Synthesis and Crystal and Molecular Structures of Mixed-valence Tetranuclear, $[Re_4I_8(CO)_6]$, and Trinuclear, $[Re_3I_6(CO)_6]$, Compounds of Rhenium† obtained by Di-iodine Oxidation of Rhenium(I) Carbonyl Complexes

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Di-iodine oxidation of $[Re_2I_2(CO)_6(thf)_2]$ (thf = tetrahydrofuran) at room temperature in heptane as solvent gave $[ReI_3(CO)_3]$ (1) and the tetranuclear $[Re_4I_8(CO)_6]$ (2). A mononuclear molecular structure of C_{3v} symmetry is suggested for (1), on the basis of spectroscopic and magnetic susceptibilty measurements. The reaction of $[Re_2I_2(CO)_8]$ with di-iodine at the reflux temperature of heptane gave the trinuclear complex $[Re_3I_6(CO)_6]$ (3). The crystal and molecular structures of both (2) and (3) have been solved by *X*-ray diffraction methods. Compound (2) is monoclinic, space group $C2/c$, $Z = 4$, with unit-cell dimensions $a = 22.316(4)$, $b = 8.679(3)$, $c = 12.705(3)$ Å, $\beta = 96.02(2)°$; $R = 0.059$ for 1 700 observed reflections. It belongs to the family of $[Re_2X_8]^{2-}$ complexes, with bridging iodine to two terminal $Re(CO)_3$ groupings. Compound (3) is trigonal, space group $R\bar{3}$, $Z = 3$, with dimensions $a = 6.915(2)$ and $c = 36.939(3)$ Å; $R = 0.068$ for 490 observed reflections. It comprises a ReI_6 central core iodide-bridged to two terminal $Re(CO)_3$ groupings in a molecular geometry of idealized D_{3d} symmetry.

DI-IODINE oxidation is the method typically employed for the oxidation of metal carbonyls to the corresponding metal iodides, accompanied by the quantitative evolution of carbon monoxide.[1] This method is usually applicable to the carbonyl derivative of 3*d* transition metals, in pyridine as solvent. Di-iodine oxidation of 4*d* and 5*d* late transition-metal derivatives is sometimes limited to the formation of iodo-carbonyl derivatives, even in pyridine, *e.g.* $[\{RuI_2(CO)_2\}_n]$ was obtained[2] from $[Ru(CO)_5]$ or $[Ru_3(CO)_{12}]$. On the other hand, incomplete carbon monoxide displacement can occur even with 3*d* elements in solvents different from pyridine, as in the preparation, for example, of $[FeI_2(CO)_4]$ from $[Fe(CO)_5]$ and I_2 in diethyl ether.[3]

This paper reports a new type of reaction exemplified by the preparation of mixed-valence complexes of rhenium, as obtained by di-iodine oxidation of a rhenium(I) carbonyl compound. A preliminary communication of these results has already appeared.[4]

EXPERIMENTAL

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified nitrogen or argon. Solvents were dried by conventional methods prior to use. The i.r. spectra were measured with a Perkin-Elmer model 283 instrument equipped with a grating and each spectrum was calibrated with CO and water vapour; the wavenumber values are believed to be accurate to ± 1 cm^{-1} for solution spectra. The magnetic susceptibilities were measured with a magnetic balance by the Faraday method, using $CuSO_4 \cdot 5H_2O$ as a calibrant. The compound $[Re_2I_2(CO)_6(thf)_2]$, thf = tetrahydrofuran, was prepared as previously described.[5a]

Preparations.—$[ReI_3(CO)_3]$ (1) *and* $[Re_4I_8(CO)_6]$ (2). The dimeric iodo-derivative $[Re_2I_2(CO)_6(thf)_2]$ (2.2 g, 2.3 mmol) in heptane (50 cm^3) was treated with di-iodine (2.32 g, 9.1 mmol) for about 2 d at 35—40 °C periodically reducing the pressure in order to remove carbon monoxide and tetrahydrofuran evolved in the reaction. The loss of solvent and di-iodine was compensated by their addition to the reacting mixture. At the end of the reaction, as monitored by i.r. spectroscopy, the solvent was evaporated under reduced pressure and the resulting solid residue was sublimed at about 70 °C (*ca.* 5×10^{-2} mmHg).‡ Deep blue compound (1) was obtained, 0.25 g (8.2%).

