub>2</sub>(Metpa)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub>·2H<sub>2</sub>O (**2a**).** A few drops of H<sub>2</sub>O<sub>2</sub> (30%) were added to 10 mL of the acetonitrile solution containing 0.05 g (0.03 mmol) of **2**. The solution changed its color from red-purple to gray in a day. Gray microcrystals deposited after standing for a few days. Yield: 0.03 g (65%). Anal. Calcd for C<sub>38</sub>H<sub>44</sub>N<sub>8</sub>F<sub>24</sub>O<sub>4</sub>P<sub>4</sub>Re<sub>2</sub> (MW 1629.09): C, 28.02; H, 2.72; N, 6.88. Found: C, 27.76; H, 2.50; N, 7.01. IR (KBr/cm<sup>-1</sup>): 720 (ν(Re-O-Re)). Recrystallization from acetonitrile-2-propanol gave green-gray crystals of [Re<sup>IV</sup><sub>2</sub>(μ-O)<sub>2</sub>(Metpa)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub>·2CH<sub>3</sub>CN·2H<sub>2</sub>O (**2a'**), which were suitable for X-ray structural determination.

**[Re<sup>III</sup>Re<sup>IV</sup>(μ-O)<sub>2</sub>(Me<sub>2</sub>tpa)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub>·2H<sub>2</sub>O (**3**).** This complex was prepared by a method similar to method B of complex **2** by using Me<sub>2</sub>tpa instead of Metpa. Yield 0.08 g (26%). Anal. Calcd for C<sub>40</sub>H<sub>46</sub>N<sub>8</sub>F<sub>18</sub>O<sub>4</sub>P<sub>3</sub>Re<sub>2</sub> (MW 1510.16): C, 31.77; H, 3.20; N, 7.41. Found: C, 31.64; H, 3.17; N, 7.25. IR (KBr/cm<sup>-1</sup>): 680 (ν(Re-O-Re)).

**[Re<sup>IV</sup><sub>2</sub>(μ-O)<sub>2</sub>(Me<sub>2</sub>tpa)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub>·H<sub>2</sub>O (**3a**).** This complex was prepared by an analogous method to that of complex **2a** except that complex **3** was used instead of complex **2**. Yield: 0.04 g (80%). Anal. Calcd for C<sub>40</sub>H<sub>44</sub>N<sub>8</sub>F<sub>24</sub>O<sub>3</sub>P<sub>4</sub>Re<sub>2</sub> (MW 1637.11): C, 31.40; H, 2.52; N, 6.66. Found: C, 31.35; H, 2.97; N, 6.59. IR (KBr/cm<sup>-1</sup>): 720 (ν(Re-O-Re)).

**[Re<sup>IV</sup><sub>2</sub>(μ-O)<sub>2</sub>(Me<sub>2</sub>tpa)<sub>2</sub>](ReO<sub>4</sub>)<sub>4</sub> (**3a'**).** A suspension of Re<sup>V</sup>OCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.33 g, 0.4 mmol) and Me<sub>2</sub>tpa (0.12 g, 0.4 mmol) in 20 mL of ethanol-H<sub>2</sub>O (1:1) was heated under reflux. The suspension changed to a green-gray solution after 8 h. When this was allowed to stand in a refrigerator, yellow-green crystals formed after a day, which were filtered off, washed with ethanol, and air dried. Yield: 0.08 g (19%). These crystals were found to be suitable for X-ray structural determination. Anal. Calcd for C<sub>40</sub>H<sub>44</sub>N<sub>8</sub>O<sub>18</sub>Re<sub>6</sub> (MW 2042.07): C, 23.53; H, 2.17; N, 5.49. Found: C, 23.50; H, 2.31; N, 5.75. IR (KBr/cm<sup>-1</sup>): 716 (ν(Re-O-Re)), 908 (ν(Re-O) of ReO<sub>4</sub><sup>-</sup>).

**3. X-ray Structural Determinations.** X-ray data for **2** were collected with graphite-monochromated Mo Kα radiation on a MacScience MXC18 diffractometer at room temperature (20 °C). Unit cell parameters were obtained by least-squares refinement of 26 reflections (30 ≤ 2θ ≤ 35°). The intensities of three standard reflections, monitored every 100 reflections, showed about 10% decay during the data collection. Correction was made for the decay and absorption. X-ray data for **2a'** and **3a'** were collected with graphite-monochromated Mo Kα radiation on a Rigaku AFC-5R diffractometer at 20 °C. Unit cell parameters were obtained by least-squares refinement of 25 reflections (25 ≤ 2θ ≤ 30°). The intensities of three standard reflections for each compound, monitored every 150 reflections, showed no appreciable decay up to 2θ < 50°, but the intensity decayed continuously up to ca. 20% during the measurement in the range of 50 ≤ 2θ ≤ 55° for **2a'**. No appreciable decay was observed for **3a'** during the data collection in the range 50 ≤ 2θ ≤ 55°. Absorption correction was applied for each compound, but no correction was made for the decay for **2a'**.

