# Electrochemical and Spectroscopic Studies on Tetranuclear $[\{Re(\mu_3\text{-}X)(CO)_3\}_4]$ (X = Cl, Br, or I) and Acetonitrile Complexes derived Therefrom

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The solid-state Raman spectra of the tetranuclear rhenium(I) carbonyl halides $[\{Re(\mu_3\text{-}X)(CO)_3\}_4]$ (X = Cl, Br, or I) have been recorded and compared with the i.r. spectra recorded previously. In acetonitrile, $[\{Re(\mu_3\text{-}Cl)(CO)_3\}_4]$ reacts to form $[ReCl(CO)_3(NCMe)_2]$ *via* the intermediacy of $[Re_2(\mu\text{-}Cl)_2(CO)_6(NCMe)_2]$. This reaction has been followed by cyclic voltammetry and the electrochemical properties of these complexes have been measured in $CH_2Cl_2$ and/or MeCN. The related electrochemical properties of $[NEt_4][Re_2(\mu\text{-}Cl)_3(CO)_6]$, *fac*-$[Re(CO)_3(NCMe)_3]PF_6$, *cis*-$[ReCl_4(NCMe)_2]$, and $[ReCl(CO)_5]$ have also been examined.

Mass spectrometric evidence suggests that the rhenium tricarbonyl halides $[\{Re(\mu_3\text{-}X)(CO)_3\}_4]$ (X = Cl or Br) are tetrameric in the vapour phase.[1,2] Together with the iodide, these complexes almost certainly possess the pseudocubane structure in the solid state that is exhibited by the structurally characterized analogue with X = SMe.[3] Upon investigating the properties of these carbonyl halides, we have noted that only limited spectroscopic data are available on this class of molecules. Thus, i.r.-active ν(CO) frequencies of the three halides[2,4] and ν(ReCl) of the chloride[4] have been documented. Interestingly, Davis[1] reported that the Raman spectrum of the chloride could not be obtained because of sample decomposition, but we have found no difficulty in recording Raman spectra of the halides using 514.5-nm excitation and the conventional 90° scattering orientation. Additionally, the i.r.-active ν(CO) fundamentals and overtones of $[\{Re(\mu_3\text{-}SPh)(CO)_3\}_4]$ have been assigned assuming $T_d$ symmetry[5] and the observed i.r. and Raman bands of $[\{Re(\mu_3\text{-}OH)(CO)_3\}_4]$ listed.[6]

In the present report we present solid-state Raman spectral data for $[\{Re(\mu_3\text{-}X)(CO)_3\}_4]$ (X = Cl, Br, or I), as well as details of the electrochemical properties of the chloride and of several of its derivatives, including $[ReCl(CO)_3(NCMe)_2]$[7] and $[NEt_4][Re_2(\mu\text{-}Cl)_3(CO)_6]$.[8]

**Table 1.** Solid-state Raman spectra ($cm^{-1}$)[a] of $[\{Re(\mu_3\text{-}X)(CO)_3\}_4]$

| X: Cl[b] | Br[c] | I[d] | Assignment |
|---|---|---|---|
| 2 077 (35) | 2 072 (32) | 2 064 (40) | ν(CO) |
| 1 956 (85) | 1 956 (70) | 1 957 (85) | |
| 1 940 (30) | 1 945 (28) | 1 943 (45) | |
| | | 1 930 (35) | |
| 648 (4) | ↑ | 635 (4) | δ(ReCO) |
| 621 (7) | not | 610 (2) | |
| 610 (3) | observed | 595 (sh) | |
| 592 (2) | ↓ | 568 (0.5) | |
| 510 (100) | 505 (100) | 503 (100) | ν(ReC) |
| 492 (70) | 486 (60) | 482 (80) | |
| 261 (20) | 182 (60) | 150 (sh) | ν(ReX) |
| 235 (65) | 151 (60) | 140 (sh) | |
| 212 (25) | | 130 (20) | |
| | | 104 (15) | |

[a] Relative intensities are given in parentheses on a scale 1—100, the most intense peak being given an arbitrary value of 100. [b] I.r. spectral data: ref. 4, ν(CO) 2 060 and 1 943; ν(ReCl) 263 and 215; ref. 2, ν(CO) 2 062 and 1 938 $cm^{-1}$. [c] I.r. spectral data: ref. 4, ν(CO) 2 059 and 1 941; ref. 2, ν(CO) 2 058 and 1 938 $cm^{-1}$. [d] I.r. spectral data: ref. 4, ν(CO) 2 050 and 1 950 $cm^{-1}$.