In another preparation of $[ReI_3(CO)_3]$, the compound was recovered by evaporation to dryness of the reaction mixture and by recrystallization from heptane between room temperature and 5 °C. After standing for about 1 month at room temperature the mother-liquor from the recrystallization yielded crystals of $[Re_4I_8(CO)_6]$, which were used for the *X*-ray structural determination.

$[Re_3I_6(CO)_6]$ (3). The dimeric octacarbonyl $[Re_2I_2(CO)_8]$[5b] (1.11 g, 1.31 mmol) in heptane (150 cm^3) was treated with di-iodine (0.35 g, 1.39 mmol) at reflux for about 10 d. The black microcrystalline precipitate obtained was filtered off and washed several times with hot heptane to remove the unreacted rhenium(I) complex. The solid was finally dried *in vacuo* (53% yield). The compound was crystallized from hot toluene to obtain the crystals used for the *X*-ray determination. It is only slightly soluble at room temperature in common hydrocarbon or halogenated solvents (Found: C, 4.4. Calc. for $C_6I_6O_6Re_3$: C, 4.8%). The i.r. spectrum (Nujol mull) has bands at 2 048s, 1 946s, 1 919m, 615m, 595w, 485w, and 470m cm^{-1}. The magnetic susceptibility at 298 K was χ_M corr. $= 5\,520 \times 10^{-6}$ c.g.s. units, diamagnetic correction $= -326 \times 10^{-6}$ c.g.s. units, corresponding to a magnetic moment $\mu_{eff.} = 3.59$ B.M. The compound dissolved in tetrahydrofuran and the resulting brown solution showed bands at 2 027m, 1 914s, and 1 895s cm^{-1}, typical[5a] of $[ReI(CO)_3(thf)_2]$ in the same solvent.

X-Ray Data Collections, Structure Determinations, and Refinements.—$[Re_4I_8(CO)_6]$. The crystal used for the *X*-ray diffractometric study was sealed under nitrogen in a

† 1,1,1,3,3,3-Hexacarbonyl-1,2;1,4;1,4;2,3;2,3;3,4-hexa-μ-iodo-2,4-di-iodo-*cyclo*-tetrarhenium(3*Re*²—*Re*⁴) and 1,1,1,3,3,3-hexacarbonyl-1,2;1,2;1,2;2,3;2,3;2,3-hexa-μ-iodo-trirhenium.

‡ Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa, 1 B.M. ≈ 9.27×10^{-24} J T^{-1}.

Lindemann capillary. Preliminary photographs showed monoclinic symmetry; the systematic absences (hkl absent for $h + k \neq 2n$, $h0l$ absent for $l \neq 2n$) led to Cc or $C2/c$ as possible space groups. The structure analysis was carried out in $C2/c$. The crystal was mounted on a Philips PW1100 automatic diffractometer equipped with graphite monochromatized Mo-K_α radiation. The cell dimensions obtained by least-squares refinement of the setting angles of 25 reflections are reported in Table 1, together with other crystal and refinement data. Integrated intensities were collected in the θ—2θ scanning mode [scan width 1.2° (θ), scan speed 0.04° s^{-1}] yielding 2 061 unique reflections, 361 of which had $I \leqslant 3\sigma(I)$. The intensity of three reflections monitored every 180 min did not show any significant variations. An absorption correction according to North *et al.*[6] was applied.

TABLE 1

Crystal data and summary of intensity data and structure refinement

Molecular formula	$[Re_4I_8(CO)_6]$ (2)	$[Re_3I_6(CO)_6]$ (3)
Crystal size (mm)	0.66 × 0.15 × 0.03	0.27 × 0.24 × 0.03
Crystal class	Monoclinic	Trigonal
Space group	$C2/c$	$R\bar{3}$
a/Å	22.316(4)	6.915(2)
b/Å	8.679(3)	
c/Å	12.705(3)	36.939(3)
β/°	96.02(2)	
U/Å^3	2 447.1	1 529.7
Z	4	3
D_c/g cm^{-3}	5.23	4.84
$\mu_{calc.}$/cm^{-1}	294.6	265.2
Scan width	1.2	1.6
Scan speed (s^{-1})	0.04	0.06
Measured reflections	2 061	909
Range 2 θ/°	6—50	4—60
Reflections used in the refinement	1 700	490
No. of variables	79	23
R	0.059	0.068
R'	0.062 [a]	0.065 [b]

In each case Mo-K_α radiation (λ = 0.710 69 Å) and the θ—2θ scan mode were employed.
[a] $w = 1/[\sigma^2(F_o) + 0.0023F_o^2]$. [b] $w = 1/[\sigma^2(F_o) + 0.0004\,F_o^2]$.

