78. *Halogenocarbonylmanganese Anions.*

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The dihalogenotetracarbonylmanganate ions $[Mn(CO)_4XY]^-$, where X and Y = Cl, Br, or I, have been isolated as their tetra-alkylammonium salts, after the action of halide ions on pentacarbonyl halides or dimeric tetracarbonyl halides of manganese. The action of halide ions on manganese carbonyl itself produced the dihalogeno-octacarbonyldimanganates $(R_4N^+)_2[Mn_2(CO)_8X_2]^{2-}$. The carbonyl stretching modes in the infrared spectra of these compounds have been recorded and in the light of them structures for the complex ions are advanced.

Direct replacement of carbonyl groups in metal carbonyls by halide ions to give halogenocarbonylmetal anions has been reported [1] for hexacarbonyl-chromium, -molybdenum, and -tungsten. We have now extended this reaction to the carbonyl and carbonyl halides of manganese.

Tetra-alkylammonium halides react directly with the carbonylmanganese halides in diethyleneglycol dimethyl ether at 120° to produce the dihalogenotetracarbonylmanganates

$$R_4N^+X^- + Mn(CO)_5X \longrightarrow R_4N^+[Mn(CO)_4X_2]^- + CO \qquad (1)$$

The products are all diamagnetic, and range from pale yellow for the dichloride to deep red for the di-iodide. They are crystalline and soluble in water, alcohol, polyoxygenated ethers, and chloroform, but are insoluble in diethyl ether, benzene, and light petroleum.

The potassium salt, $K^+[Mn(CO)_4I_2]^-$, is obtained by the action of potassium iodide on iodopentacarbonylmanganese but is too unstable for analysis and does not give good solution spectra. A Nujol mull spectrum of the crystals is, however, almost identical with those of the corresponding tetra-alkylammonium salts (Table 1).

In addition to these symmetrical dihalogenomanganates, we obtained ions with two different halogens attached to manganese:

$$\left.\begin{array}{l} R_4N^+X^- + Mn(CO)_5Y \\ R_4N^+Y^- + Mn(CO)_5X \end{array}\right] \longrightarrow R_4N^+[Mn(CO)_4XY]^- + CO \qquad (2)$$

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[1] (*a*) Fischer and Öfele, *Z. Naturforsch.*, 1959, **14**b, 763; *Chem. Ber.*, 1960, **93**, 1156; Abel, Bennett, and Wilkinson. *Chem. and Ind.*, 1960, 442; (*b*) Abel, Butler, and Reid, *J.*, 1963, 2068.

Identical products are always obtained by the two routes of reactions (2). These dihalogenotetracarbonylmanganates with two different halogen atoms are similar in every way to those containing only one type of halogen, and show no tendency to disproportionate to the two symmetrical ions.

A second method for the preparation of both types of dihalogenotetracarbonylmanganate involves fission of the halogen bridge in the dimeric tetracarbonylmanganese halides:

$$2R_4N^+X^- + \{Mn(CO)_4X\}_2 \longrightarrow 2R_4N^+[Mn(CO)_4X_2]^- \tag{3}$$

$$\left.\begin{array}{l}2R_4N^+X^- + \{Mn(CO)_4Y\}_2\\ 2R_4N^+Y^- + \{Mn(CO)_4X\}_2\end{array}\right] \longrightarrow 2R_4N^+[Mn(CO)_4XY]^- \tag{4}$$

These bridge-breaking reactions take place more quickly and at a lower temperature than those [reactions (1) and (2)] requiring evolution of carbon monoxide, as in corresponding reactions with other ligands.[2,3] The products are identical with those obtained from the corresponding pentacarbonyl halides.

Manganese carbonyl reacts with tetra-alkylammonium halides, evolving carbon monoxide and producing the tetra-alkylammonium dihalogeno-octacarbonyldimanganates

$$2R_4N^+X^- + Mn_2(CO)_{10} \longrightarrow (R_4N^+)_2[Mn_2(CO)_8X_2]^{2-} + 2CO \tag{5}$$

These salts are isolated as yellow (chloride) to red (iodide) diamagnetic crystals. They behave similarly to the dihalogenotetracarbonylmanganates, but are in general rather less soluble.

