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THE PREPARATION AND CHARACTERISATION OF TRI- μ -HALOGENOHEXACARBONYLDIMETALLATE(I) ANIONS OF MANGANESE AND RHENIUM

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Summary

The final products of the reactions between $Mn(CO)_5X$ and Et_4NX (X = Cl or Br) in boiling chloroform and between $Re(CO)_5X$ and Et_4NX (X = Cl, Br or I) in boiling decalin are the compounds $Et_4N[M_2(CO)_6(\mu\text{-}X)_3]$. Vibrational spectroscopic results indicate that the anions possess bi-confacial octahedral geometry with three bridging halogen atoms.

Introduction

A wide range of mono- and bi-nuclear halogenocarbonyl anions are known for both manganese and rhenium. The mononuclear anions are of the types cis-$[M(CO)_4XY]^-$ (M = Mn; X = Y = Cl, Br or I; X = Cl, Y = Br or I; X = Br, Y = I [1,2]; M = Re, X = Y = Cl, Br or I; X = Br, Y = I [3-5]) and fac-$[Re(CO)_3X_3]^{2-}$ (X = Cl, Br or I) [3-6]. For the binuclear anions, the metal-metal bonded $[M_2(CO)_8X_2]^{2-}$ (M = Mn, X = Cl, Br or I [1]; M = Re, X = I [3]) and the bis-μ-halogeno-types $[Re_2(CO)_7X_2Y]^-$ (X = Y = Cl, Br or I; X = Cl, Y = Br) [3,5] and $[Re_2(CO)_6X_4]^{2-}$ (X = Cl or Br) [6] are known. Recent reports have indicated that the tri-μ-halogenoanions $[M_2(CO)_6X_3]^-$ may also be prepared. Thus, Levenson and co-workers [7] have isolated $Et_4N[Mn_2(CO)_6(\mu\text{-}Cl)_3]$ as the product of a photochemical reaction between $Mn_2(CO)_{10}$ and Et_4NCl in chloroform. The bromo-analogue was also formed in a similar manner but could not be separated from other products produced simultaneously. An X-ray diffraction study [8] of the product obtained from the reaction of either $Re(CO)_5Br$ or $Re_2(CO)_8Br_2$ with toluene has shown it to be $[Re(CO)_3(\eta\text{-}C_6H_5Me)][Re_2(CO)_6(\mu\text{-}Br)_3]$, and $[Re(CO)_3(\eta\text{-}C_6Me_6)][Re_2(CO)_6(\mu\text{-}Cl)_3]$ was similarly characterised. The only other complexes known [9] to contain such anions are $[H_3OEP][Re_2(CO)_6(\mu\text{-}Cl)_3]$, prepared from $Re(CO)_5Cl$ and H_2OEP in refluxing decalin (H_2OEP = octaethylporphine), and $[H_3MPDE][Re_2(CO)_6(\mu\text{-}Br)_3]$, prepared analogously using H_2MPDE, (H_2MPDE = mesoporphine IX dimethylester).

Thus apart from $Et_4N[Mn_2(CO)_6(\mu\text{-}Cl)_3]$ which was obtained at best in 19% yield from chloroform and in only 1% yield from diglyme [7], all other pure complexes containing such anions also involve either carbonyl-containing cations which confuse a study of the ν(CO) infrared bands of the anions, or very complex porphinium cations. We are therefore prompted by the above reports to present details of simple high-yield preparations of $Et_4N[M_2(CO)_6(\mu\text{-}X)_3]$ (M = Mn, X = Cl or Br; M = Re, X = Cl, Br or I) and their characterisation particularly by vibrational spectroscopy.

Experimental

$M(CO)_5X$ (M = Mn, X = Cl or Br; M = Re, X = Cl, Br or I) and $Et_4N[Mn(CO)_4X_2]$ (X = Cl or Br) were prepared by published methods [2,10]. All reactions were carried out under dry nitrogen gas, using anhydrous solvents.