Each crystal structure of **2**, **2a'**, and **3a'** was solved by standard heavy-atom procedures. The positional and thermal parameters were refined by the block-diagonal-matrix least-squares method. The minimized function was  $\sum w(|F_o| - |F_c|)^2$ , where  $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$ . No attempt was made to locate hydrogen atoms in the structure analysis. In the final cycle of the refinement, parameter shifts were less than 0.2σ except for F(11), F(13), F(14), and F(15), which were less than 0.5σ for **2**, less than 0.1σ except N(21), F(23), and F(25) which were less than 0.2σ for **2a'**, and less than 0.1σ for **3a'**. No correction was made for secondary extinction. The atomic scattering factors for neutral atoms, with correction for anomalous dispersion of Re<sup>0</sup>, P<sup>0</sup>, and F<sup>0</sup>, were used throughout the analysis.<sup>33</sup> Computational work was carried out by using standard programs in UNICS III<sup>34</sup> and

(33) Ibers, J. A.; Hamilton, W. C. *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C.; Kynoch: Birmingham, England, 1974; Vol. IV.

**Table 2.** Selected Bond Lengths and Bond Angles for **2**, **2a'**, and **3a'**

	Bond Lengths (Å)		
	<b>2</b>	<b>2a'</b>	<b>3a'</b>
Re(1)–Re(1')	2.426(1)	2.368(1)	2.383(1)
Re(1)–O(1)	1.965(12)	1.932(8)	1.946(8)
Re(1)–O(1')	1.934(14)	1.952(7)	1.915(9)
Re(1)–N(1)	2.130(16)	2.163(9)	2.137(12)
Re(1)–N(11)	2.167(16)	2.141(10)	2.149(10)
Re(1)–N(21)	2.054(16)	2.125(9)	2.135(9)
Re(1)–N(31)	2.092(16)	2.130(7)	2.145(10)
	Bond Angles (deg)		
	<b>2</b>	<b>2a'</b>	<b>3a'</b>
O(1)–Re(1)–O(1')	103.1(6)	104.9(3)	103.8(4)
O(1)–Re(1)–N(1)	86.0(6)	84.7(3)	85.9(4)
O(1)–Re(1)–N(21)	93.9(6)	93.5(4)	94.4(3)
O(1)–Re(1)–N(31)	92.0(6)	93.3(4)	92.7(4)
O(1)–Re(1)–N(11)	166.5(5)	165.1(3)	165.3(4)
O(1')–Re(1)–N(1)	170.7(6)	170.4(3)	170.3(4)
O(1')–Re(1)–N(21)	97.6(6)	100.9(3)	101.1(4)
O(1')–Re(1)–N(31)	104.9(6)	101.8(4)	102.7(4)
O(1')–Re(1)–N(11)	90.4(6)	89.9(4)	90.9(4)
N(1)–Re(1)–N(21)	79.2(6)	77.7(3)	77.7(4)
N(1)–Re(1)–N(31)	76.8(6)	77.8(4)	76.5(4)
N(1)–Re(1)–N(11)	80.5(6)	80.5(4)	79.5(4)
N(21)–Re(1)–N(31)	154.8(6)	153.8(4)	152.7(5)
N(21)–Re(1)–N(11)	82.8(6)	85.6(4)	82.1(4)
N(31)–Re(1)–N(11)	85.8(6)	81.4(4)	84.4(4)
Re(1)–O(1)–Re(1')	76.9(5)	75.1(3)	76.2(3)

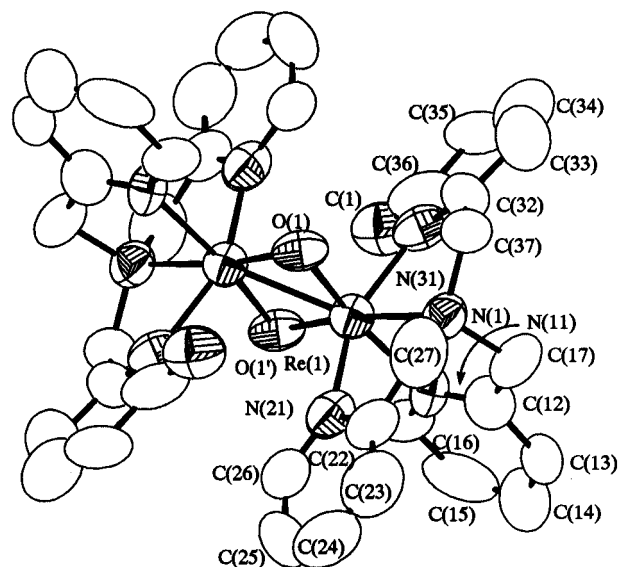
ORTEP.<sup>35</sup> Further crystallographic data are given in Table 1. Selected bond distances and angles are summarized in Table 2. Listings of the non-hydrogen atom coordinates and full listings of bond distances and angles are provided as Supporting Information.

**4. Electrochemical Measurements.** Cyclic voltammetry was performed with a Hokuto HA-501G potentiostat and a Hokuto HB-105 function generator equipped with a Graphtec WX2400 X-Y recorder. The working and the counter electrodes were a glassy-carbon disk and a platinum wire, respectively. Cyclic voltammograms were recorded at a scan rate of 50 mV/s. The sample solutions (ca. 1.0 mM) in 0.1 M TBAP–acetonitrile were deoxygenated with a stream of nitrogen gas. The reference electrode was Ag/AgCl and the half-wave potential of  $\text{Fc}^+/\text{Fc}$  ( $E_{1/2}(\text{Fc}^+/\text{Fc})$ ) vs Ag/AgCl was 0.435 V).

