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Crown Ethers in Inorganic Chemistry. Preparation of Monohalide Derivatives of Manganese Carbonyl

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The anions ax-$Mn_2(CO)_9X^-$*(X = F, Cl, Br, I), in association with cations consisting of crown ethers and potassium ions, have been prepared photochemically. The infrared and ultraviolet–visible spectra have been recorded; the* $\sigma \rightarrow \sigma^*$ *electronic transition has been assigned.*

Introduction

Crown ethers have been utilized to increase the solubility of inorganic salts in organic media[1–6]. A crown ether is a cyclic ether with a ring of oxygen atoms capable of binding a cation (*e.g.,* K^+) in the ring. Pedersen has synthesized many crown ether complexes of simple inorganic salts[1,2,7]. The size of the bound cation is dependent on the size of the crown ring. The larger the ring, the less tightly bound would be Li^+ compared to a larger cation such as Cs^+. Recently the use of crown ethers has been reported in the preparation of the carbonyl derivatives $M(CO)_5X^-$ (M = Cr, W; X = F, OH)[8].

The photochemical preparation of complexes of formula $(OC)_5M–M(CO)_4L$ and $L(OC)_4M–M(CO)_4L$ have been reported[9–14] (reaction 1).

$$M_2(CO)_{10} + L \xrightarrow{h\nu} (OC)_5MM(CO)_4L + L \xrightarrow{h\nu} L(OC)_4MM(CO)_4L \quad (1)$$

Substitution *cis* or *trans* to the metal–metal bond is both solvent and ligand dependent. Several Lewis base complexes have been prepared and some structures have been determined[13,14]. It appears that good π acceptor and σ donor ligands add *trans*[15]. Ruff has reported anionic species where L is $SnCl_3$ and $GeCl_3$; these are π acceptor ligands but only monosubstituted derivatives were obtained. The reason for the product being limited to monosubstituted species only was postulated to be related to the charge on the complexes[16]. Several axially di-substituted dimetaldecacarbonyls of manganese and rhenium have been prepared by reaction of the appropriate decacarbonyl with tetraalkylammonium halide salts at elevated temperatures (*ca.* 120°C)[17,18]. The rhenium complexes were prepared in much lower yields than were the manganese analogues, and a completely satisfactory characterization is still lacking[18].

This paper reports the photochemical preparation of the axially substituted species $Mn_2(CO)_9X^-$ (X = F, Cl, Br, I) in association with a cation consisting of a crown ether and a potassium ion. The crown salts were used to surmount the oiling problem encountered by Ruff[16].

Experimental

$Mn_2(CO)_{10}$ was prepared by the method of King *et al.*[19] and sublimed before use. Dibenzo-18-crown-6 was prepared by the method of Pedersen[20]. All preparative work was carried out in a nitrogen atmosphere. Solvents were deoxygenated by purging with nitrogen.

Infrared spectra were recorded in the carbonyl region on a Beckman IR-12 spectrophotometer; KBr plates were used with the samples in $CHCl_3$. Ultraviolet–visible spectra in CH_3CN were recorded on a Cary 14 spectrometer.

[*Dibenzo-18-crown-6*][$Mn_2(CO)_9Br$]

$Mn_2(CO)_{10}$ (0.20 g, 0.51 mmol), dibenzo-18-crown-6 (0.20 g, 0.56 mmol) and KBr (0.20 g, 1.7 mmol) with 20 ml CH_2Cl_2 in a 100 ml flask were stirred together while irradiating with a Hanovia high pressure mercury vapor lamp at room temperature for 2 h. After filtration, petroleum ether (30–60°C) was added to the yellow filtrate to produce a fluffy pale yellow precipitate which was recrystallized twice from ethanol/petroleum ether to rid the product of uncomplexed dibenzo-18-crown-6. The yellow solid obtained was recrystallized from CH_2Cl_2/petroleum ether to give a bright yellow powder. The preparation and purification of the other derivatives were similar. Yields, decomposition points and elemental analyses are given in Table I.

An attempt to exchange Et_4N^+ for the crown-K^+ moiety on a Dowex 50 cation exchange column with methanol as the solvent resulted in decomposition of the anion. The crown-K^+ derivative (0.1 g) was stirred in a 20 ml aqueous solution of KX (0.1 g) (X = F,

TABLE I. Analytical Data on [Dibenzo-18-crown-6-K][$Mn_2(CO)_9X$].

X	% Yield	Decomposition Point (°C)[a]	Analysis %					
			Calcd.			Found		
			C	H	X	C	H	X
F	11	160–170	44.62	3.08	2.44	45.38	4.03	1.59
Cl	27	160–165	43.69	3.01	4.46	45.05	3.53	3.99
Br	60	165–170	41.38	2.85	9.51	41.78	3.31	9.90
I	70	175–180	39.19	2.70	14.30	38.51	3.13	14.26

[a] Gas evolution at approximately 150°C for all derivatives.