Melting points were determined using a Kofler heating block. Infrared spectra were recorded on a Perkin-Elmer 597 spectrophotometer. Far-infrared spectra of samples dispersed in polyethylene were obtained on a Beckman - R.I.I.C. FS 720 interferometer. Raman spectra were recorded using a Spex 1401 spectrometer in conjunction with a Spectra-Physics 125 He-Ne laser. Spectra were measured on solid samples held in capillary tubes. Conductance measurements at 25°C were carried out using a Wayne-Kerr Autobalance bridge and a dip-type cell with platinum electrodes.

Preparation of $Et_4N[Mn_2(CO)_6(\mu\text{-}X)_3]$, (X = Cl or Br).

(a) The reactions between $Mn(CO)_5X$ (2 mmol) and Et_4NX (1 mmol) were allowed to proceed for 5 h. in refluxing chloroform (30 cm^3). After cooling, the products were filtered off, washed with a little ethanol and water and dried *in vacuo*. (Yields: X = Cl, 91%; X = Br, 93%). Samples could be recrystallised from acetone-diethyl ether as orange needles. (Found for X = Cl: C, 32.5; H, 4.33; N, 2.52. $C_{14}H_{20}Cl_3Mn_2NO_6$ calcd: C, 32.7; H, 3.92; N, 2.72%. Found for X = Br: C, 25.9; H, 3.24; N, 1.92. $C_{14}H_{20}Br_3Mn_2NO_6$ calcd: C, 25.9; H, 3.11; N, 2.16%).

(b) $Et_4N[Mn_2(CO)_6(\mu\text{-}X)_3]$, (X = Cl or Br), could also be obtained from the decomposition of $Et_4N[Mn(CO)_4X_2]$ in refluxing chloroform. However separation of the desired products from Et_4NX also formed in the decomposition, and subsequent recrystallisation from acetone-diethyl ether reduced the yields to below 10%.

Preparation of $Et_4N[Re_2(CO)_6(\mu\text{-}X)_3]$, (X = Cl, Br or I).

The reactions between $Re(CO)_5X$ (2 mmol) and Et_4NX (1 mmol) were carried out in refluxing decalin (30 cm^3) for 18 h. The resulting grey solids were filtered off and washed with light petroleum (40-60°) before dissolution in anhydrous dichloromethane (80 cm^3). The dichloromethane solutions were then filtered and the volume of the filtrates reduced to *ca*.10 cm^3 to afford colourless crystalline products which were recrystallised from further dichloromethane and dried *in vacuo*. (Yields: X = Cl, 77%; X = Br, 68%; X = I, 78%). (Found for X = Cl: C, 21.6; H, 2.84; N, 1.74. $C_{14}H_{20}Cl_3NO_6Re_2$ calcd: C, 21.6; H, 2.59; N, 1.80%. Found for X = Br: C, 18.7; H, 2.40; N, 1.38. $C_{14}H_{20}Br_3NO_6Re_2$ calcd: C, 18.5; H, 2.21; N, 1.54%. Found for X = I: C, 16.1; H, 2.09; N, 1.22. $C_{14}H_{20}I_3NO_6Re_2$ calcd: C, 16.0; H, 1.92; N, 1.33%).

Results and Discussion

The thermal reactions between $M(CO)_5X$ (M = Mn, X = Cl or Br; M = Re, X = Cl, Br or I) and Et_4NX in a 2:1 molar ratio lead to the isolation of $Et_4N[M_2(CO)_6X_3]$.

$$2\ M(CO)_5X\ +\ Et_4NX\ \rightarrow\ Et_4N[M_2(CO)_6X_3]\ +\ 4\ CO$$

As will be shown below the anions contain three bridging halogen atoms and it is therefore reasonable to suppose that our lack of success in preparing $Et_4N[Mn_2(CO)_6I_3]$ is associated with the incompatibility of three bulky iodine bridges linking two small manganese atoms. As we have shown that $Et_4N[Mn_2(CO)_6X_3]$ (X = Cl or Br) can also be obtained by decomposition of $Et_4N[Mn(CO)_4X_2]$, and that the latter anion may be detected spectroscopically in the $Mn(CO)_5X$ - Et_4NX reaction mixtures, the reactions employing $M(CO)_5X$ must proceed <u>via</u> $[M(CO)_4X_2]^-$ and may possibly involve the bis-μ-halogenoanions $[M_2(CO)_7X_3]^-$ before finally affording $[M_2(CO)_6X_3]^-$. Other anions such as $[M(CO)_3X_3]^{2-}$ and $[M_2(CO)_6X_4]^{2-}$ are unlikely to be involved as intermediates as insufficient halide ion is present in the reaction mixture to generate these anions.