**5. Other Measurements.** UV–visible spectra were recorded on a Jasco Ubest-30 spectrophotometer at 20 °C. IR spectra were recorded on a Hitachi 270-50 infrared spectrophotometer. The  $^1\text{H}$  NMR spectra were obtained at 270 MHz with a JEOL JNM-EX270 spectrometer.

## Results and Discussion

**Preparation of the Complexes.** No general preparation route to access to bis( $\mu$ -oxo)dirhenium complexes has been established. Various starting materials such as  $\text{Re}^{\text{IV}}\text{O}_2$ ,  $[\text{Re}^{\text{IV}}\text{Cl}_6]^{2-}$ , and  $[\text{Re}^{\text{V}}(\text{O})\text{Cl}_5]^{2-}$ , have been used for the preparation of the bis( $\mu$ -oxo)dirhenium(IV) complexes of nonbridging ligands, edta<sup>13</sup> and oxalate.<sup>10,36</sup>  $[\text{Re}_2(\mu\text{-O})_2\text{X}_2(\text{tacn})_2]^{2+}$  ( $\text{tacn} = 1,4,7$ -triazacyclononane) ( $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$ ) was obtained from  $\text{Re}^{\text{V}}(\text{O})\text{Cl}_3(\text{PPh}_3)_2$  through intermediate mononuclear complexes,  $[\text{Re}^{\text{V}}(\text{O})(\text{ethyleneglycolato})(\text{tacn})]\text{X}$  or  $\text{Re}^{\text{III}}\text{X}_3(\text{tacn})$ .<sup>12</sup> We have found that the reactions of  $\text{Re}^{\text{V}}\text{OCl}_3(\text{PPh}_3)_2$  with bpy (2,2'-bipyridine), phen (1,10-phenanthroline) and tpa in acetonitrile or ethanol–H<sub>2</sub>O (30:1 in volume) give single-bridged  $\mu$ -oxo rhenium(III) dimers,  $[\text{Re}_2(\mu\text{-O})\text{Cl}_2(\text{L})_n]^{2+}$  ( $(\text{L})_n = (\text{bpy})_4, (\text{phen})_4$ ,<sup>37</sup> and  $(\text{tpa})_2$ ,<sup>27</sup> respectively). When tpa was used as a nonbridging



**Figure 1.** ORTEP view of the complex cation in  $[\text{Re}^{\text{III}}\text{Re}^{\text{IV}}(\mu\text{-O})_2(\text{Metpa})_2](\text{PF}_6)_3$  (**2**) with the atom-numbering scheme. The non-hydrogen atoms are represented by 50% probability thermal ellipsoids.

ligand, a bis( $\mu$ -oxo) dimer,  $[\text{Re}^{\text{IV}}_2(\mu\text{-O})_2(\text{tpa})_2]^{4+}$  was obtained as a minor byproduct. This complex was structurally characterized by the single-crystal X-ray diffraction method.<sup>26</sup> Subsequently we have found that, when 6-methyl derivatives of tpa were used under similar experimental conditions in an ethanol–water mixture, bis( $\mu$ -oxo) complexes rather than single-bridged dimers were obtained. By careful examination of the reaction conditions by adding  $\text{CH}_3\text{COOH}$ – $\text{CH}_3\text{COONa}$  to control effective pH of the ethanol solution, it was found that at pH = 4.0–4.5 the reaction mixture of tpa and  $\text{Re}^{\text{V}}\text{OCl}_3(\text{PPh}_3)_2$  gives the bis( $\mu$ -oxo) tpa complex **1** in the oxidation state (III,IV) (yield, 6%). Since, under similar reaction conditions with  $\text{Me}_2\text{tpa}$  as a ligand, we have isolated an  $\text{ReO}_4^-$  salt of the bis( $\mu$ -oxo)dirhenium complex (**3a'**), it is possible that the tetravalent rhenium is formed through a disproportionation reaction. In fact, Wieghardt and coworkers reported that in 0.5 M HX ( $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$ ) aqueous solution,  $\text{Re}(\text{V})$  ( $[\text{Re}^{\text{V}}\text{O}(\text{ethyleneglycolato})(\text{tacn})]^{2+}$ ) disproportionates to  $\text{Re}(\text{IV})$  and  $\text{Re}(\text{VII})$  and produces the  $\text{Re}_2(\mu\text{-O})_2$  complexes.<sup>12</sup> Higher yield of the bis( $\mu$ -oxo) complexes is not expected by the disproportionation mechanism.

A different route to the bis( $\mu$ -oxo) complexes was sought and eventually we found that the bis( $\mu$ -oxo) complexes are obtained in much higher yield by using *cis*- $[\text{ReCl}_2(\text{L})]^+$  ( $\text{L} = \text{tpa}$  or  $\text{Metpa}$ )<sup>32</sup> as a starting material. The *cis*-dichloro complex was prepared from  $\text{Re}^{\text{V}}(\text{O})\text{Cl}_3(\text{PPh}_3)_2$ , and the total yield of the bis( $\mu$ -oxo) complexes is ca. 45% based on  $\text{Re}^{\text{V}}(\text{O})\text{Cl}_3(\text{PPh}_3)_2$ .

