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# Synthesis and Molecular Structure of Mixed-valence Compounds of Rhenium Obtained by Di-iodine Oxidation of Rhenium(I) Carbonyl Complexes; X-Ray Crystal Structure of $\text{Re}_3\text{I}_6(\text{CO})_6$

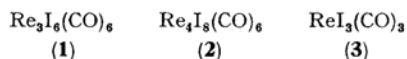
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**Summary** Mixed-valence iodide-bridged compounds of rhenium have been obtained by the di-iodine oxidation of rhenium(I) carbonyl complexes; the X-ray crystal and molecular structure of  $\text{Re}_3\text{I}_6(\text{CO})_6$ , a  $\text{Re}^{\text{I}}\text{-Re}^{\text{IV}}$  complex of  $S_6$  symmetry, is presented.

MIXED-VALENCE compounds of Class I<sup>1</sup> have usually been obtained by oxygen or halogen oxidation of metals at elevated temperatures. To the best of our knowledge, no mixed-valence compounds of Class I are known which have been obtained by halogen oxidation of metal carbonyl compounds and, moreover, no such rhenium mixed-valence compounds have been reported, although technetium<sup>2</sup> and rhenium<sup>3</sup> complexes, which have been assumed to belong to Class II or III, are known.

We report herein that new rhenium mixed-valence complexes can be obtained by the di-iodine oxidation of rhenium(I) carbonyl complexes. A solution of  $\text{Re}_2\text{I}_2(\text{CO})_8$ <sup>4</sup> (ca.  $10^{-2}$  M) in n-heptane was refluxed for several days with  $\text{I}_2$  (1 mol. equiv.). The black, microcrystalline solid which was obtained (54% yield) was recrystallized from toluene and shown to be  $\text{Re}_3\text{I}_6(\text{CO})_6$ , (1), by X-ray diffraction methods.

**Crystal Data:**  $\text{C}_6\text{I}_6\text{O}_6\text{Re}_3$ ,  $M = 1488$ , trigonal,  $R\bar{3}$  space group,  $a = 6.915(2)$ ,  $c = 36.939(3)$  Å,  $U = 1529.7$  Å<sup>3</sup>,  $D_c = 4.844$  g cm<sup>-3</sup>,  $Z = 3$ ,  $\mu(\text{Mo-K}\alpha, 0.71069 \text{ Å}) = 265.2$  cm<sup>-1</sup>. The intensity data were measured with a Philips PW1100 diffractometer and corrected for absorption.†



The structure was solved by standard Patterson and Fourier methods<sup>5</sup> and was initially solved to an  $R$  factor of 0.16. Twinning of the crystal was suggested by the presence of spurious peaks on the electron-density map and by systematic disagreements between  $F_0$  and  $F_c$  of two groups of reflections, namely those having  $hkl$  with  $l = 3n$  or  $l \neq 3n$ ; the twinning operator is the (100) mirror plane. After correction of the data the final  $R$  factor by least-squares methods was refined to 0.068 for 490 observed reflections.

Compound (1) is a trinuclear iodide-bridged  $S_6$  complex (idealized  $D_{3d}$  symmetry), with the rhenium atoms on the threefold axis of symmetry; it is a Class I mixed-valence compound because the formal oxidation states of +I and +IV can be assigned to the terminal and to the inter-