The structure was solved by the automatic centrosymmetric routine of SHELX,[7] by which an E map yields the positions of the rhenium and iodine atoms. The remaining carbon and oxygen atoms were found by the heavy-atom method. Full-matrix least-squares refinement led to convergence with $R = 0.059$ for 1 700 observed reflections and 79 parameters. (The thermal parameters of the rhenium and iodine atoms were refined anisotropically.) The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$ with the final weighting scheme $w = 1/[\sigma^2(F_o) + 0.0023\,F_o^2]$. Scattering factors and corrections for anomalous dispersion for Re and I were taken from ref. 8, while those for C and O were taken from the SHELX program.

$[Re_3I_6(CO)_6]$. The crystals of this compound were thin hexagonal plates belonging to the trigonal system, Laue class $\bar{3}$. The possible space groups (systematic extinctions: $hkil$ present for $-h + k + l = 3n$) are $R3$ and $R\bar{3}$. The latter was chosen for structure determination also on the basis of the intensity statistics and it was found to be correct. The unit-cell parameters were obtained with one of the standard programs of the Philips PW1100 automatic diffractometer. With this program (LAT) the rows ($h00$), ($0k0$), and ($00l$) were investigated by scanning the four most intense reflections in the positive and in the negative region. The centres of gravity of the eight profiles were used in the least-squares refinement yielding the cell constants reported in Table 1, together with other crystal and refinement data. Integrated intensities were collected by the same method as for the tetranuclear compound: scan width 1.6° (θ), scan speed 0.06 s^{-1}. The intensity data were corrected for Lorentz and polarization factors. A numerical absorption correction was applied, the transmission factors being in the range 0.434—0.045.

TABLE 2

Fractional co-ordinates of $[Re_4I_8(CO)_6]$

Atom	X/a	Y/b	Z/c
Re(1)	0.338 80(4)	0.659 67(10)	0.245 69(7)
Re(2)	0.508 04(4)	0.862 73(9)	0.162 91(7)
I(1)	0.402 04(7)	0.744 17(17)	0.074 79(12)
I(2)	0.447 36(7)	0.576 13(16)	0.362 29(12)
I(3)	0.374 50(7)	0.951 02(16)	0.326 67(13)
I(4)	0.474 93(8)	1.144 53(17)	0.104 11(14)
C(1)	0.295(1)	0.613(3)	0.362(2)
C(2)	0.266(1)	0.715(2)	0.164(2)
C(3)	0.329(1)	0.455(3)	0.191(2)
O(1)	0.268(1)	0.586(2)	0.431(2)
O(2)	0.224(1)	0.754(2)	0.115(2)
O(3)	0.323(1)	0.330(2)	0.163(2)

The structure was solved by the Patterson method and by successive Fourier syntheses and refined by a least-squares method. The convergence stopped at $R = 0.16$. At this stage some ghost maxima similar to echoes of the actual structure appeared on the electron-density map at unreasonable positions. Examination of the observed and calculated structure factors showed that all reflections with $l \neq 3n$ were underestimated, while those with $l = 3n$ appeared systematically overestimated. This led to the conclusion that the crystal used for data collection was twinned. The symmetry of the molecular model, $\bar{3}m$, is greater than that of the rhombohedral lattice, $\bar{3}$. According to Holser,[9] the extra elements of symmetry are possible twin operations. On this basis, the twin operator was identified as the (100) mirror plane. Taking into account the geometry of the reciprocal lattice, reflections from individuals A and B are not superimposable on the layers $l = 3n + 1$ and $3n + 2$. On the contrary, the reciprocal lattice layers with $l = 3n$ have $hkil$ reflections of the A component exactly superimposed on the $hikl$ reflections of the B component. Thus, we had two different sets of data: reflections with $l \neq 3n$ ascribable separately to the A and B individuals, and reflections with $l \neq 3n$ overlapped by twinning. Several cycles of refinement were then carried out with the first set of reflections, lowering R to 0.07. At this stage the volume