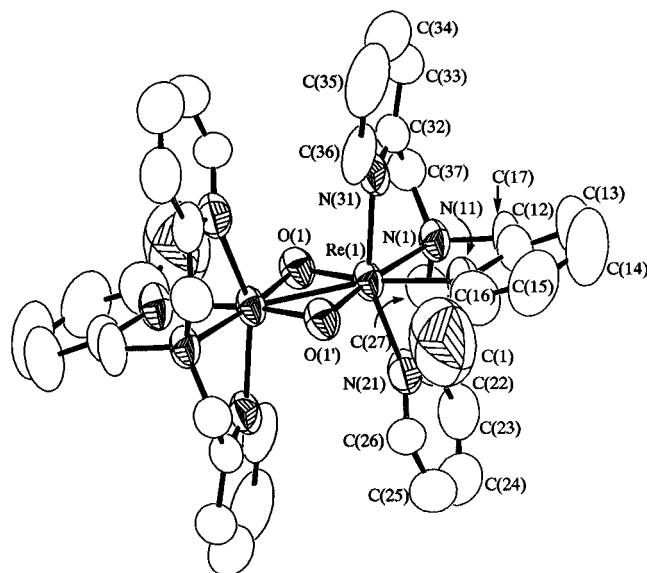
**Structures of the Bis( $\mu$ -oxo)dirhenium Complexes.** Figures 1–3 show the ORTEP drawings of the three complex cations in **2**, **2a'**, and **3a'**. These complexes are structurally very similar to one another having an edge-shared bioctahedral structure with two bridging oxide ions. Each rhenium ion is coordinated by the tetradentate ligand Metpa or  $\text{Me}_2\text{tpa}$  to complete a distorted octahedral coordination sphere. All the complex cations have a centrosymmetric configuration, with two tertiary amine nitrogens occupying positions trans to the different bridging oxide. Thus the mixed-valence complex **2** is a structurally delocalized type. It should be noted that the geometrical configurations of the cations in **2** and **2a'** are different with respect to the coordination sites of 6-methylpyridyl groups. The 6-methylpyridyl moieties occupy the positions *cis* to the both oxide bridges in **2** and *trans* to one of the oxide bridges in **2a'**. Judging from the following observations, the difference should

(34) Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyusho Hokoku (Rep. Inst. Phys. Chem. Res.)* **1979**, 55, 69.

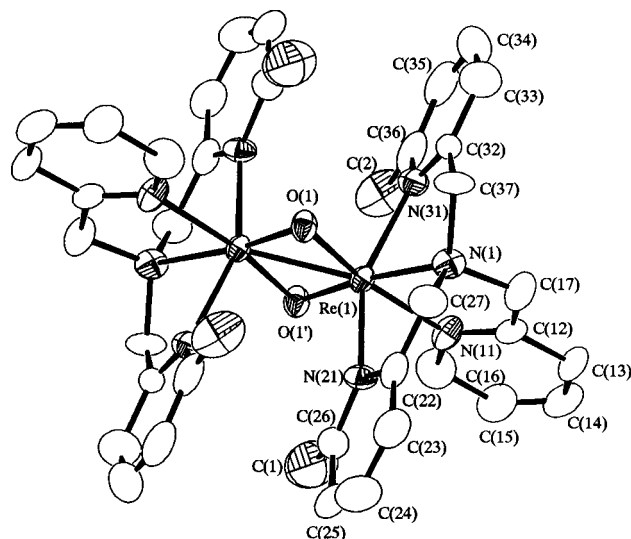
(35) Johnson, C. K. ORTEP II. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(36) Atkinson, J. W.; Hong, M.-C.; Housem, D. A.; Kyritsis, P.; Li, Y.-J.; Nasreldin, M.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1995**, 3317.

(37) Takahira, T.; Umakoshi, K.; Sasaki, Y. *Chem. Lett.* **1994**, 1870.



**Figure 2.** ORTEP view of the complex cation in  $[\text{Re}^{\text{IV}}_2(\mu\text{-O})_2\text{-(Metpa)}_2](\text{PF}_6)_4 \cdot 2\text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$  (**2a'**) with the atom-numbering scheme.



**Figure 3.** ORTEP view of the complex cation in  $[\text{Re}^{\text{IV}}_2(\mu\text{-O})_2(\text{Me}_2\text{tpa})_2](\text{ReO}_4)_4$  (**3a'**) with the atom-numbering scheme.

not be caused by the different oxidation states, (III,IV) for **2** and (IV,IV) for **2a'**. Namely,  $^1\text{H}$  NMR spectrum indicated the existence of at least two geometrical isomers in the powdered product of **2a**.<sup>38</sup> Also, a preliminary result of the X-ray structural analysis of **3a** disclosed a different geometrical isomer (two 6-methylpyridyl groups occupy one in-plane and one out-of-plane positions to the  $\text{Re}_2(\mu\text{-O})_2$  plane)<sup>39</sup> from the complex cation in **3a'**. Thus at least two geometrical isomers are formed by the preparation methods employed for the Metpa and  $\text{Me}_2\text{tpa}$  complexes. It may be that crystals of different geometrical isomers have been selected for the structural studies.

