Electronic Spectra of some Pentacarbonylhalogenometal Complexes and Related Species

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U.v. and visible absorption spectra of the complexes [M(CO)$_5$X] (M = Mn, Re, Cr, Mo, or W; X = Cl, Br, or I) are reported. These and spectra of [Mn(CO)$_5$X] (X = H, Me, CF$_3$, and SiH$_3$) and other metal carbonyl halide complexes are assigned using a molecular-orbital bonding picture based on recent approximate calculations and photoelectron spectra of these species. The highest-filled orbital of the halogeno-complexes is considered to have part metal d_π and part halogen p_π character. The unique lowest-energy band, which gives rise to the colour of these complexes and is not present in the other metal pentacarbonyl species discussed, is assigned to a $^1A_1\rightarrow{}^1E$ transition with electron transfer from this highest-filled orbital to a mainly σ^* orbital of the metal–halogen bond. This is in contrast to earlier assignments which considered the acceptor orbital to have mainly π^*(CO) character.

ALTHOUGH a considerable amount of work has been done on the interpretation of vibrational spectra [1] of metal carbonyl complexes, until recently very few assignments of electronic spectra of these species had been attempted. This is quite contrary to the situation with most metal complexes and needs rectification. The appearance of good molecular-orbital (m.o.) calculations [2-6] and photoelectron (p.e.) spectra [7-10] of some metal carbonyl complexes has prepared the way for a more thorough study of their electronic spectra.[11]

The first electronic spectra of metal carbonyl halide species reported were those of [Fe(CO)$_4$Br$_2$] and [Fe(CO)$_4$I$_2$] by Hieber and Bader.[12] In contrast to the parent Fe(CO)$_5$, these species have strong bands in the visible region, a standard feature of electronic spectra of metal carbonyl halides. In 1941, Schuh,[13] in a paper which seems to have been passed over by later workers, carried out a thorough study of electronic spectra of pentacarbonylhalogenorhenium complexes. Although he made the erroneous assignment of bands to transitions of radical decomposition products, he made some interesting observations on solvent shifts.

Lundquist and Cais [14] made some attempt at assignment of electronic spectra of metal carbonyls, but the first attempt at assignment based on m.o. theory was by

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Gray *et al.*[15] They assigned the lowest-energy band in pentacarbonylhalogenomanganese complexes to a transition from the highest-filled metal d_{xy} orbital (b_2) to the lowest π^* CO orbital (e) which was postulated to be situated mainly on the unique axial CO group. This one-electron m.o. picture was challenged by Braterman *et al.*[16-19] On the basis of a simple Hückel picture neglecting overlap and inter-ligand repulsion, they postulated that the metal $d_{xz,yz}$ was the highest-filled orbital and that the lowest-empty orbital had a_1 symmetry (*i.e.* situated on the equatorial CO groups). Comparison of spectra of $[\mathrm{M(CO)_5L}]$ and *trans*-$[\mathrm{M(CO)_4L_2}]$ species [M = Cr, Mo, or W; L = $\mathrm{(PhO)_3P}$, $\mathrm{(Me_2N)_3P}$, or $\mathrm{Ph_3P}$] seemed to add support to the view that the unique CO π^* levels were not involved in the lowest-energy electronic transition.[17,19] P.e. spectra of some $[\mathrm{Mn(CO)_5X}]$ species[10] indicated that the symmetry of the highest-energy orbital was in fact e.

However, although this orbital would be mainly metal $d_{xz,yz}$ for most ligand-substituted pentacarbonyls, for pentacarbonyliodomanganese it clearly has considerable iodine p character because of the observed spin-orbit splitting of the p.e. band. This was also indicated by broadening of the first band in the electronic spectrum of the complex $[\mathrm{Mn(CO)_5I}]$ compared to those in $[\mathrm{Mn(CO)_5Br}]$ and $[\mathrm{Mn(CO)_5Cl}]$.[11] P.e. spectra of $[\mathrm{Mn(CO)_5X}]$ species (X = Cl, Br, or I)[10b] indicated the following order for ionisation from the highest-filled orbitals, *e.g.* in $[\mathrm{Mn(CO)_5Cl}]$ $8e(p_\pi\ \mathrm{X})$ — 8·94 eV $>$ $9a_1(\sigma\ \mathrm{Mn{-}X})$ — 9·56 eV $>$ $7e(d_{xz}d_{yz}\ \mathrm{Mn})$ — 10·56 eV $>$ $2b_2(d_{xy}\ \mathrm{Mn})$ — 11·18 eV. Since in simple metal carbonyls* and carbonyl nitrosyls the d electrons are ionised normally between 8 and 9·5 eV (*e.g.* in $\mathrm{Cr(CO)_6}$ — 8·4 eV[8]) and no other chlorine p_π orbital has been ionised below 10·5 eV, this order seems a little odd, at least for the pentacarbonylchloro-complex.