## Results and Discussion

As a result of a number of constraints, assignments of the Raman spectra of $[\{Re(\mu_3\text{-}X)(CO)_3\}_4]$ (X = Cl, Br, or I) can be given only in general terms. Thus, satisfactory solution spectra and hence polarization data could not be obtained, the halides only being soluble enough in those donor solvents with which they react to produce monomeric complexes. Also, no single-crystal *X*-ray structure determinations have been carried out so assured assignments from solid-state spectra, which usually require a knowledge of site symmetry, are not possible.

The number of ν(CO) and ν(ReX) bands detected in the Raman spectra (Table 1) is not entirely consistent on changing from one halide to another. Also, the number of observed bands is not totally in agreement with either $T_d$ molecular symmetry [ν(CO), ν(ReC), and ν(ReX), all $A_1 + E + 2T_2$: $A_1$ and $E$ being Raman-active, $T_2$ both i.r.- and Raman-active] or the $C_{3v}$ symmetry of an isolated $Re(\mu_3\text{-}X)_3(CO)_3$ unit [ν(CO), ν(ReC), and ν(ReX), all $A_1 + E$: these are both i.r.- and Raman-active]. A similar problem has been reported[9] for the related pseudocubane molecule $[\{Os(\mu_3\text{-}O)(CO)_3\}_4]$ of known crystal structure.[10] The number and intensities of the ν(CO) bands in the solid-state vibrational spectrum could not be rationalized using $C_{3v}$ symmetry of an isolated $Os(CO)_3$ group, molecular $T_d$ symmetry, site-group ($D_{2d}$) or factor-group ($D_{4h}$) symmetry. An explanation of the observed Raman spectrum was based upon the bond-polarizability approach of Wolkenstein.

The highest-frequency band observed in the Raman spectra of $[\{Re(\mu_3\text{-}X)(CO)_3\}_4]$ can undoubtedly be assigned to a totally symmetric mode[11] and is well separated by more than 100 $cm^{-1}$ from the other two (X = Cl or Br) or three (X = I) well resolved ν(CO) bands. The lack of coincidences with the previously reported i.r. ν(CO) bands[2,4] again emphasizes the invalidity of assignments based on $T_d$ symmetry. Indeed, like $[\{Os(\mu_3\text{-}O)(CO)_3\}_4]$, these halides appear to be examples of non-centrosymmetric molecules displaying centrosymmetric i.r. and Raman activity patterns.

**Table 2.** Summary of electrochemical properties of rhenium carbonyl chloride complexes

| Complex | Voltammetric potentials* |
|---|---|
| $[\{Re(\mu_3\text{-}Cl)(CO)_3\}_4]$ | $+1.9(E_{p,a})$, $+2.35(E_{p,a})$ |
| $[NEt_4][Re_2(\mu\text{-}Cl)_3(CO)_6]$ | $+1.51[E_{\frac{1}{2}}(ox)]$, $+1.94(E_{p,a})$ |
| $[Re_2(\mu\text{-}Cl)_2(CO)_6(NCMe)_2]$ | $+1.81(E_{p,a})$ |
| $[ReCl(CO)_5]$ | $+2.2(E_{p,a})$, $+2.4(E_{p,a})$ |
| $[ReCl(CO)_3(NCMe)_2]$ | $+1.50[E_{\frac{1}{2}}(ox)]$, $+2.16(E_{p,a})$ |
| *fac*-$[Re(CO)_3(NCMe)_3]^+$ | $+1.37(E_{\frac{1}{2}})$, $+1.8(E_{p,a})$ |
| *cis*-$[ReCl_4(NCMe)_2]$ | $+0.04\,[E_{\frac{1}{2}}(red)]$, $+1.95\,[E_{\frac{1}{2}}(ox)]$ |

* Measured for 0.1 mol $dm^{-3}$ $NBu^n{}_4PF_6$–$CH_2Cl_2$ solutions by the cyclic voltammetric technique (V *vs.* Ag–AgCl). Scan rate ν = 200 mV $s^{-1}$.