(38) See footnote 46.

(39) X-ray data for the crystal of **3a** with a molecular formula of  $[\text{Re}_2(\text{O})_2(\text{C}_{20}\text{H}_{22}\text{N}_4)_2](\text{PF}_6)_4 \cdot 2\text{CH}_3\text{CN}$  were collected with graphite-monochromated Mo  $\text{K}\alpha$  radiation on a MacScience MXC18 diffractometer at 163 K. The triclinic space group  $P\bar{1}$  was observed with  $a = 12.191(5)$  Å,  $b = 22.373(6)$  Å,  $c = 12.000(4)$  Å,  $\alpha = 100.29(2)^\circ$ ,  $\beta = 99.06(3)^\circ$ , and  $\gamma = 78.28(3)^\circ$ . The structure was solved and refined to a conventional  $R$  factor of 0.12. The standard deviations of bond lengths and angles are large, but the general feature of the structure are clear enough to recognize the isomer.

(40) Shaik, S.; Hoffman, R.; Fisel, C. R.; Summerville, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4555.

Structures of the three complex cations are very similar to that of **1a** whose structure was reported previously.<sup>26</sup> The Re–Re distances of the three  $\text{Re}^{\text{IV}}_2$  complexes, **1a**, **2a'**, and **3a'**, are 2.364(1), 2.368(1), and 2.383(1) Å, respectively. These distances are in the range of the corresponding ones reported for other  $\text{Re}^{\text{IV}}_2(\mu\text{-O})_2$  complexes.<sup>10–13</sup> Short Re–Re distances have been accounted for by considering multiple Re–Re bonds for  $d^5$   $\text{Re}^{\text{IV}}_2(\mu\text{-O})_2$  complexes,<sup>12,13</sup> where the electronic configuration, whether  $\sigma^2\pi^2\delta^2$  or  $\sigma^2\pi^2\delta^{*2}$ , has not been determined unambiguously. The distances are also similar to the Tc–Tc bond lengths in the  $\text{Tc}^{\text{IV}}_2(\mu\text{-O})_2$  complexes<sup>8,9</sup> where the  $\sigma^2\pi^2\delta^{*2}$  formalism rather than the  $\sigma^2\pi^2\delta^2$  one has been proposed to explain relatively “long” Tc–Tc distances as compared with metal–metal triple bond distances found for complexes of other structural types. The  $\sigma^2\pi^2\delta^{*2}$  configuration has been supported by molecular orbital calculations; i.e. interaction with orbitals of bridging ligands could place the energy level of  $\delta^*$  orbital lower than that of  $\delta$ .<sup>8</sup> Thus the question is whether the ground state configuration is  $\sigma^2\pi^2\delta^{*2}$  (formal bond order 1) or  $\sigma^2\pi^2\delta^2$  (formal bond order 3)<sup>25,40</sup> in the present case. Comparison of the Re–Re distances of **2a'** and **2** supports the latter configuration. The Re–Re distance in **2a'**, a  $\text{Re}^{\text{III}}\text{Re}^{\text{IV}}$  dimer, is 2.426(1) Å, which is clearly longer than the one in **2**. The trend is reasonable if the mixed-valence dimer has the Re–Re bond order of 2.5 ( $\sigma^2\pi^2\delta^2\delta^{*1}$ ) rather than a bond order of 1.5 ( $\sigma^2\pi^2\delta^{*2}\delta^1$ ), and the  $\text{Re}^{\text{IV}}_2$  dimer has a bond order of 3 ( $\sigma^2\pi^2\delta^2$ ). Judging from the similarity between the metal–metal distances of the  $\text{Re}^{\text{IV}}_2$  and the  $\text{Tc}^{\text{IV}}_2$  bis( $\mu$ -oxo) complexes, the bond order of the latter could also be 3 ( $\sigma^2\pi^2\delta^2$ ) rather than 1 ( $\sigma^2\pi^2\delta^{*2}$ ). It is interesting that the  $\sigma^2\pi^2\delta^{*2}$  formalism has been suggested for the type of complexes  $\text{M}_2(\mu\text{-Cl})_2\text{Cl}_4(\mu\text{-dppm})_2$  (dppm = diphenylphosphino)ethane) on the basis of the trend of the M–M distances among the three complexes with M = Ta, W, and Re.<sup>25,41</sup>

