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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 $\text{Re}_3\text{I}_6(\text{CO})_6$

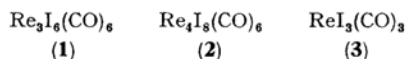
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Summary Mixed-valence iodide-bridged compounds of rhenium have been obtained by the di-iodine oxidation of rhenium(I) carbonyl complexes; the X-ray crystal and molecular structure of $\text{Re}_3\text{I}_6(\text{CO})_6$, a $\text{Re}^{\text{I}}\text{-Re}^{\text{IV}}$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

MIXED-VALENCE compounds of Class I¹ 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 technetium² and rhenium³ 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 $\text{Re}_2\text{I}_2(\text{CO})_8$ ⁴ (ca. 10^{-2} M) in n-heptane was refluxed for several days with 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, $U = 1529.7$ Å³, $D_c = 4.844$ g cm⁻³, $Z = 3$, $\mu(\text{Mo-K}\alpha, 0.71069 \text{ Å}) = 265.2$ cm⁻¹. The intensity data were measured with a Philips PW1100 diffractometer and corrected for absorption.†



The structure was solved by standard Patterson and Fourier methods⁵ 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-

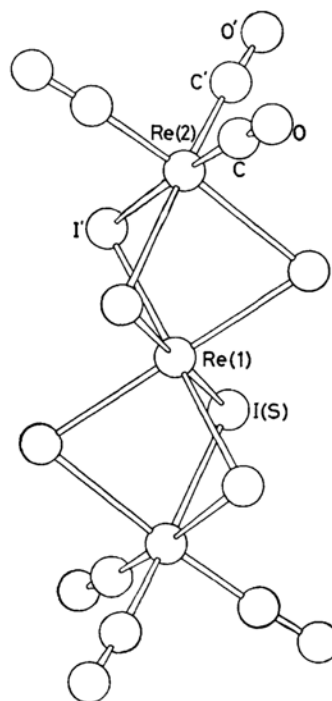


FIGURE. ORTEP view of $\text{Re}_3\text{I}_6(\text{CO})_6$ (1).⁶ Relevant bond distances, contacts, and angles (e.s.d. in parentheses) are: $\text{Re}(1)\text{-I}$, 2.714(2); $\text{Re}(2)\text{-I}$, 2.797(2); $\text{Re}(2)\text{-C}$, 1.94(4); C-O , 1.18(5) Å; $\text{Re}(1)\text{-I-Re}(2)$, 75.6(1); $\text{I-Re}(1)\text{-I}(S)$, 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 μ_{eff} 3.59 BM for the whole trinuclear molecule, consistent with the value expected⁷ for a magnetically dilute hexaco-ordinate $d^3 \text{Re}^{4+}$ cation.

By the reaction of the tetrahydrofuran adduct $\text{Re}_2\text{I}_2(\text{CO})_6\text{(THF)}_2$ ⁸ 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.⁹ 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 bonded¹¹ 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 [ν_{CO} (n-heptane) 2012s and 1982s cm^{-1}] which sublimed (ca. 75 °C/10⁻² 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 μ vs. $T^{\frac{1}{2}}$ plot, characteristic of a $5d^4 t_{2g}^4$ configuration.^{7,12–14}

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 AuCl_3 and $\text{AuCl}(\text{CO})$.

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