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The Aquopentacarbonylmanganese(I) Cation

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The aquopentacarbonylmanganese(I) cation, $[Mn(CO)_5(H_2O)]^+$, has been postulated [1] as one of the products of the acidic hydrolysis of the 3- and 4-pyridiomethylmanganesepentacarbonyl cations in aqueous solution. The workers did not isolate or characterize the complex. However, recent work [2] suggests that this compound may need to be reformulated as $[Mn(CO)_3(H_2O)_3]^+$. We have shown [3] that the perchlorato complex, $Mn(CO)_5(OClO_3)$, is a versatile reagent for the preparation of cationic pentacarbonyl complexes of manganese(I), and the aforementioned work prompts us to report the reaction of this complex with water.

When a dichloromethane solution of $Mn(CO)_5(OClO_3)$ [3] was vigorously stirred for 30 minutes with a small amount of water at room temperature under an atmosphere of nitrogen, the yellow colour disappeared from the organic phase and was transferred to the aqueous phase. The reaction is shown in equation (1):

$$Mn(CO)_5(OClO_3) + H_2O \rightarrow [Mn(CO)_5(H_2O)]ClO_4 \qquad (1)$$

The aqueous solution of the product slowly evolved carbon monoxide on standing at room temperature and attempts to concentrate the solution in a vacuum resulted in vigorous effervescence (presumably of carbon monoxide). The product is very soluble in water and could only be precipitated by adding solid sodium tetraphenylborate; this gave bright yellow microcrystals of $[Mn(CO)_5(H_2O)]BPh_4 \cdot nH_2O$ in low yield (25%).† The solid complex is unstable at room temperature and decomposes over a period of 24 hours, giving brown crystals. $[Mn(CO)_5(H_2O)]BPh_4 \cdot nH_2O$ is soluble in both polar organic (Me_2CO, MeOH, MeCN, $MeNO_2$) and chlorinated hydrocarbon (CH_2Cl_2, $CHCl_3$) solvents and even in wet diethyl-

TABLE I. Infrared Spectrum of $[Mn(CO)_5(H_2O)]BPh_4$.

Assignment	Nujol	Frequency (cm^{-1})	Acetone
		Wet ether	
lattice H_2O, ν(OH) free	3632 w,shp 3561 w,shp		
lattice H_2O, ν(OH) H bonded	3425 sh		
coord. H_2O, ν(OH)	3386 ms,br		
aromatic ν(C–H)	3055 mw		
ν(CO), (A_1^{1b})	2169 w	2148 w	2146 w
ν(CO), (B_1)	2122 ms	2092 sh	
ν(CO), (E)	2079 vs 2066 vs	2060 vs	2059 vs
ν(CO), (A_1^{1a})	2036 vs	2008 s	2020 s
		1945 ms	
δ(H_2O	1610 w		
ν(C=C)	1580 w		
C–H out of plane def.	744 s 715 s		
δ(MCO)	630 s 543 w		
ν(M–C)	399 ms		

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†Complete precipitation of the product could not be achieved.

ether, although it is insoluble in dry ether and benzene.

The carbonyl stretching frequencies of the complex in various media are recorded in Table I. The local symmetry of the carbonyl groups is C_{4v} and hence, three carbonyl stretching fundamentals ($2A_1$ + E) are expected [4, 5]. Three of the four bands observed in the solid-state spectrum can be assigned to these modes of vibration, while the band at 2122 cm^{-1} is assigned as the B_1 mode, which is infra-red inactive for rigorous C_{4v} symmetry. Its appearance may be due to crystal effects lowering the symmetry of the complex. Alternatively, the hydrogen bonding between the lattice water and the co-ordinated water molecules (see below) will result in a reduction in the symmetry of the complex. Under these conditions, splitting of the E mode should occur [4, 5] and this is indeed observed. The B_1 absorption is also present in the infra-red spectra of the fluoro anions $[M(CO)_5F]^-$ (M = Cr, W) [6, 7] and of phosphine-substituted complexes of the type $Cr(CO)_5PR_3$ [5].

The infra-red spectrum in wet diethylether shows, in addition to the three expected modes of vibration, a shoulder due to the B_1 mode and a band of medium intensity at 1945 cm^{-1}; the origin of the latter band is at present uncertain. Extra bands in this region have been observed in the spectra of acyl complexes of the formula $RCORe(CO)_5$ [4]. The carbonyl stretching frequencies of the aquo complex in acetone are similar to those of $[Mn(CO)_5(Me_2CO)]^+$ [8] and this may be indicative of substitution by the solvent. The aquo ligand is displaced in acetonitrile solution giving $[Mn(CO)_5(MeCN)]^+$.

The solid-state spectrum shows bands due to both co-ordinated water [9, 10] and lattice water, one arm of which is hydrogen bonded and the other is free [11]. Hydrogen bonding between the lattice water molecules and the aquo ligand is thought to be responsible for the reduction in the symmetry of the complex as mentioned above.

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