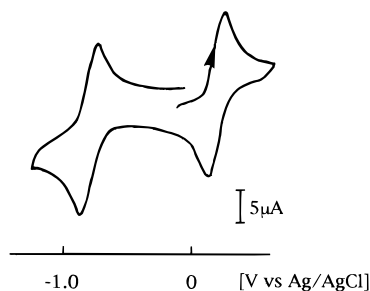
The metal–metal distances of our complexes are considerably shorter than those of the bis( $\mu$ -oxo) dimers of manganese,  $\text{Mn}^{\text{IV}}_2$ ,  $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ , and  $\text{Mn}^{\text{III}}_2$ .<sup>7</sup> It should be noted that the trend of the Re–Re distances ( $[\text{IV,IV}] < [\text{III,IV}]$ ) is in sharp contrast to the case of the two dimanganese pairs; i.e. the bispicen ( $N,N'$ -bis(2-pyridylmethyl)ethylenediamine) complexes of bis( $\mu$ -oxo)-manganese(III)manganese(IV) and -dimanganese(IV) and the pair of phen analogs. The Mn–Mn distances increase on going from (III,IV) to (IV,IV); i.e. Mn–Mn distances of the (III,IV) ( $n = 3$ ) and (IV,IV) ( $n = 4$ ) states of  $[\text{Mn}_2(\mu\text{-O})_2(\text{bispicen})_2]^{n+}$  are 2.659 and 2.672 Å, respectively, and those of  $[\text{Mn}_2(\mu\text{-O})_2(\text{phen})_4]^{n+}$  are 2.700 and 2.748 Å, respectively.<sup>18–20</sup> Since direct metal–metal bond is absent in these cases, electrostatic repulsion at higher oxidation states is considered as a main factor to control the Mn–Mn distances.

The Re–O(bridge) distances are not distinguishable among the four dirhenium complexes within uncertainties. The different Re–Re distances are thus accompanied by the different Re–O–Re angles,  $76.9(5)^\circ$  for the  $\text{Re}^{\text{III}}\text{Re}^{\text{IV}}$  complex **2** and  $75.1(3)^\circ$  for the  $\text{Re}^{\text{IV}}_2$  complex **2a'**. The Re–Re distances of the three dirhenium(IV) complexes with different nonbridging ligands, tpa, Metpa, and  $\text{Me}_2\text{tpa}$ , are not significantly different, but the distance tends to increase with increasing number of 6-methylpyridyl groups.

#### Redox Properties of the Bis( $\mu$ -oxo)dirhenium Complexes.

Figure 4 shows the cyclic voltammogram (CV) of **2** in acetonitrile. Two reversible redox waves are observed at  $-0.66$  and  $+0.14$  V vs Ag/AgCl. They are one-electron steps as confirmed by coulometric measurements, and assigned to  $\text{Re}^{\text{III}}_2/$

(41) Canich, J. A. M.; Cotton, F. A.; Daniels, L. M.; Lewis, D. B. *Inorg. Chem.* **1987**, *26*, 4046.



**Figure 4.** Cyclic voltammogram of  $[\text{Re}^{\text{III}}\text{Re}^{\text{IV}}(\mu\text{-O})_2(\text{Metpa})_2](\text{PF}_6)_3$  (**2**) in 0.1M TBAP- $\text{CH}_3\text{CN}$  at a glassy-carbon electrode with a scan rate of 50 mV/s.

**Table 3.** Electrochemical Data of  $[\text{Re}_2(\mu\text{-O})_2\text{L}_2]^{n+}$  and  $[\text{Mn}_2(\mu\text{-O})_2\text{L}_2]^{n+}$  (L = tpa, Metpa and  $\text{Me}_2\text{tpa}$ )<sup>a</sup>

complex	$E_{1/2}^b$ V vs Ag/AgCl ( $\Delta E_p^c$ )		ref
	(III,III)/(III,IV)	(III,IV)/(IV,IV)	
$[\text{Re}_2(\mu\text{-O})_2(\text{tpa})_2]^{n+}$	-0.77 (60)	0.09 (60)	e
$[\text{Re}_2(\mu\text{-O})_2(\text{Metpa})_2]^{n+}$	-0.66 (60)	0.14 (60)	e
$[\text{Re}_2(\mu\text{-O})_2(\text{Me}_2\text{tpa})_2]^{n+}$	-0.64 (60)	0.20 (60)	e
$[\text{Mn}_2(\mu\text{-O})_2(\text{tpa})_2]^{n+}$	0.29 <sup>d</sup>	1.09 <sup>d</sup>	20, 44
$[\text{Mn}_2(\mu\text{-O})_2(\text{Metpa})_2]^{n+}$	0.44 <sup>d</sup>	1.28 <sup>d</sup>	20
$[\text{Mn}_2(\mu\text{-O})_2(\text{Me}_2\text{tpa})_2]^{n+}$	0.68 <sup>d</sup>	1.45 <sup>d</sup>	30

<sup>a</sup> tpa = tris(2-pyridylmethyl)amine, Metpa = ((6-methyl-2-pyridyl)-methyl)bis(2-pyridylmethyl)amine and  $\text{Me}_2\text{tpa}$  = bis((6-methyl-2-pyridyl)methyl)(2-pyridylmethyl)amine. <sup>b</sup>  $E_{1/2} = (E_{pa} + E_{pc})/2$ , where  $E_{pa}$  and  $E_{pc}$  are anodic and cathodic peak potentials, respectively. <sup>c</sup>  $\Delta E_p = E_{pa} - E_{pc}$ . <sup>d</sup> Quasi-reversible process. <sup>e</sup> This work.