TABLE 3

Fractional co-ordinates of $[Re_3I_6(CO)_6]$

Atom	X/a	Y/b	Z/c
Re(1)	0.0	0.0	0.0
Re(2)	0.0	0.0	0.091 47(8)
I	0.002 6(3)	0.316 1(3)	0.043 91(8)
C	0.233(5)	0.227(5)	0.122(1)
O	0.384(5)	0.370(5)	0.138(1)

ratio between the components A and B was computed through the scale factor between observed and calculated structure factors of about 70 reflections of the type $hh\bar{2}hl$. This ratio (A : B = 1.43 : 1) allowed the composite intensities of the overlapped reflections to be subdivided into the intensities of A and B by solving the system below

$$I_{hkl} = I_{hkl}^{A} + I_{khl}^{B}$$
$$I_{khl} = I_{khl}^{A} + I_{hkl}^{B}$$

where I is the observed intensity of the twinned crystal and I^A and I^B are the intensities of the two superimposed reflections. In this way a homogeneous set of data as from a single crystal was obtained and used in the final cycles of refinement. The R factor converged to 0.068, for 490 observed reflections [$I \geqslant 3\sigma(I)$] and 23 parameters. (The thermal parameters of Re and I were refined anisotropically.) The weighting scheme was $w = 1/[\sigma^2(F_o) + 0.0004 F_o^2]$. The atomic scattering factors and anomalous dispersion corrections were the same as for compound A.

Fractional atomic co-ordinates for (2) and (3) are listed in Tables 2 and 3 respectively. Thermal parameters, observed structure amplitudes, and calculated structure factors are available as Supplementary Publication No. SUP 23307 (17 pp.).*

RESULTS AND DISCUSSION

Mixed-valence compounds which usually have interesting electric and magnetic properties [10] have become accessible by several preparative procedures. Class I [10] complexes have usually been synthesized by oxygen or halogen oxidation of metals at elevated temperatures. On the other hand, dichlorine or dibromine oxidation of iron metal [11] in a solvent led to the formation of $[Fe(solvent)_6]^{2+}[FeX_4]^{2-}$ regarded [10] as Class I complexes, with no shared ligands. On the other hand, electrochemical, dihalogen, or silver(I) oxidation of iron carbonyl complexes [12] led to one-electron metal–metal bonded compounds regarded as Class II or III mixed-valence species. Finally, di-iodine oxidation of nickel and palladium stacked systems considerably increased the electrical conductivity [13] in the solid state.

With the concept [14] in mind that metal carbonyls can be regarded as easily accessible compounds exhibiting, under much milder conditions, a reactivity similar to that of isolated metal atoms, we have been able to prepare mixed-valence complexes of rhenium by di-iodine oxidation of carbonyl complexes of rhenium(I). We believe that an important intermediate in these reactions is the tri-iodo-derivative $[ReI_3(CO)_3]$ obtained according to equation (i).

Compound (1) was isolated and characterized by its i.r. spectrum in the carbonyl stretching region and by magnetic susceptibility measurements. It is a deep blue solid, whose i.r. spectrum [ν(CO) at 2 012s and 1 982s cm^{-1} in n-heptane] is consistent with a *fac* geometry for which two i.r.-active carbonyl absorptions ($A_1 + E$) are expected. The spectrum is to be compared with that reported for $[ReF_3(CO)_3]$ [15] [ν_{CO} 2 120m, 2 070s, and 2 040(sh) cm^{-1}] and for $[ReI_3(CO)_3]$ [2-16] [ν(CO) 2 005s and 1 886s cm^{-1}]. The shift to lower wavenumber for our compound (1) and for the anionic one is understandable in terms of increased electron density at the metal. It is, however, to be noted that the existence of the trifluoro-complex of rhenium(III) was later questioned,[17] the alternative formulation presented being $[Re(CO)_6]^+[ReF_6]^-$.