The infrared spectra of all these compounds in the C–O stretching region are reported in Table 1, together with the corresponding spectra of the tetracarbonyliron halides.

TABLE 1.

Infrared spectra in the C–O stretching region of the halogenocarbonylmanganates and tetracarbonyliron halides.

Compound	ν(C=O) (cm.$^{-1}$)				Solvent
$Et_4N^+[Mn(CO)_4Cl_2]^-$	2040w	2002s	1969m	1915m	Nujol mull
$Et_4N^+[Mn(CO)_4Br_2]^-$	2090w	2013s	1989m	1941m	Chloroform
$Et_4N^+[Mn(CO)_4I_2]^-$	2075w	2001s	1982m	1940m	Chloroform
$Bu_4N^+[Mn(CO)_4I_2]^-$	2072w	1997s	1980m	1936m	Chloroform
$(C_{10}H_{10}N)^+[Mn(CO)_4I_2]^-$ *	2075w	2000s	1983m	1940m	Chloroform
$K^+[Mn(CO)_4I_2]^-$	2065m	2000s	1970s	1930s	Nujol mull
$Et_4N^+[Mn(CO)_4ClBr]^-$	2093m	2014s	1989m	1941s	Chloroform
$Et_4N^+[Mn(CO)_4BrI]$	2079w	2002s	1985m	1941m	Chloroform
$Et_4N^+[Mn(CO)_4ClI]^-$	2076w	2001s	1982m	1941m	Chloroform
$(Et_4N^+)_2[Mn_2(CO)_8Cl_2]^{2-}$		2022s	1931s		Chloroform
		2016s	1908s		Nujol mull
$(Et_4N^+)_2[Mn_2(CO)_8Br_2]^{2-}$		2002s	1922s		Chloroform
		2019s	1905s		Nujol mull
		2020s	1913s		KBr disc
$(Et_4N^+)_2[Mn_2(CO)_8I_2]^{2-}$		2020s	1910s		Chloroform
		2017s	1913s		Nujol mull
$Fe(CO)_4Br_2$ †	2152w	2108s	2100m	2073m	Carbon tetrachloride
$Fe(CO)_4I_2$ †	2130m	2083s	2061s	2120w	Carbon tetrachloride
	2137m	2090s	2067m	2028w	Iso-octane

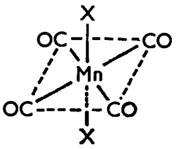
* 1-Methylquinolinium salt. † Measurements by Mr. B. C. Crosse.

The profiles of the spectra of the $[Mn(CO)_4X_2]^+$ ions are similar to those of the corresponding neutral tetracarbonyliron halides $Fe(CO)_4X_2$. In general, however, the anionic species absorb at wavelengths about 100 cm.$^{-1}$ lower than the neutral compounds. This weaker carbon–oxygen bond, in comparison with that in a neutral isoelectronic and isostructural species, due to the presence of an excess of negative charge, had already been

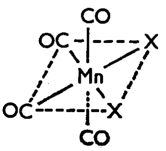
[2] Abel and Wilkinson, *J.*, 1959, 1501.

[3] Abel, Hargreaves, and Wilkinson, *J.*, 1958, 3149.

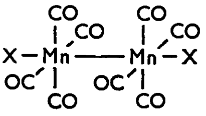
noted[1b] for the anionic carbonyl halides of Group VI metals and for many other metal carbonyl derivatives.[4]



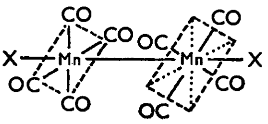
(I)



(II)



(III)



(IV)