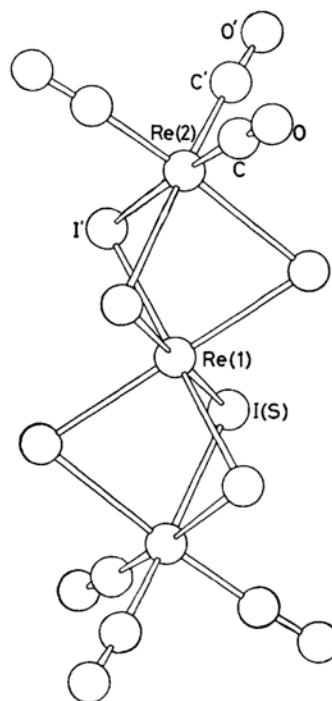


FIGURE. ORTEP view of  $\text{Re}_3\text{I}_6(\text{CO})_6$  (1).<sup>6</sup> Relevant bond distances, contacts, and angles (e.s.d. in parentheses) are:  $\text{Re}(1)\text{-I}$ , 2.714(2);  $\text{Re}(2)\text{-I}$ , 2.797(2);  $\text{Re}(2)\text{-C}$ , 1.94(4);  $\text{C-O}$ , 1.18(5) Å;  $\text{Re}(1)\text{-I-Re}(2)$ , 75.6(1);  $\text{I-Re}(1)\text{-I}(s)$ , 92.0(1);  $\text{C-Re}(2)\text{-C'}$ , 90(2);  $\text{Re}(2)\text{-C-O}$ , 175(4)°;  $\text{Re}(1)\dots\text{Re}(2)$ , 3.379(3) Å. The atoms marked ' and (S) are related to those of the asymmetric unit by the  $C_3$  and  $S_6$  symmetry operations.

mediate rhenium atoms, respectively. Furthermore, the two non-equivalent hexaco-ordinate rhenium atoms have different sets of donor atoms. In agreement with this, the magnetic susceptibility of (1) at 18 °C corresponds to  $\mu_{\text{eff}}$  3.59 BM for the whole trinuclear molecule, consistent with the value expected<sup>7</sup> for a magnetically dilute hexaco-ordinate  $d^3 \text{Re}^{4+}$  cation.

By the reaction of the tetrahydrofuran adduct  $\text{Re}_2\text{I}_2(\text{CO})_6\text{(THF)}_2$ <sup>8</sup> with di-iodine in n-heptane at room temperature a small yield of the black tetranuclear  $\text{Re}_4\text{I}_8(\text{CO})_6$  (2) was also obtained. Compound (2) is also a mixed-valence compound, as shown by an X-ray diffraction study of a single crystal.<sup>9</sup> Its molecular structure consists of a central

† The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

$\text{Re}_2\text{I}_8^{10}$  unit iodide-bridged to two hexaco-ordinate  $\text{Re}(\text{CO})_3$  groups. The two central rhenium atoms are best described as being formally in a +III oxidation state; consistent with this, they are multiply bonded<sup>11</sup> at a distance of 2.279(1) Å.

We believe that an important role in the formation of compounds (1) and (2) is played by  $\text{ReI}_3(\text{CO})_3$  (3), which is suggested to have a *fac* geometry and was isolated from the room temperature reaction of  $\text{Re}_2\text{I}_2(\text{CO})_6(\text{THF})_2$  with diiodine in n-heptane as a hydrocarbon soluble, deep blue solid [ $\nu_{\text{CO}}$  (n-heptane) 2012s and 1982s  $\text{cm}^{-1}$ ] which sublimed (ca. 75 °C/10<sup>-2</sup> mmHg), and the magnetic susceptibility ( $\chi_{\text{M}}^{\text{corr}} + 850 \times 10^{-6}$  cgsu, diamagnetic correction  $- 164 \times 10^{-6}$  cgsu) of which was substantially independent of temperature in the range 80–298 K and had a linear  $\mu$  vs.  $T^{\frac{1}{2}}$  plot, characteristic of a 5d  $t_{2g}^4$  configuration.<sup>7,12–14</sup>

Thus, mixed-valence complexes are obtained by the diiodine oxidation of low valent carbonyl complexes. An alternative route to mixed-valence compounds is the reduction, by co-ordinated CO, of metal halides of relatively high oxidation states, as in the case of the already reported preparation of  $\text{Au}_4\text{Cl}_8^{15}$  from  $\text{AuCl}_3$  and  $\text{AuCl}(\text{CO})$ .

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