Very weak bands in the 650—550 $cm^{-1}$ region are assigned to δ(ReCO) modes, although in the case of X = Br these bands were too weak to be located (Table 1). In the 510—480 $cm^{-1}$ region each complex has two intense bands which, although showing *minor* shifts in agreement with halide mass change, can be assigned to ν(ReC) stretches. The detection of only two well resolved sharp bands, of which the higher frequency is the most intense for each halide, is as predicted for isolated $Re(CO)_3$ groups of $C_{3v}$ symmetry.

Colton and Garrard[4] assigned two bands in the 300—200 $cm^{-1}$ region of the mull i.r. spectrum of $[\{Re(\mu_3\text{-}Cl)(CO)_3\}_4]$ to ν(ReCl) stretches. These are almost coincident with two of the three bands similarly assigned in the Raman spectrum. Only two bands in the Raman spectrum of the bromide can be assigned to ν(ReBr) and for the iodide again two bands are assignable to ν(ReI) although the higher-frequency band shows two prominent shoulders.

In spite of the poor solubility of $[\{Re(\mu_3\text{-}Cl)(CO)_3\}_4]$ in solvents with which it does not react, it was soluble enough in $CH_2Cl_2$ to permit an examination of its electrochemical redox behaviour. The electrochemical properties of $[\{Re(\mu_3\text{-}Cl)(CO)_3\}_4]$ conform to those expected based upon previous measurements[12,13] on rhenium(I) carbonylphosphine complexes such as $[ReCl(CO)_2(PMe_2Ph)_3]$ and *mer*- and *fac*-$[ReCl(CO)_3(PMe_2Ph)_2]$ in 0.2 mol $dm^{-3}$ $NBu_4PF_6$–$CH_2Cl_2$ and 0.1 mol $dm^{-3}$ $NaClO_4$–MeCN, namely oxidation processes which occur at quite high positive potentials. In the case of $[\{Re(\mu_3\text{-}Cl)(CO)_3\}_4]$, cyclic voltammetry (c.v.) on solutions in 0.1 mol $dm^{-3}$ $NBu_4PF_6$–$CH_2Cl_2$ show oxidation waves ($E_{p,a} \approx +1.9$ and $+2.35$ V *vs.* Ag–AgCl) which occur very close to the solvent limit (Table 2). These processes, which are chemically irreversible, most likely correspond either to a two-electron oxidation per metal centre ($E_{p,a} = +1.9$ V) with a subsequent rapid chemical step to give an unstable product with $E_{p,a} = +2.35$ V, or to two sequential one-electron oxidations. Upon addition of an excess of acetonitrile to this solution, the c.v. showed the growth (with time) of processes characterized by $E_{\frac{1}{2}} = +1.49$ V, $E_{p,a} = +1.79$ V, and $E_{p,a} = +2.18$ V. There is also a very weak feature at $E_{p,a} = +1.06$ V which is due to the release of a *trace* of $Cl^-$ {this assignment was confirmed by adding $[NEt_3(CH_2Ph)]Cl$ to the solution}. The oxidations at +1.49 and +2.18 V are due to the formation of mononuclear $[ReCl(CO)_3(NCMe)_2]$ as the majority species. This is clearly shown by c.v. measurements of a chemically synthesized sample of $[ReCl(CO)_3(NCMe)_2]$[7] in 0.1 mol $dm^{-3}$ $NBu_4PF_6$–$CH_2Cl_2$ which gave $E_{\frac{1}{2}} = +1.50$ V* and $E_{p,a} = +2.16$ V (Table 2). The former process is believed to correspond to a one-electron change, based upon a comparison of the peak currents associated with the one-electron oxidation and reduction of *cis*-$[ReCl_4(NCMe)_2]$ (see Table 2),[14] a complex whose diffusion coefficient was judged to be very similar to that of $[ReCl(CO)_3(NCMe)_2]$. The wave at $E_{p,a} = +1.79$ V in the c.v. of $[\{Re(\mu_3\text{-}Cl)(CO)_3\}_4]$ in $CH_2Cl_2$–MeCN is due either to an intermediate or to a minor by-product. We favour it being $[Re_2(\mu\text{-}Cl)_2(CO)_6(NCMe)_2]$,[15,†] since an authentic sample of this complex when dissolved in 0.1 mol $dm^{-3}$ $NBu_4PF_6$–$CH_2Cl_2$ has an oxidation at $E_{p,a} = +1.81$ V (Table 2). When acetonitrile is added to this latter solution, $[Re_2(\mu\text{-}Cl)_2(CO)_6(NCMe)_2]$ is converted into $[ReCl(CO)_3(NCMe)_2]$. Accordingly, in the presence of acetonitrile, the tetranuclear structure of $[\{Re(\mu_3\text{-}Cl)(CO)_3\}_4]$ is disrupted to give $[ReCl(CO)_3(NCMe)_2]$, *via* the intermediacy of $[Re_2(\mu\text{-}Cl)_2(CO)_6(NCMe)_2]$.