The complexes are air-stable over a period of some weeks and may be stored indefinitely under nitrogen. Melting points are given in Table 1. Dichloromethane solutions were stable for at least a few days for the rhenium compounds and a few hours for the manganese compounds, so infrared carbonyl stretching frequencies were obtained in this solvent. Decomposition was found to be more rapid in solvents of greater coordinating power such as acetonitrile and nitromethane, the manganese complexes again being more susceptible than the rhenium complexes. Of these two solvents a slower decomposition rate was found in nitromethane, so conductivity measurements were made in this solvent at 25°C, the measurements being carried out as rapidly as possible after solution preparation. The results obtained (Table 1) are in good agreement with expectations for uni-univalent electrolytes in this solvent, (75-95 $S\ cm^2\ mol^{-1}$ for $10^{-3}M$ solutions [11]). Levenson et al. [7] also found $Et_4N[Mn_2(CO)_6(\mu\text{-}Cl)_3]$ to be stable in ethanol only for periods of up to 1 h.

The decomposition of $Et_4N[Mn_2(CO)_6(\mu\text{-}Cl)_3]$ in acetonitrile solution was briefly studied by monitoring changes in the infrared ν(CO) region with time. Initially only the two strong ν(CO) bands of the $[Mn_2(CO)_6(\mu\text{-}Cl)_3]^-$

TABLE 1

MELTING POINTS, CONDUCTIVITIES AND SOLUTION INFRARED ν(CO) FREQUENCIES

Complex	M.p. °C.	Λ_M, 25°C, S cm^2 mol^{-1} 10^{-3}M, MeNO$_2$	ν(CO), cm^{-1} CH$_2$Cl$_2$ solutions	
			A_2''	E'
$Et_4N[Mn_2(CO)_6Cl_3]$	190 dec.	78.9	2030	1936
$Et_4N[Mn_2(CO)_6Br_3]$	196 dec.	74.4	2029	1937
$Et_4N[Re_2(CO)_6Cl_3]$	191	70.3	2030	1917
$Et_4N[Re_2(CO)_6Br_3]$	206	70.3	2028	1915
$Et_4N[Re_2(CO)_6I_3]$	> 260 dec.	68.8	2012	1914

anion, (see below), are observed. The spectrum subsequently becomes more complex, the bands associated with this anion decaying, and three new ν(CO) bands increasing in intensity. The new ν(CO) bands were found to be in positions in good agreement with literature values [12] for $[Mn(CO)_3Cl(NCMe)_2]$, so presumably Et_4NCl is also formed. If the decomposition followed this route exclusively the molar conductance in acetonitrile should not markedly change, one uni-univalent electrolyte being replaced by another. However the conductance slowly increases with time and all ν(CO) infrared bands decay suggesting that other non-carbonyl electrolyte species may form, perhaps by disproportionation. In view of these observations we feel that the electronic spectrum of $Et_4N[Mn_2(CO)_6(\mu\text{-}Cl)_3]$ recorded by Levenson et al. [7] in acetonitrile is of doubtful value, and indeed we have been unable to reproduce the results quoted.

The solution infrared spectra of the complexes in the ν(CO) region, (Table 1), and the solid state infrared spectra in the ν(MX) region, (Table 2), are consistent with the presence of a bi-confacial octahedral anion of D_{3h} local symmetry with three bridging halogen atoms. Since this type of anion