It had earlier been shown that approximate m.o. treatments could give a satisfactory picture of the bonding, p.e. and electronic spectra of simple metal carbonyls,[20-22] and be in reasonable agreement with a more accurate treatment.[2] Four sets of calculations have been carried out recently on $[\mathrm{M(CO)_5X}]$ species.[3-6] In agreement with the p.e. results and the theory of Braterman *et al.*,[16-19] it has been shown[5] that in the species $[\mathrm{Mn(CO)_5H}]$ the filled d orbitals are in the order $e(d_{xz,yz}) > b_2(d_{xy})$. The same result was obtained with all the other $[\mathrm{M(CO)_5X}]$ species studied by Fenske and his co-workers.[3-5] For the pentacarbonylhalogeno-complexes the calculations indicate that the highest-filled energy level has mainly halogen p_π character. However calculations of Fenske and his co-workers[3,4,11] showed the highest-filled a_1 level ($9a_1$) to be in the same region as the metal d_π and halogen p_π electrons and remeasurement of the p.e. spectrum[10b] confirmed this. These calculations therefore appear to give a better picture of the bonding in $[\mathrm{M(CO)_5X}]$ species and should be used for assignment of electronic spectra.

After much of this paper had been written, Hall and Fenske's m.o. calculations[3] on many of the molecules discussed here were published. In this work, they modified earlier calculations on $[\mathrm{Mn(CO)_5X}]$ species[5] and extended them to corresponding anionic and cationic complexes, $[\mathrm{Cr(CO)_5X}]^-$ and $[\mathrm{Fe(CO)_5X}]^+$. Excellent agreement was found between trends in non-rigorous carbonyl force constants and 5σ and 2π orbital occupancies, so one can have some confidence in the other results produced. As we shall see in the discussion of the m.o. picture for $[\mathrm{M(CO)_5X}]$ species, there is considerable support for our earlier qualitative arguments[11] in the results of these calculations.

Recently the spectra of $[\mathrm{Mn(CO)_5X}]$ (X = Cl, Br, I, H, Me, or $\mathrm{CF_3}$) species have been remeasured and reassigned.[23] The spectra of the halides are in agreement with those obtained by the present author, but show some differences to those reported earlier.[15] The assignments were based on a simple one-electron molecular picture taking due note of the p.e. results and calculations. There is little justification for this type of approach which neglects electron correlation and configuration interaction. However, it should be suitable for assigning a band or group of bands of similar origin which are well separated from the others and for comparing isoelectronic series of molecules. The present approach is to give data on a number of pentacarbonylhalogenometals (particularly the anions of Group VI) and related species and to make appropriate qualitative correlations and comparison with recent m.o. calculations, to aid assignment.

Besides the tetracarbonyldihalogenoiron and Group VII pentacarbonylhalogeno-complexes, a number of other carbonyl halide species have had their electronic spectra published. Examples are as follows: $[\mathrm{Mn(CO)_4(L)Br}]$ [L = $\mathrm{P(OR)_3}$, $\mathrm{PR_3}$, $\mathrm{P(OPh)_3}$, $\mathrm{PPhCl_2}$, $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$, or $\mathrm{SbPh_3}$];[24] *cis*- and *trans*-$[\mathrm{Mn(CO)_3\{P(OPh)_3\}_2Br}]$;[25] $[\mathrm{(cp)Mo(CO)_3Cl}]$ and $[\mathrm{(cp)Mo(CO)_3I}]$ (cp = η-cyclopentadienyl) and Lewis-base substituted derivatives;[26,27] $[\mathrm{(cp)Co(CO)X}]$;[28] and $[\mathrm{Ir(CO)(X)L_2}]$ and $[\mathrm{Ir(CO)(X)L_2H_2}]$.[29]