There is no evidence for the presence of alternative species such as *fac*-$[Re(CO)_3(NCMe)_3]^+$[16] or $[ReCl(CO)_5]$ when solutions of $[\{Re(\mu_3\text{-}Cl)(CO)_3\}_4]$ in 0.1 mol $dm^{-3}$ $NBu_4PF_6$–$CH_2Cl_2$ are treated with an excess of acetonitrile. Solutions of *fac*-$[Re(CO)_3(NCMe)_3]PF_6$ in 0.1 mol $dm^{-3}$ $NBu_4PF_6$–$CH_2Cl_2$ show coupled waves at $E_{p,a} = +1.44$ V and $E_{p,c} = +1.31$ V (with $E_{\frac{1}{2}} \approx +1.37$ V and $i_{p,a} > i_{p,c}$), and an irreversible process at *ca.* +1.8 V, whereas c.v. of $[ReCl(CO)_5]$ in 0.1 mol $dm^{-3}$ $NBu_4PF_6$–$CH_2Cl_2$ yields $E_{p,a} \simeq +2.4$ V with a 'shoulder' at *ca.* +2.2 V (see Table 2). When acetonitrile is added to the latter solution a feature at $E_{p,a} = +2.27$ V represents the only discernible oxidation process up to the solvent limit.

As a consequence of the preceding results, we also examined the electrochemical properties of $[NEt_4][Re_2(\mu\text{-}Cl)_3(CO)_6]$. In 0.1 mol $dm^{-3}$ $NBu_4PF_6$–$CH_2Cl_2$, c.v. shows a reversible oxidation at $E_{\frac{1}{2}} = +1.51$ V and a second oxidation process, albeit irreversible, at $E_{p,a} = +1.94$ V. The process at $E_{\frac{1}{2}} = +1.51$ V is characterized by $i_{p,c}/i_{p,a}$ ratios of 1.0(±1) and $i_{p,a} \propto v^{\frac{1}{2}}$ over the range of sweep rates from 100 to 500 mV $s^{-1}$. A comparison of peak currents associated with the c.v. of $[Re_2Cl_4(PMe_3)_4]$,[17] a complex which shows two reversible one-electron oxidations, indicates that the oxidation at +1.51 V is a one-electron process. Upon addition of acetonitrile to the solution of $[NEt_4][Re_2(\mu\text{-}Cl)_3(CO)_6]$ in 0.1 mol $dm^{-3}$ $NBu_4PF_6$–$CH_2Cl_2$, there is the rapid growth of waves corresponding to the generation of $Cl^-$ ($E_{p,a} = +1.06$ V) and $[ReCl(CO)_3(NCMe)_2]$ (see above), together with appearance of an oxidation close to +1.8 V which signals the appearance of the same intermediate {*viz.* $[Re_2(\mu\text{-}Cl)_2(CO)_6(NCMe)_2]$} as is formed upon treating acetonitrile with $[\{Re(\mu_3\text{-}Cl)(CO)_3\}_4]$ in $CH_2Cl_2$. Thus the reaction of $[Re_2(\mu\text{-}Cl)_3(CO)_6]^-$ with acetonitrile apparently proceeds according to equations (1) and (2).