$\text{Re}^{\text{III}}\text{Re}^{\text{IV}}$  and  $\text{Re}^{\text{III}}\text{Re}^{\text{IV}}/\text{Re}^{\text{IV}}_2$  processes, respectively.<sup>42</sup> Redox potentials of the new complexes are summarized in Table 3 together with those of relevant bis( $\mu$ -oxo) dinuclear complexes. The data of **1**, **2**, and **3** in Table 3 show that the methyl substituent on the pyridyl ring has no meaningful influence to the redox potentials of the  $\text{Re}_2(\mu\text{-O})_2$  complexes. In the case of corresponding dimanganese complexes, differences in the redox potentials between the tpa and the  $\text{Me}_2\text{tpa}$  complexes are 0.39 (+0.29 and +0.678 V vs Ag/AgCl for the tpa and  $\text{Me}_2\text{tpa}$  complexes, respectively) and 0.36 V (+1.09<sup>43</sup> and +1.446 V, respectively) for the (III,III)/(III,IV) and the (III,IV)/(IV,IV) processes, respectively, in acetonitrile.<sup>30,44</sup> It should be noted that a negative shift in the redox potentials would be expected if the electronic effect of the methyl substituent were the important factor. Since the observation is in reverse direction, it is concluded that the difference in redox potentials of the series of bis( $\mu$ -oxo)dimanganese complexes are predominantly of steric origin. The steric structure of the  $\text{Mn}_2(\mu\text{-O})_2$  unit would be significantly affected by the methyl substituent, although precise comparable structural information is not available.<sup>20,29</sup> It appears that the strong Re-Re bonding interaction in the  $\text{Re}_2(\mu\text{-O})_2$  core overwhelms the steric influence of the methyl substituted tripodal ligands.

The redox potentials of the present  $\text{Re}_2(\mu\text{-O})_2$  complexes are significantly more negative as compared with those of the corresponding  $\text{Mn}_2(\mu\text{-O})_2$  complexes; the difference for the (III,III)/(III,IV) process being ca. 1.32 V for the  $\text{Me}_2\text{tpa}$  and ca. 0.85 V for the tpa complexes, respectively. Thus the higher

(42) The samples of **2** and **3** must be a mixture of geometrical isomers. The shape of redox waves, in particular, peak-to-peak separations are those of a typical single redox process, and analogous to **1** where no geometrical isomer is possible. Thus we conclude that the geometrical isomers do not give meaningful difference in the redox behavior. We neglect the possible difference arisen from the different geometrical isomers for further discussion.

(43) Converted the literature value reported with reference to SCE.

(44) Suzuki, M.; Tokura, S.; Suhara, M.; Uehara, A. *Chem. Lett.* **1988**, 477.

**Table 4.** Electronic Spectral Data of  $[\text{Re}_2(\mu\text{-O})_2\text{L}_2]^{n+}$  ( $n = 3, 4$ ) (L = tpa, Metpa and  $\text{Me}_2\text{tpa}$ )<sup>a</sup>

complex	$\lambda_{\text{max}}$ , nm ( $\epsilon$ , $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ )
$[\text{Re}_2(\mu\text{-O})_2(\text{tpa})_2]^{3+}$ ( <b>1</b> )	900 (2000), 572 (11900), 477 (8700), 372 (4400), 327 (5500)
$[\text{Re}_2(\mu\text{-O})_2(\text{tpa})_2]^{4+}$ ( <b>1a</b> )	565 (2400), 477 (9200)
$[\text{Re}_2(\mu\text{-O})_2(\text{Metpa})_2]^{3+}$ ( <b>2</b> )	928 (2100), 670 (4700), 570 (11500), 476 (8300), 370 (4600), 333 (5500)
$[\text{Re}_2(\mu\text{-O})_2(\text{Metpa})_2]^{4+}$ ( <b>2a</b> )	583 (2100), 482 (11200)
$[\text{Re}_2(\mu\text{-O})_2(\text{Me}_2\text{tpa})_2]^{3+}$ ( <b>3</b> )	951 (1100), 556 (7200)
$[\text{Re}_2(\mu\text{-O})_2(\text{Me}_2\text{tpa})_2]^{4+}$ ( <b>3a</b> )	582 (1800), 485 (8700)

<sup>a</sup> tpa = Tris(2-pyridylmethyl)amine, Metpa = ((6-methyl-2-pyridyl)-methyl)bis(2-pyridylmethyl)amine, and  $\text{Me}_2\text{tpa}$  = bis((6-methyl-2-pyridyl)methyl)(2-pyridylmethyl)amine.

oxidation states are significantly more stable for the dirhenium complexes. Stability of the mixed valence state  $\text{Re}^{\text{III}}\text{Re}^{\text{IV}}$  is represented by the comproportionation constant ( $K_{\text{com}}$ ) defined by eq 1. The  $K_{\text{com}}$  values were calculated from the separation

$$K_{\text{com}} = [\text{Re}^{\text{III}}\text{Re}^{\text{IV}}] / [\text{Re}^{\text{III}}]_2 [\text{Re}^{\text{IV}}]_2 \quad (1)$$

of the two redox potentials ( $\Delta E$ ) of the (III,III)/(III,IV) and (III,IV)/(IV,IV) processes (eq 2). The values are  $1.5 \times 10^{13}$ ,

$$K_{\text{com}} = \exp(F\Delta E/RT) \quad (2)$$

$3.3 \times 10^{13}$ , and  $1.6 \times 10^{14}$  for the tpa, Metpa, and  $\text{Me}_2\text{tpa}$  complexes, respectively. Interestingly, the  $K_c$  values are of a similar order of magnitude to that ( $1.1 \times 10^{12}$ ) for the corresponding  $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}(\mu\text{-O})_2$  complex of tpa, whose X-ray structural analysis disclosed that the mixed-valence state is a fully localized type.<sup>45</sup> Thus neither the metal-metal bond nor structural delocalization is a predominant factor to stabilize the mixed-valence state at least for the type of complexes discussed here.