TABLE 2 SOLID STATE INFRARED SPECTRA BELOW 700 cm^{-1}

Complex	δ(MCO)	ν(MC)	ν(MX)	δ(XMX)	Et_4N^+
	A_2'' + 2E'	A_2'' + E'	A_2'' + E'	E'	Skeletal Deformations
$Et_4N[Mn_2(CO)_6Cl_3]$	680 s, 663 s, 628 s	504 s, 486 ms	278 s, 239 s	173 s	415 vw, 358 vw
$Et_4N[Mn_2(CO)_6Br_3]$	673 s, 630 s, 623 s	504 s, 485 ms	212 s, 176 s	161 s	415 w, 350 vw
$Et_4N[Re_2(CO)_6Cl_3]$	648 s, 635 s	510 sh, 499 s	269 s, 251 s	159 s	414 w, 355 vw
$Et_4N[Re_2(CO)_6Br_3]$	642 s, 629 s	506 s, 495 s	190 s, 171 s	117 s	414 w[a]
$Et_4N[Re_2(CO)_6I_3]$	640 s, 630 sh	510 sh, 493 s	156 s, 137 s	100 ms	412 vw, 355 vw

[a] Raman spectrum; 417 m, 413 sh

has high local symmetry and the number of atoms involved is low, we have attempted to carry out a reasonably complete vibrational spectroscopic study. Attempts to obtain Raman spectra of the manganese anions were unfortunately thwarted by decomposition of the compounds in the laser beam, but a satisfactory Raman spectrum of $Et_4N[Re_2(CO)_6(\mu\text{-}Br)_3]$ was obtained.

The vibrational representations for an isolated $[M_2(CO)_6(\mu\text{-}X)_3]^-$ anion of D_{3h} symmetry reduce as follows:

$$\begin{aligned}
\Gamma_{vib} &= 6A_1' + 2A_2' + 8E' + 2A_1'' + 5A_2'' + 7E'' \\
\Gamma_{\nu(CO)} \text{ or } \Gamma_{\nu(MC)} &= A_1' + E' + A_2'' + E'' \\
\Gamma_{\delta(MCO)} &= A_1' + 2E' + A_2'' + 2E'' \\
\Gamma_{\nu(MX)} &= A_1' + E' + A_2'' + E'' \\
\Gamma_{\delta(XMX)} &= A_1' + E'
\end{aligned}$$

In D_{3h} symmetry, A_1' and E'' modes are Raman-active only, E' modes are infrared- and Raman-active, A_2'' modes are infrared-active only, whilst A_2' and A_1'' modes are inactive.

The assignments of the $\nu(CO)$ bands, (Tables 1 and 3), are straightforward, the band assigned to the infrared- and Raman-active E' mode showing considerable splitting in the solid state spectra, but appearing unsplit in the dichloromethane solution infrared spectra. Assignments of the bands in the $\nu(MC)$ and $\delta(MCO)$ region are less obvious. We have taken the widely held view that $\delta(MCO)$ modes generally appear at higher energies than $\nu(MC)$ modes, as established for other fac-tricarbonyl species such as $[M(CO)_3(\eta\text{-arene})]$ (M = Cr, Mo, or W) [13] and $[Mn(CO)_3(\eta\text{-}C_5H_4R)]$ (R = H or Me) [14]. The results of Table 2 show that although the manganese anions exhibit the predicted three infrared-active $\delta(MCO)$ bands, only two such bands are evident for the rhenium anions. It is known that the highest-frequency $\delta(MCO)$ bands of, for example, $[M(CO)_6]^+$ [15], $[M(CO)_5X]$ [16] and $[M(CO)_3(NCMe)_3]^+$ [17], (M = Mn or Re), show a substantial mass effect on changing from manganese to rhenium (e.g. 52 cm^{-1} for the hexacarbonyl cations), but for the remaining $\delta(MCO)$ bands this effect is much less apparent and may even be reversed. We therefore incline to the view that the A_2'' δ(MCO) mode found at ca.680 cm^{-1} for the manganese anions suffers a similar mass shift for the rhenium analogues and becomes accidentally co-incident with the highest infrared-active E' mode, only two δ(MCO) infrared bands thereby being observed for the rhenium anions. Inspection of the infrared spectra shows that the highest energy δ(ReCO) bands are indeed somewhat broader than the δ(MnCO) bands of intermediate energy. The E' δ(MCO) bands are easily assigned because of their correspondence in the infrared and Raman spectra of $Et_4N[Re_2(CO)_6(\mu\text{-}Br)_3]$. The ν(MC) bands are assigned without difficulty, (Tables 2 and 3), although it could be argued from a consideration of merely the solid state infrared spectra that the two bands observed, being of closely similar frequency, could both be assigned to the E' mode split by solid state effects, leaving the A_2'' mode undetected. However, a dichloromethane solution infrared spectrum of $Et_4N[Re_2(CO)_6(\mu\text{-}Br)_3]$ in the δ(ReCO) and ν(ReC) region also shows four bands (647, 633, 509 and 501 cm^{-1}) thereby supporting the assignments of Table 2.