$$[Re_2(\mu\text{-}Cl)_3(CO)_6]^- + 2MeCN \rightleftharpoons [Re_2(\mu\text{-}Cl)_2(CO)_6(NCMe)_2] + Cl^- \quad (1)$$

$$[Re_2(\mu\text{-}Cl)_2(CO)_6(NCMe)_2] + 2MeCN \rightleftharpoons 2[ReCl(CO)_3(NCMe)_2] \quad (2)$$

## Experimental

*Starting Materials.*—Samples of the following complexes were prepared by standard literature methods: $[\{Re(\mu_3\text{-}$

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* This value is estimated since we find that $i_{p,c}$ is slightly less than $i_{p,a}$ for the coupled processes with $E_{p,c} = +1.45$ V and $E_{p,a} = +1.55$ V, respectively.

† The previous assignment of the $C_{2h}$(*trans*) structure of $[Re_2(\mu\text{-}Cl)_2(CO)_6(NCMe)_2]$ has now been confirmed by measurements of its Raman spectrum: ν(CO), i.r. 2 060s, 1 940(sh), and 1 920s ($A_u + 2B_u$); Raman 2 051m, 1 916vs, and 1 896vs ($2A_g + B_g$): ν(ReC), i.r. 524s, 508s, and 482s ($A_u + 2B_u$); Raman 514vs, 504s, and 476s ($2A_g + B_g$): ν(ReCl), i.r. 286s and 262s ($A_u + B_u$); Raman 269vs and 246s ($A_g + B_g$): ν(ReN), i.r. 229s ($B_u$); Raman 195m $cm^{-1}$ ($A_g$).

X)(CO)$_3$}$_4$] (X = Cl, Br, or I),[4] the reflux in n-heptane being extended to 72 h; [ReCl(CO)$_3$(NCMe)$_2$];[7] [NEt$_4$][Re$_2$(μ-Cl)$_3$(CO)$_6$];[8] [Re$_2$(μ-Cl)$_2$(CO)$_6$(NCMe)$_2$];[15] *fac*-[Re(CO)$_3$(NCMe)$_3$]PF$_6$;.[16] and *cis*-[ReCl$_4$(NCMe)$_2$].[14]

*Physical Measurements.*—Cyclic voltammetric measurements were carried out by the use of the procedures and instrumentation we have described previously.[18] A Bioanalytical Systems Inc. model CV-1A instrument was used in conjunction with a Hewlett-Packard model 7035 x-y recorder. Measurements were made with $CH_2Cl_2$ or MeCN as solvent and tetra-n-butylammonium hexafluorophosphate as supporting electrolyte. A platinum-bead working electrode and a Bioanalytical Systems Inc., 3M, Ag–AgCl reference electrode were used. The $E_{\frac{1}{2}}$ values were determined as $(E_{p,a} + E_{p,c})/2$, and a scan rate (ν) of 200 mV s$^{-1}$ was used in all measurements (see Table 2). Under our experimental conditions, $E_{\frac{1}{2}} = +0.47$ V and $E_{p,a} - E_{p,c} = 90 \pm 10$ mV at ν = 200 mV s$^{-1}$ for the ferrocenium–ferrocene couple which was used as a reference redox standard. Spectroscopic grade Burdick and Jackson solvents were carefully dried prior to use.

Raman spectra on the solids [{Re(μ$_3$-X)(CO)$_3$}$_4$] were recorded by the usual means.[19]

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