Cyclic voltammograms of **1**, **2**, and **3** in acetonitrile are not affected by the addition of up to 2 equivalent of *p*-toluenesulfonic acid. For the  $\mu$ -oxo-bis( $\mu$ -acetato)dirhenium complex  $[\text{Ru}_2(\mu\text{-O})(\mu\text{-CH}_3\text{COO})_2(\text{bpy})_2(1\text{-methylimidazole})_2]^{2+}$  in acetonitrile, addition of the acid causes significant positive shift of the redox potentials of the  $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}_2$  and the  $\text{Ru}^{\text{II}}/\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$  processes.<sup>4</sup> The proton-coupled redox behavior has been accounted for by the protonation at the oxide bridge at the (II,III) and the (II,II) oxidation states. The oxide bridge of the  $\text{Re}^{\text{III}}_2$  states would not be a base strong enough to accept proton from the added acid. We can not access to the  $\text{Re}^{\text{II}}\text{Re}^{\text{III}}$  and  $\text{Re}^{\text{II}}_2$  states where the protonation at the oxide bridges may be expected.

**Spectroscopic Results.** The UV-visible absorption spectra of the  $\text{Re}_2(\mu\text{-O})_2$  complexes were obtained by controlled potential electrolysis for the (III,IV) and the (IV,IV) oxidation states.<sup>46</sup> The  $\text{Re}^{\text{III}}_2$  state was not stable in the time scale of the electrolysis. Numerical data of the absorption spectra are summarized in Table 4. A strong absorption band at ca. 480

(45) Towle, D. K.; Botsford, C. A.; Hodgson, D. J. *Inorg. Chem. Acta* **1988**, 141, 167.

(46) It was difficult to obtain fully quantitative absorption spectra of the complexes by dissolving the isolated solid, since (III,IV) and (IV,IV) are always contaminated with each other even under argon atmosphere. Thus the electrochemical technique was employed to obtain a quantitative spectrum of each oxidation state. <sup>1</sup>H NMR spectral measurements of the  $\text{Re}^{\text{IV}}_2$  complexes also suffered from the contamination of the (III,IV) species. <sup>1</sup>H NMR spectrum of the (IV,IV) state was obtained in the presence of the oxidizing reagent,  $\text{H}_2\text{O}_2$ , but this case also suffered from the contamination of some unknown decomposition products. Nevertheless, we obtained evidence for the existence of at least two geometrical isomers as typically seen in the 6H of the py ring which shows splitting.

nm with an  $\epsilon$  of ca.  $10\,000\text{ cm}^{-1}\text{ mol}^{-1}\text{ dm}^3$  is characteristic of  $\text{Re}_2(\mu\text{-O})_2$  complexes in the (IV,IV) states.<sup>12,13</sup> This strong band has been assigned to the  $\pi\text{-}\pi^*$  transition within the Re–Re bond.<sup>12</sup> Weaker absorption bands ( $\epsilon < 5000$ ) observed in the lower energy region would correspond to the transitions involving  $\delta$  and  $\delta^*$  orbitals. For the (III,IV) state, a strong band appeared in the longer wavelength region, 550–570 nm. It is possible that the weaker metal–metal bond in the (III,IV) state causes the decrease in energy gap between  $\pi$  and  $\pi^*$  levels and therefore in  $\pi\text{-}\pi^*$  transition energy. Some bands in the near-infrared region are noted for the mixed-valent (III,IV) state, and should be related to the half-filled  $\delta^*$  orbital.

**Conclusions.** The present work provides the first example of the structural studies of two neighboring oxidation states of the metal–metal bonded bis( $\mu$ -oxo) dinuclear rhenium complexes. The increase in the Re–Re distance from the (IV,IV) to (III,IV) oxidation states is consistent with the decrease in

the bond order from 3 to 2.5, suggesting the  $\sigma^2\pi^2\delta^2$  configuration for the former. Two reversible one-electron redox waves corresponding to the (III,III)/(III,IV) and the (III,IV)/(IV,IV) states have been observed for the first time for  $\text{Re}_2(\mu\text{-O})_2$  complexes. The electronic spectra of the  $\text{Re}^{\text{III}}\text{Re}^{\text{IV}}$  as well as the  $\text{Re}^{\text{IV}}_2$  states have been measured.

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**Supporting Information Available:** Tables of atomic coordinates and  $B_{\text{eq}}$  values (Tables S1–S3), anisotropic thermal parameters (Tables S4–S6), and bond lengths and bond angles (Tables S7–S9), of the three complexes, **2**, **2a'**, and **3a'**, and a figure showing electronic spectra of the Metpa complex both in  $\text{Re}^{\text{III}}\text{Re}^{\text{IV}}$  and  $\text{Re}^{\text{IV}}_2$  states (15 pages). Ordering information is given on any current masthead page.

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