The two possible forms of the dihalogenotetracarbonylmanganate ions $[Mn(CO)_4X_2]^-$ are (*cis*) C_{2v} (II) and (*trans*) D_{4h} (I) structures. Group-theoretical arguments[5] have been used to predict the number of infrared-active carbonyl-stretching modes that each of these structures should produce. The D_{4h} form should have only one (E_u) mode, and the less symmetrical C_{2v} form should have four ($2A_1 + B_1 + B_2$) modes. All the measured spectra of the $[Mn(CO)_4X_2]^-$ ions have four well-resolved absorptions in this region, and are in accordance with the *cis*-structure for these compounds. Arguments based on the *trans*-effect[6] and the lower reactivity[7] of the carbonyl group *trans* to the halogen atom in the pentacarbonylmanganese halides support this assignment, as also does formation of the compounds from the *cis*-bridged[8] dimeric tetracarbonyl halides.

The dihalogenotetracarbonylmanganate ions $[Mn(CO)_4XY]^-$, containing two different halogens, also appear to have the *cis*-configuration. The four absorption peaks in the C–O stretching region is in accordance with the group-theoretical prediction of four such active modes ($3A' + A''$) for these C_{1h} species. The alternative (*trans*) C_{4v} structure would only be expected to have two ($A_1 + E$) active modes.

The observed infrared spectra of the dihalogeno-octacarbonyldimanganate ions $[Mn_2(CO)_8X_2]^{2-}$ are remarkably simple, only two peaks being observed in the C–O stretching region. Nujol-mull spectra of these compounds are unaffected on storage, but after even a short time the solution spectra in the C–O stretching region becomes more complex, owing to isomerisation or decomposition of the complex anions.

If we assume initially that any two carbonyl groups in manganese carbonyl[9] can be replaced by two halogen ions, several configurations are possible for the resulting anion.[8] As there are only two C–O stretching modes in the infrared spectra of these compounds, the ions must possess very high symmetry. We find that no structure in which both halide ions are co-ordinated to only one metal atom has sufficient symmetry to possess only two infrared-active C–O stretching modes. Further, of the possible structures in which one halogen is attached to each metal atom, only two of these appear to be suitable from group-theoretical considerations. The D_{4h} structure (III) would be predicted to have two ($A_{2u} + E_u$) modes, and the D_{4d} structure (IV) would have only two infrared-active stretching modes ($B_2 + E_1$). We believe tentatively that the D_{4d} (IV) form would have the lower energy.

As the action of halogen on manganese carbonyl itself causes fission of the metal–metal bond and formation of a metal–halogen bond,[2,10] it was considered possible that reaction of the dihalogeno-octacarbonyldimanganates (III and IV) with halogen could produce the dihalogenotetracarbonylmanganates. From this reaction, provided no rearrangement took place, the *trans*-isomers (I) should be obtained. However, in all the conditions tried,

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[4] Abel, *Quart. Rev.*, 1963, **17**, 133.

[5] Eyring, Walter, and Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, 1944, p. 383.

[6] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4456; Orgel, *J. Inorg. Nuclear Chem.*, 1956, **2**, 137.

[7] Basolo and Wojcicki, *J. Amer. Chem. Soc.*, 1961, **83**, 520.

[8] El-Sayed and Kaesz, *Inorg. Chem.*, 1963, **1**, 158.

[9] Dahl and Rundle, *Acta Cryst.*, 1963, **16**, 419.

[10] Brimm, Lynch, and Sesney, *J. Amer. Chem. Soc.*, 1954, **76**, 3831.

halogens appear to cause complete decomposition of the dihalogeno-octacarbonyldimanganates.

EXPERIMENTAL

Infrared spectra were recorded on a Unicam S.P. 100 spectrophotometer with sodium chloride optics. Tetra-ethylammonium chloride tetrahydrate was dehydrated at 120°/0·1 mm., and other tetra-alkylammonium halides were dried over phosphorus pentoxide.