The initially blue solution of $[ReI_3(CO)_3]$ in tetrahydrofuran rapidly loses its colour, while the i.r. spectrum changes finally to a spectrum similar but not identical to that of $[ReI(CO)_3(thf)_2]$. This observation, together with the fact that di-iodine does not appear to be liberated during this treatment, suggests that thf is initially added to the 16-electron species $[ReI_3(CO)_3]$ to give the seven co-ordinate $[ReI_3(CO)_3(thf)]$, which then undergoes a rearrangement to $[Re(I_3)(CO)_3(thf)_2]$ containing the tri-iodo-ligand I_3. A few cases of co-ordinated I_3 have been reported.[18]

Compound (1) is soluble in hydrocarbon solvents and can be sublimed with some decomposition *in vacuo*: this is in agreement with its monomeric formulation. Indirect confirmation was also provided by the magnetic measurements: the magnetic susceptibility is substantially independent of temperature in the range 80—298 K, which is typical of $5d\ t_{2g}^4$ configurations.[19,20] A least-squares linear plot obeyed the expression $\mu = (0.081 \pm 0.0003)\sqrt{T} + (0.023 \pm 0.003)$.

Another product of the di-iodine oxidation of the rhenium(I) complex is the tetranuclear $[Re_4I_8(CO)_6]$, see equation (ii). Its crystal and molecular structure has been established by X-ray diffraction methods, see Figure 1. The compound can be regarded as a mixed-valence derivative of rhenium(III) and rhenium(I), the two central rhenium(III) atoms being bonded by a multiple metal–metal bond. The interatomic distances and angles are in Table 4. The tetranuclear compound belongs to the class of $[Re_2X_8]^{2-}$ complexes, which have been studied extensively, especially by Cotton and Haas.[21] The co-ordination around each rhenium atom can be visualized as that of a distorted square pyramid with three bridging and one terminal iodine

$$[Re_2I_2(CO)_6(thf)_2] + 2\ I_2 \longrightarrow \underset{(1)}{2\ [ReI_3(CO)_3]} + 2\ thf \quad (i)$$

$$2[Re_2I_2(CO)_6(thf)_2] + 2\ I_2 \longrightarrow \underset{(2)}{[Re_4I_8(CO)_6]} + 6\ CO + 4\ thf \quad (ii)$$

$$3[Re_2I_2(CO)_8] + 3\ I_2 \longrightarrow \underset{(3)}{2[Re_3I_6(CO)_6]} + 12\ CO \quad (iii)$$

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

forming the base of the pyramid. As is clearly shown in Figure 2, the two square pyramids are joined together through a rhenium–rhenium bond in a non-eclipsed configuration. Both the non-eclipsed configuration and

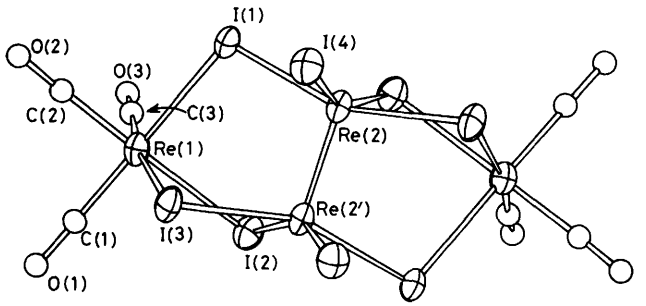

FIGURE 1 ORTEP view of $[Re_4I_8(CO)_6]$ with the atom-numbering system used

the observed Re–Re bond length of 2.279(1) Å are in agreement with the available bonding description.[21] In an eclipsed configuration four metal–metal bonds will be formed by overlapping of the appropriate four atomic orbitals. In a staggered configuration, on the other hand, the overlapping of the d_{xy} atomic orbitals will be negligible and a triple metal–metal bond will result for a d^4 cation such as rhenium(III). In agreement with this, the present bond distance is intermediate between that of the doubly bonded Re_3Cl_9 [2.489(6) Å][22] and those of

TABLE 4

Bond distances (Å) and angles (°) for $[Re_4I_8(CO)_6]$*

Re(1)–I(1)	2.808(2)	Re(2)–I(3')	2.721(2)
Re(1)–I(2)	2.799(2)	Re(1)–C(1)	1.89(3)
Re(1)–I(3)	2.813(2)	Re(1)–C(2)	1.90(2)
Re(2)–Re(2')	2.279(1)	Re(1)–C(3)	1.91(3)
Re(2)–I(1)	2.712(2)	C(1)–O(1)	1.14(4)
Re(2)–I(2')	2.711(2)	C(2)–O(2)	1.12(3)
Re(2)–I(4)	2.640(2)	C(3)–O(3)	1.15(3)

