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 $Re_3I_6(CO)_6$

By FAUSTO CALDERAZZO, FABIO MARCHETTI, RINALDO POLI, and DARIO VITALI
(*Istituto Chimica Generale, University of Pisa, Via Risorgimento* 35, 56100 *Pisa, Italy*)

and PIER FRANCESCO ZANAZZI
(*Istituto di Mineralogia, University of Perugia, Piazza Università,* 06100 *Perugia, Italy*)

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 $Re_3I_6(CO)_6$, a Re^{I}–Re^{IV} complex of S_6 symmetry, is presented.

MIXED-VALENCE compounds of Class I[1] 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[2] and rhenium[3] 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 $Re_2I_2(CO)_8$[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 $Re_3I_6(CO)_6$, (**1**), by *X*-ray diffraction methods.

Crystal Data: $C_6I_6O_6Re_3$, $M = 1488$, trigonal, $R\bar{3}$ space group, $a = 6{\cdot}915(2)$, $c = 36{\cdot}939(3)$ Å, $U = 1529{\cdot}7$ Å^3, $D_c = 4{\cdot}844$ g cm^{-3}, $Z = 3$, μ(Mo-K_α, 0·71069 Å) = 265·2 cm^{-1}. The intensity data were measured with a Philips PW1100 diffractometer and corrected for absorption.†

$Re_3I_6(CO)_6$	$Re_4I_8(CO)_6$	$ReI_3(CO)_3$
(**1**)	(**2**)	(**3**)

The structure was solved by standard Patterson and Fourier methods[5] 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 *hkil* 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 intermediate 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 expected[7] for a magnetically dilute hexaco-ordinate d^3 Re^{4+} cation.

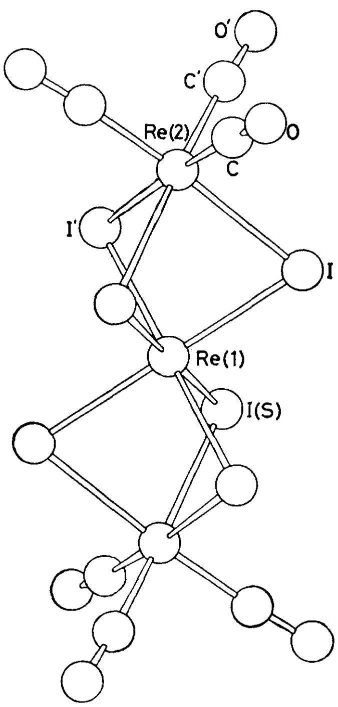

FIGURE. ORTEP view of $Re_3I_6(CO)_6$ (**1**).[6] Relevant bond distances, contacts, and angles (e.s.d. in parentheses) are: Re(1)-I, 2·714(2); Re(2)-I, 2·797(2); Re(2)-C, 1·94(4); C-O, 1·18(5) Å; Re(1)-I-Re(2), 75·6(1); I-Re(1)-I(s), 92·0(1); C-Re(2)-C′, 90(2); Re(2)-C-O, 175(4)°; Re(1)...Re(2), 3·379(3) Å. The atoms marked ′ and (S) are related to those of the asymmetric unit by the C_3 and S_6 symmetry operations.

By the reaction of the tetrahydrofuran adduct $Re_2I_2(CO)_6(THF)_2$[8] with di-iodine in n-heptane at room temperature a small yield of the black tetranuclear $Re_4I_8(CO)_6$ (**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.

Re_2I_8[10] unit iodide-bridged to two hexaco-ordinate $Re(CO)_3$ groups. The two central rhenium atoms are best described as being formally in a +III oxidation state; consistent with this, they are multiply bonded[11] 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 $ReI_3(CO)_3$ (**3**), which is suggested to have a *fac* geometry and was isolated from the room temperature reaction of $Re_2I_2(CO)_6(THF)_2$ with di-iodine 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 (χ_M^{corr} + 850 × 10^{-6} cgsu, diamagnetic correction − 164 × 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 t_{2g}^4 configuration.[7,12–14]

Thus, mixed-valence complexes are obtained by the di-iodine 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 Au_4Cl_8[15] from $AuCl_3$ and AuCl(CO).

We thank the National Research Council (C.N.R., Rome) and the C.N.R. Programma Finalizzato for support of this work, and Prof. L. Sacconi for providing diffractometry facilities.

(*Received*, 29*th April* 1981; *Com.* 511.)

[1] M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.

[2] F. A. Cotton and L. W. Shive, *Inorg. Chem.*, 1975, **14**, 2032.

[3] J. R. Ebner and R. A. Walton, *Inorg. Chem.*, 1975, **14**, 1987.

[4] E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1959, 1501.

[5] G. M. Sheldrick, Programme for Crystal Structure Determination, SHELX, University of Cambridge, England, 1976.

[6] C. K. Johnson, 'ORTEP,' Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.

[7] B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, 1964, **6**, 37.

[8] F. Calderazzo, D. Vitali, R. Poli, J. L. Atwood, R. D. Rogers, J. M. Cummings, and I. Bernal, *J. Chem. Soc., Dalton. Trans.*, 1981, 1004.

[9] F. Calderazzo, F. Marchetti, R. Poli, D. Vitali, and P. F. Zanazzi, to be published.

[10] H. D. Glicksman and R. A. Walton, *Inorg. Chem.*, 1978, **11**, 3197; W. Preetz and L. Rudzik, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 150.

[11] F. A. Cotton, *Inorg. Chem.*, 1965, **4**, 334.

[12] H. P. Gunz and G. J. Leigh, *J. Chem. Soc., A*, 1971, 2229.

[13] M. Freni, P. Romiti, V. Valenti, and P. Fantucci, *J. Inorg. Nucl. Chem.*, 1972, **34**, 1195.

[14] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' J. Wiley, New York, 4th Edn, 1980, pp. 650—652.

[15] D. Belli Dell'Amico, F. Calderazzo, F. Marchetti, S. Merlino, and G. Perego, *J. Chem. Soc., Chem. Commun.*, 1977, 31.