(*A*) *Reaction of Tetra-alkylammonium Halides with Manganese Pentacarbonyl Halides.*—The halide (~0·3 g.) was heated with a slight excess of the pentacarbonylmanganese halide (~0·5 g.) in diethyleneglycol dimethyl ether (20 c.c.) at 120° until evolution of carbon monoxide ceased. The mixture was filtered hot under nitrogen. Slow addition of light petroleum (b. p. 40—60°) (50 c.c.) to the cooled filtrate gave crystals of the *tetra-alkylammonium dihalogenotetracarbonylmanganate* (see Table 2). After decantation, the crystals were rapidly washed with light petroleum (2 × 20 c.c.) and any remaining solvent was removed at 20°/0·1 mm. Finally treatment at 60°/0·1 mm. for a short time ensured removal of any remaining excess of pentacarbonylmanganesehalide.

TABLE 2.

Method of prep.	$R_4N^+[Mn(CO)_4XY]^-$ R	X	Y	Yield (%)	Found (%) C	H	N	Mn	Hal	Required (%) C	H	N	Mn	Hal
A	Et	Cl	Cl	*										
A	Et	Br	Br	51	30·6	4·48		13·1	34·4	31·5	4·41		12·0	34·9
A	Et	I	I	40	25·7	3·72		9·1		26·2	3·66		10·0	
A	Bu	I	I	49	36·4	5·68	2·2	7·9	38·1 †	36·2	5·5	2·4	7·8	38·3 †
B	Et	I	I	66	25·9	3·89				26·2	3·66			
B	Et	I	Br	39	27·9	4·12				28·6	3·96			
B	Et	Br	I	31	27·6	3·86				28·6	3·96			
A	Et	Cl	Br	46	33·2	4·41				34·9	4·86			
A	Et	Br	Cl	76	33·5	4·37				34·9	4·86			
A	Et	Cl	I	55	31·7	4·68				31·4	4·35			
A	Et	I	Cl	41	31·6	4·50				31·4	4·35			
A	Et	Br	I	50	27·6	3·73	3·03	11·1		28·6	3·96	2·78	10·9	
A	Et	I	Br	60	27·6	4·04	2·63	10·7	15·8 ‡	28·6	3·96	2·78	10·9	15·9 ‡

* Not enough material for analysis, but spectrum recorded (Table 1). † Found: O, 9·7. Reqd.: O, 9·8%. ‡ Bromine.

(*B*) *Reaction of Tetra-alkylammonium Halides with the Dimeric Tetracarbonylmanganese Halides.*—The procedure was that described above. No carbon monoxide was evolved; however, as the temperature was raised from 20° to 110° there was a gradual darkening. Heating was continued until all the tetra-alkylammonium halide had disappeared (~2 hr.) and a slight evolution of carbon monoxide, due to decomposition, had started.

Reaction of Tetra-alkylammonium Halides with Manganese Carbonyl.—The halide (~0·5 g.) was heated with an excess (~1 g.) of manganese carbonyl in diethyleneglycol dimethyl ether (25 c.c.) at 140° until evolution of carbon monoxide ceased. The mixture was filtered hot under nitrogen. Addition of light petroleum (b. p. 40—60°) (50 c.c.) to the cooled filtrate caused precipitation of a coloured oil. After decantation, the oil was taken up in the minimum amount of chloroform. Slow addition of light petroleum then precipitated crystals of the *tetra-alkylammonium dihalogeno-octacarbonyldimanganates* (see Table 3). Solvent was decanted and the product washed with light petroleum (2 × 20 c.c.) and dried at 20°/0·1 mm.

TABLE 3.

X in $(Et_4N^+)_2[Mn_2(CO)_8X_2]^{2-}$	Yield (%)	Found (%) C	H	Mn	Hal	Required (%) C	H	Mn	Hal
Cl *	—								
Br	12·5	38·4	5·33			38·3	5·35		
I	40·0	33·9	4·71	12·0	29·2	33·9	4·75	12·9	29·9

* Insufficient obtained for analysis, but the spectrum is recorded in Table 1.

We thank the D.S.I.R. for financial support (I. S. B.) and the Ethyl Corporation for a generous gift of manganese carbonyl.

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[*Received, June* 15*th*, 1963.]