I(1)–Re(1)–I(2)	89.98(6)
I(1)–Re(1)–I(3)	84.38(5)
I(2)–Re(1)–I(3)	80.97(5)
I(1)–Re(1)–C(1)	177.2(9)
I(1)–Re(1)–C(2)	89.2(8)
I(1)–Re(1)–C(3)	90(1)
I(2)–Re(1)–C(1)	91.0(9)
I(2)–Re(1)–C(2)	179(1)
I(2)–Re(1)–C(3)	90.6(9)
I(3)–Re(1)–C(1)	93.2(8)
I(3)–Re(1)–C(2)	99.7(6)
I(3)–Re(1)–C(3)	170.1(9)
I(1)–Re(2)–Re(2')	100.46(5)
I(1)–Re(2)–I(2')	85.31(5)
I(1)–Re(2)–I(3')	157.11(7)
I(1)–Re(2)–I(4)	91.64(5)
I(2)–Re(2')–Re(2)	102.23(5)
I(3)–Re(2')–Re(2)	101.64(5)
I(4)–Re(2)–Re(2')	101.94(6)
I(2)–Re(2')–I(3)	84.28(5)
I(4)–Re(2)–I(2')	155.79(8)
I(4)–Re(2)–I(3')	89.57(5)
C(2)–Re(1)–C(1)	90(1)
C(3)–Re(1)–C(1)	92(1)
C(3)–Re(1)–C(2)	89(1)
Re(1)–C(1)–O(1)	179(3)
Re(1)–C(2)–O(2)	177(2)
Re(1)–C(3)–O(3)	177(3)

* Primed atoms are related to unprimed ones by the symmetry operation $1 - x, y, \frac{1}{2} - z$.

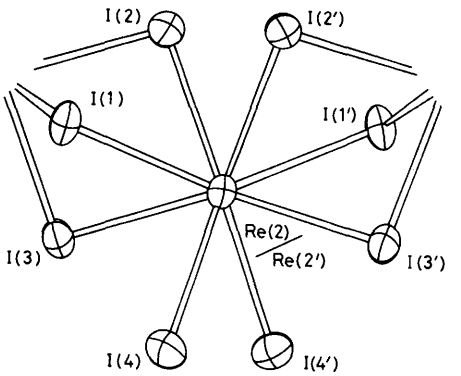

FIGURE 2 View of $[Re_4I_8(CO)_6]$ along the rhenium–rhenium bond showing the co-ordination around the metal. Dihedral angles: I(2')–Re(2)–Re(2')–I(2), 40.2; I(2)–Re(2')–Re(2)–I(1), 47.2; I(1)–Re(2)–Re(2')–I(3), 39.4; I(3)–Re(2')–Re(2)–I(4), 54.5; I(4)–Re(2)–Re(2')–I(4'), 37.5°. Primed atoms are related to unprimed ones by the symmetry operation $1 - x, y, \frac{1}{2} - z$