Cl, Br, I) in an attempt to draw off the crown to yield water soluble $KMn_2(CO)_9X$ with no success. An attempt to extract the crown-K^+ complex from CH_2Cl_2 into a 0.1 g KX in 20 ml H_2O solution was also unsuccessful. Attempts to separate the crown$_n$-K$_x$ (n = 1, 2, 3; X = 1, 2) species on an alumina column with CH_3CN as the solvent resulted in decomposition.

$Et_4N[Mn_2(CO)_9Br]$

$Mn_2(CO)_{10}$ (0.20 g, 0.51 mmol), Et_4NBr (0.20 g, 0.11 mmol) and 20 ml CH_2Cl_2 in a 100 ml flask were irradiated for 2 h. Petroleum ether (30–60°C) was added slowly to the resulting solution to produce a reddish oil. A small amount of a solid product whose infrared spectrum in the carbonyl stretching region matched that of the crown-K^+ derivative was obtained only with difficulty. Tetrabutylammonium salts were substituted for Et_4N^+ with no improvement of the oiling problem. Similar reactions were obtained for all halides except fluoride for which no isolatable product was obtained. All reactions led to the same oiling problem.

Our attempts to prepare the disubstituted species $Mn_2(CO)_8X_2^-$ (X = Cl, Br, I) according to the method of Abel and Butler[17] always led to the monosubstituted product. No evidence for the disubstituted material was found in the photochemical studies.

Discussion

The solid complexes are stable for several days at room temperature in air. All derivatives are of comparable stability. Once isolated in a pure form they are stable in $CHCl_3$ or CH_3CN solution over periods of 30 min to 1 h at room temperature and longer at 0°C. The crown-K derivatives do not have the oiling problem commonly found for R_4N^+ and $As(PPh)_4^+$[16] salts. Side products in the R_4N^+ reactions were obtained in trace quantities for the crown-K^+ complexes and were easily removed by recrystallization. A cleaner and higher yield is obtained for the crown-K^+ cation than in the Et_4N^+ synthesis. The disadvantages of K-crown salts have previously been discussed[8]. In the present work there is the possibility that mixed crown species may occur in the product purification. Evidence for this is seen in the elemental analyses (Table I), in analogy with data from Pedersen's work[1]. This phenomenon has been illustrated by Pedersen by varying the crown to K^+ ratio to yield crown-K^+, crown$_2$-K^+ and crown$_3$-K_2^{2+} salts simply by recrystallizing the product from various solvents[1]. A method for the purification of the crown-K^+ species would be very useful. The difficulty arises in that the method must be mild enough so as not to destroy the anionic complex.

The synthesis has its best results in solvents such as CH_2Cl_2, a non-coordinating solvent which leads primarily to the loss of CO and the formation of the axially substituted species in the $SnCl_3$ and $GeCl_3$ cases[16]. For the coordinating solvent tetrahydrofuran, the Mn–Mn bond is split, resulting in the formation of $Mn(CO)_5$[22,23].

The infrared spectra in the carbonyl stretching region are reported in Table II. The position, relative intensity and number of peaks match well with the $GeCl_3$, $SnCl_3$[16] and PPh_3[15] derivatives. Peak assignments are made by comparison to the $Mn_2(CO)_9PPh_3$ derivative[15]. The low intensity high energy band, only seen in the $GeCl_3$, $SnCl_3$, Br, and I derivatives, was also not assigned by Ruff[16]. The lowest energy band (~1900 cm^{-1}), which appears as a weak shoulder in all four complexes, does not appear in the PPh_3, $GeCl_3$ or $SnCl_3$ derivatives. While it may be a contaminant, it shows up consistently in the infrared even after a fresh sample is prepared; also, the intensity does not change with time. Another possibility is the production of a small amount of equatorially substituted[15] or disubstituted[17] product which could have bands in this range. The infrared is free of other peaks which may be attributed to these species, but it is possible they could be buried by the bands from the axially substituted species which is present in higher concentration. The intensities of the first and last weak bands are consistent with the

TABLE II. Infrared Data for $Mn_2(CO)_9X^-$ (X = F, Cl, Br, I) in $CHCl_3$[a].

X = F	Cl	Br	I	Assignment
–	–	2107 w	2078 w	–
2058 m	2057 m	2057 m	2055 m	$A_1(1)$
2014 ms	2016 ms	2015 s	2009 ms	$A_1(2)$
1988 s	1990 s	1985 s	1981 s	E(1)
1969 msh	1966 m	1968 m	–	$A_1(3)$
1945 msh	1947 msh	1942 msh	1944 msh	E(2)
1911 wsh	1910 wsh	1897 wsh	1901 wsh	–

[a] Energy in cm^{-1}.

infrared inactive B_1 and B_2 modes, but because of the previously mentioned possibilities the bands are not definitely assigned.