Apart from the absence of the E" Raman-active ν(ReBr) band of $Et_4N[Re_2(CO)_6(\mu\text{-}Br)_3]$, the ν(MX) and δ(XMX) bands are readily assignable as shown in Tables 2 and 3, and display the expected sensitivity to change of mass of the halogen. The ν(MBr)/ν(MCl) and ν(MI)/ν(MCl) ratios of 0.68-0.76 and 0.53-0.58 respectively give added confidence to these assignments. The frequencies of the ν(MX) bands are in the expected regions for bridging halogen atoms and are closely similar in frequency to such bands observed [18] for the neutral $[M_2(CO)_8(\mu\text{-}X)_2]$ (M = Mn or Re; X = Cl, Br, or I) carbonyl halides.

In the Raman spectrum of $Et_4N[Re_2(CO)_6(\mu\text{-}Br)_3]$ the A_1' ν(CO), δ(ReCO), ν(ReC) and ν(ReBr) bands have been assigned to the highest frequency bands of the particular group both on intensity grounds and by comparison with the spectra of other fac-tricarbonyl species [13,14] in which the A_1 modes are consistently of higher energy than the E modes.

Weak bands in the infrared spectra of the compounds at ca.415 and ca.355 cm^{-1}, (Table 2), can be assigned [19] to skeletal deformations of the tetraethylammonium cation.

These anions are therefore further examples of the established structural type $[M_2(CO)_6(\mu\text{-}X)_3]^-$ for Group VII anions (M = Mn, X = N_3 or NCO [20]; M = Re, X = H, OEt, or OPr^i [21]; M = Re, X = OR, R = H, Me, Et, Bu^n, Bu^t, or Cy [22]), and are isostructural and isoelectronic with

TABLE 3

VIBRATIONAL SPECTRA OF SOLID $Et_4N[Re_2(CO)_6(\mu\text{-}Br)_3]$, ($cm^{-1}$)

I.R.	Raman [a]	Proposed Assignments	
	2040 ms	A_1'	ν(CO)
2020 vs		A_2''	
	1951 m	E''	
1915 sh	1909 ms		
1904 vs	1902 ms	E'	
1890 sh	1891 ms		
	671 m	A_1'	δ(MCO)
642 s[b]	642 vw	E'	
629 s	631 vw	E'	
	565 w	E''	
	554 vw	E''	
	520 vs	A_1'	ν(MC)
	512 sh	E''	
506 s	508 ms	E'	
495 s		A_2''	
	212 m	A_1'	$\nu(MBr)_{bridge}$
190 vs		A_2''	
	not observed	E''	
171 vs	170 m	E'	
	123 m	A_1'	δ(BrMBr)
117 s	117 ms	E'	

[a] Other low-energy Raman bands: 110, 104, 98, 91 and 85 cm^{-1}

[b] A_2'' mode may be co-incident, (see text)

the Group VI anions $[M_2(CO)_6(\mu\text{-}X)_3]^{3-}$ (M = Cr, Mo, or W; X = F, Cl, Br, I, OH, SCN, N_3, or OEt [23]; M = Mo or W, X = Cl [24]).

Finally, it is pertinent to note that reactions of $[Re_2(CO)_6(\mu\text{-}X)_3]^-$ (X = H, OEt, or OPr^i) with hydrogen halides [6] do not lead to the tri-μ-halogenoanions prepared in this work, but rather to $[Re_2(CO)_6X_4]^{2-}$ or $[Re(CO)_3X_3]^{2-}$ (X = Cl, Br, or I). A deficiency of halide ion therefore appears necessary for the successful preparation of the dinuclear tri-μ-halogenoanions.

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