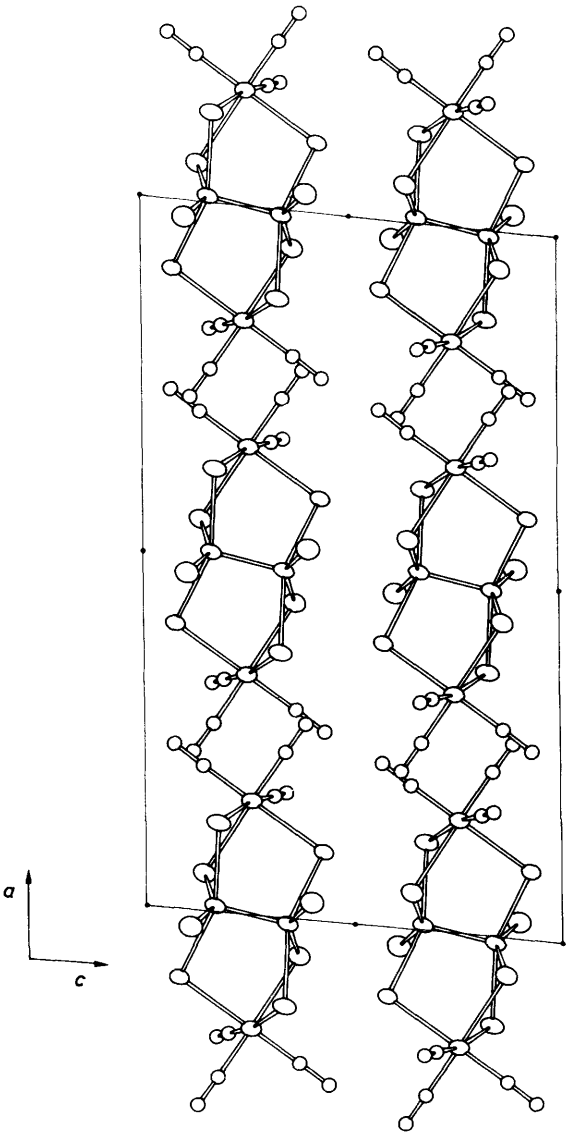

FIGURE 3 ORTEP view of the crystal packing of $[Re_4I_8(CO)_6]$ along the b axis direction

the quadruply bonded complexes, *e.g.* 2.222 (3) Å in $[Re_2Cl_6(PEt_3)_2]$ [23] and 2.228 (4) Å in $Cs_2Re_2Br_8$.[24] The molecular orbitals which do not form the metal–metal bond will become non-bonding and, since they are degenerate, a triplet ground state for the molecule is expected. Unfortunately, we could not verify this experimentally, since the amount of product obtained was insufficient for magnetic susceptibility determination.

Several attempts have been made to increase the yields of $[Re_4I_8(CO)_6]$ by independent synthetic procedures: (*a*) oxidation of $[Re_2I_2(CO)_6(thf)_2]$ with di-iodine at the reflux temperature of pentane; (*b*) reaction of $[ReI_3(CO)_3]$ with $[Re_2I_2(CO)_6(thf)_2]$ in the appropriate stoicheiometric ratio; and (*c*) reaction of $[NBu_4]_2[Re_2I_8]$ [25] with $[Re_2I_2(CO)_6(thf)_2]$. In all cases mixed-valence complexes have been obtained; but none of them could be identified with certainty with $[Re_4I_8(CO)_6]$.

A crucial point in the preparation of $[Re_4I_8(CO)_6]$ is probably the elimination of tetrahydrofuran and CO, which have to be evolved before the formation of the tetranuclear complex takes place.

By operating under more drastic conditions at the reflux temperature of heptane and with $[Re_2I_2(CO)_8]$ as starting material, another mixed-valence compound of rhenium was obtained, namely $[Re_3I_6(CO)_6]$, (3), see equation (iii). The molecular structure of this trinuclear compound is shown in Figure 4. It can be described as a central octahedral core of rhenium(IV), $[ReI_6]^{2-}$, iodide-bridged to two terminal $[Re(CO)_3]^+$ units. The idealized molecular symmetry is D_{3d}. The molecular structure can be thought as being built of successive staggered $(CO)_3$–I_3–I_3–$(CO)_3$ layers around the three Re atoms, thus leading to two sets of staggered terminal CO groups. The distance from the central rhenium atom to the bridging iodine, Re(1)–I, is 2.714(2) Å (see Table 5). In agreement with the assumed presence of an isolated rhenium(IV) centre, the magnetic moment of 3.59 B.M. for the whole trinuclear molecular complex is consistent with the expected value [19] for a magnetically diluted six-co-ordinate rhenium(IV) cation of d^3 electronic configuration. The observed magnetic moment, which is somewhat lower than the spin-only value for three unpaired electrons (3.87 B.M.), is presumably due to a negative contribution from spin–orbit coupling.[19]

The i.r. spectrum of (3) as a Nujol mull shows two main carbonyl bands, in agreement with local C_{3v} symmetry of the carbonyl groups ($A_1 + E$). On the other hand, the compound dissolved, with reaction, in tetrahydrofuran: the i.r. spectrum of the resulting brown solution has bands typical of $[ReI(CO)_3(thf)_2]$. This, and the colour of the solution, suggest reaction (iv). It is known [26] that

$$[Re_3I_6(CO)_6] + 6\ thf \longrightarrow 2[ReI(CO)_3(thf)_2] + [ReI_4(thf)_2] \quad (iv)$$

ReI_4 is soluble in oxygenated solvents giving brown solutions, presumably due to the formation of bis adducts with the solvent.