UV–visible data for the halide derivatives (Table III) match that for $Mn_2(CO)_9PPh_3$[23] with respect to position, number, and relative intensity of bands. Band I, a shoulder on the more intense second band, is assigned $d_\pi \rightarrow \sigma^*$. This transition is expected to decrease in energy as the halides are changed from fluoro to iodo. From the arguments of Coffey *et al.* Band I is predicted to shift to lower energy with a weaker ligand replacing a CO since the d_π electrons should be destabilized[24]. As the ligand is changed the X_π orbitals shift to higher energy, destabilizing the d_π electrons and thus lowering the energy of the transition. This assignment assumes the X_π orbitals to be below the d_π levels (Figure 1) as in the Group VI pentacarbonyl derivatives[25,26]. This is not unreasonable since the manganese is zerovalent. Were the first band an $X_\pi \rightarrow \sigma^*$ transition, the halo derivatives would be expected to shift to lower energy with ligand than is seen, by analogy to the spectra of the $Mn(CO)_5X$ (X = Cl, Br, I) complexes. Also, for the iodo complex the peak would be expected to split from spin–orbit coupling as noted for $Mn(CO)_5I$[27]. This behavior is not seen, supporting the correctness of the present assignment. Transitions from the X_π level are expected to occur at higher energy and to be buried under the more intense peaks. Not surprisingly, the fluoro derivative appears as an anomaly in the series; in recent photochemical studies on Cr(III) complexes this ligand does not fit into the pattern of reactivity or electronic structure[28] predicted by the spectrochemical series. The band in the fluoro complex has the lowest energy of the derivatives, possibly due to its small size which would allow closer approach to the metal and thus increase the X_π–d_π repulsion above that otherwise expected.

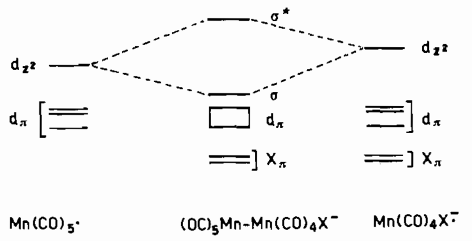

Figure 1. Scheme of orbital energy levels.

Band II, assigned as the $\sigma \rightarrow \sigma^*$ transition, is independent of substituted ligand. Both σ and σ* levels can be

TABLE III. Electronic Spectra and Assignments of [Dibenzo-18-crown-6-K][$Mn_2(CO)_9X$] (X = F, Cl, Br, I) in CH_3CN.

X	Band I $d_\pi \rightarrow \sigma^*$	Band II $\sigma \rightarrow \sigma^*$	Band III $\sigma \rightarrow \pi^*(CO)$	Band IV crown	Band V crown	Band VI $M(d\pi,\sigma) \rightarrow \pi^*(CO)$
F	20,300[a] (1,780)	27,700 (5,340)	–	35,500 (11,000)	36,480 (12,800)	44,070 (48,500)
Cl	21,800 (2,360)	27,820 (6,000)	–	35,760 (8,950)	36,740 (10,950)	44,270 (41,160)
Br	21,640 (1,822)	27,820 (5,590)	–	35,710 (11,930)	36,710 (14,260)	44,500 (58,528)
I	21,370 (1,940)	27,090 (5,390)	33,160 (6,000)	35,770 (15,200)	36,820 (17,540)	44,310 (31,280)

[a] Peak position in cm^{-1} (ε).

expected to shift uniformly as the ligand is varied, thereby maintaining a reasonably constant transition energy, independent of ligand.

Band III, assigned as $\sigma \rightarrow \pi^*$ (CO), is seen only in the iodo derivative. This band may be more sensitive to halide than Band 1 because of X_π–d_σ interaction; that is, while the σ level may change in energy as noted for Band II, the π^*(CO) level will remain relatively constant. If this assignment is correct, then the ligand destabilizing the σ electrons the most should yield the lowest energy band; this is predicted and observed for the iodo derivative. The other derivatives probably have this peak buried under Bands IV and V.

Bands IV and V are derived from the crown-K^+ complex and shift slightly with anion as discussed by Pedersen[7]. Band VI is assigned as $M(d_\pi,\sigma) \rightarrow \pi^*(CO)$. The intensity of the band shows it to be CT and probably the result of many overlapping bands.

Only the monoaxially substituted species could be isolated from the reaction, with no indication of the diaxially substituted derivative reported for the thermal preparation[17]. Ruff could not obtain the disubstituted anion with π acceptor anionic ligands[15]. An attempt to irradiate $Mn_2(CO)_9X^-$ in the presence of X^- led only to rapid decomposition with small amounts of a tribridged material being produced[29]; no diaxially substituted product was formed. The ligands which form diaxially substituted derivatives differ from the present ligands in that they are neutral and π acceptors. The lack of, or decreased π acceptor ability of the anionic ligands indicates a lesser d_π stabilization than in $Mn_2(CO)_9PPh_3$. This destabilization would have the d_π electrons more available to the π^*(CO) orbitals. Increased d_π backbonding would then decrease the possibility of further loss of CO from the complex. The inability to photochemically prepare the diaxially substituted species and the failure to repeat the thermal preparation[17] leave the existence of the $Mn_2(CO)_8X_2^{2-}$ derivatives open to question.

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