Conclusion.—This paper discloses the possibility of obtaining mixed-valence compounds by di-iodine oxidation of rhenium(I) carbonyl complexes. Compounds (2) and (3) can be regarded as co-ordination compounds of the bases $[Re_4I_8]^{2-}$ and $[ReI_6]^{2-}$ towards the acid $[Re(CO)_3]^+$, respectively. The successful isolation of these products presumably resides in the reluctance of rhenium(I) to be readily oxidized by di-iodine, thus

TABLE 5

Interatomic distances (Å) and angles (°) for $[Re_3I_6(CO)_6]$ *

Re(1)–I	2.714(2)	Re(1)–I–Re(2)	75.6(1)	I–Re(2)–C′	92(2)
Re(2)–I	2.797(2)	I–Re(1)–I′	88.0(1)	C–Re(2)–C′	90(2)
Re(1)–Re(2)	3.379(3)	I–Re(2)–I′	84.7(1)	Re(2)–C–O	175(4)
Re(2)–C	1.94(4)	I–Re(1)–I″	92.0(1)		
C–O	1.18(5)	I–Re(2)–C	93(2)		

* Primed atoms are related to unprimed ones by the symmetry operation $-y, x-y, z$ and doubly primed atoms by $x-y, x, -z$.

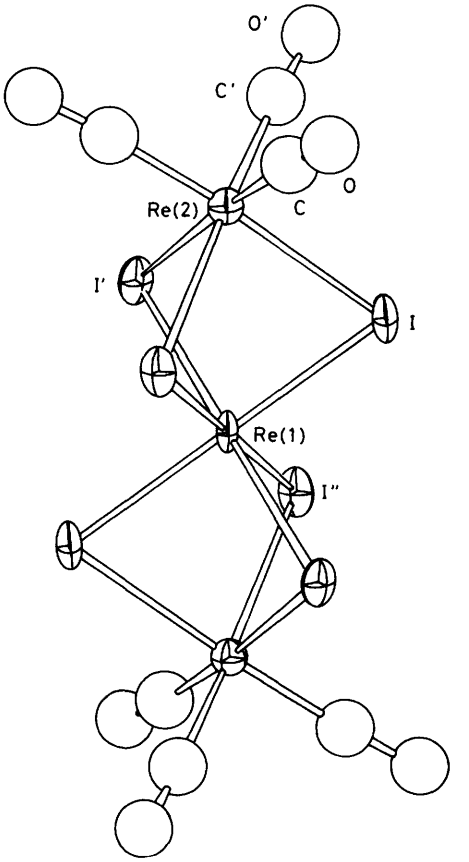

FIGURE 4 ORTEP view of $[Re_3I_6(CO)_6]$ with the atom-numbering system employed

permitting the presence of unreacted rhenium(I) carbonyl in the course of the oxidation. It is interesting to note that with dichalcogenides and P_2Ph_4 no oxidative addition across the E–E (E = chalcogen or P) bond was observed* for $[Re_2X_2(CO)_6(thf)_2]$, in agreement with the lower oxidizing power of these species.

It is conceivable that similar reactions of di-iodine to produce mixed-valence compounds can be carried out with other 4*d* and 5*d* metal carbonyls and experiments of this kind are presently being carried out. Another approach to the preparation of mixed-valence compounds is the reduction of metal halides by carbon monoxide. This synthetic approach has been successfully employed with gold. Thus gold(III) chloride reacts with CO to give, under certain conditions,[27,28] the tetranuclear Au_4Cl_8, which is a gold(III)-gold(I) halogeno-complex. The oxidation product of carbon monoxide is, in this case, phosgene $COCl_2$. The di-iodine attack of 3*d* metal carbonyls must result in carbon monoxide evolution since COI_2 is unstable with respect to its decomposition to CO and I_2.

* See references cited in ref. 5*a*.

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