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EXPERIMENTAL

Electronic Spectra.—Electronic spectra were recorded on Cary 14 and Unicam SP 700 spectrophotometers using solutions in 1, 2, 5, or 10 mm ' Spectrosil ' quartz cells, and were calibrated with a holmium standard. Preliminary spectra were run on a Unicam SP 800 spectrophotometer and rerun on the other instruments to check for reproducibility. All solvents used (cyclohexane, hexane, iso-octane, methanol, chloroform, and water) were Spectrosol grade, purged and stored under a nitrogen atmosphere. Between 185 and 200 nm spectra were recorded on the SP 700 with constant purging of the optical path of the instrument with dry nitrogen. Errors in the positions of the distinct maxima given in the Tables are estimated as ± 100 cm^{-1} with a reproducibility of ± 50 cm^{-1}. Gaussian analyses were carried out by hand on all spectra to resolve shoulders and for these the errors are estimated as ± 100 cm^{-1}. Previous attempts to use a curve-fitting computer program to analyse electronic spectra of the metal carbonyls failed to produce significantly better results than this.[19] Solutions were made up using *ca.* 2 mg of complex in 10 cm^3 solvent in a standard flask and diluted with standard syringes and flasks. With this technique, errors in absorption coefficients are estimated to be *ca.* 10%.

TABLE 1

Analyses (%) *

Complex	C	H	Halogen
$[Mn(CO)_3\{(Ph_2PCH_2)_2\}Cl]$	60·55 (60·79)	4·35 (4·19)	6·25 (6·20)
$[Mn(CO)_3\{(MeSCH_2)_2\}Cl]$	28·75 (28·34)	3·4 (3·37)	12·3 (11·98)
$[Mn(CO)_3\{(MeSeCH_2)_2\}Cl]$	21·1 (21·51)	2·45 (2·56)	9·35 (9·09)
$[Mn(CO)_3\{(MeSeCH_2)_2\}Br]$	19·55 (19·31)	2·25 (2·30)	18·7 (18·37)

* Calculated values are given in parentheses.

Preparation of Complexes.—The following complexes were prepared by standard methods: $[Mn(CO)_5X]$ (X = Cl, Br, or I);[30,31] $[Re(CO)_5X]$ (X = Cl, Br, or I);[31,32] $[Et_4N][M(CO)_5X]$ (M = Cr, Mo, or W; X = Cl, Br, or I);[33] $[Mn(CO)_3(L_2)Cl]$ [L_2 = 2 pyridine (py), $\{(MeSCH_2)_2\}$, $\{(MeSeCH_2)_2\}$, or 2,2′-bipyridine (bipy)];[30] $[Mn(CO)_3(L_2)X]$ [L_2 = bipy, $\{(MeSCH_2)_2\}$, $\{(MeSeCH_2)_2\}$, or $\{(Ph_2PCH_2)_2\}$; X = Br or I];[30] $[Mn(CO)_5(SiMe_3)]$;[34] $[Mn(CO)_5(GeMe_3)]$;[35] $[Mn(CO)_5(SnMe_3)]$;[36] $[Mn(CO)_5Et]$;[37] and $[Mn(CO)_5H]$.[38] The complex $[Mn(CO)_3\{(Ph_2PCH_2)_2\}Cl]$ could not be prepared by the standard thermal method.[39] It was prepared by irradiation of an equimolar quantity of 1,2-bis(diphenylphosphino)ethane and pentacarbonylchloromanganese in methanol with a Hanovia medium-pressure mercury lamp for 3 h at room temperature. Evaporation of the solvent and recrystallisation of the yellow product from light petroleum produced an almost quantitative yield of $[Mn(CO)_3\{(Ph_2PCH_2)_2\}Cl]$. The new *compounds* $[Mn(CO)_3\{(MeSCH_2)_2\}Cl]$, $[Mn(CO)_3\{(MeSeCH_2)_2\}Cl]$, $[Mn(CO)_3\{(MeSeCH_2)_2\}Br]$, and $[Mn(CO)_3\{(Ph_2PCH_2)_2\}Cl]$ gave satisfactory elemental analyses as listed in Table 1.

RESULTS

All spectra listed in this work were measured immediately and then further measurements were made over a period of time to determine the presence of bands due to decomposition products (*e.g.* tetracarbonyldihalogenomanganese dimers in the case of pentacarbonylhalogenomanganese [23]).

(a) $[Mn(CO)_5R]$ (R = H,[23,40,41] Me, Et, CF_3, $SiMe_3$, $GeMe_3$, *and* $SnMe_3$ [42]).—There is good agreement between the different sets of published data [14,23] for the complexes $[Mn(CO)_5Me]$ and $[Mn(CO)_5(CF_3)]$ so only the most recent results [23] are quoted in Table 2. For the complex $[Mn(CO)_5H]$ there is excellent agreement for the high-intensity maximum below 50 000 cm^{-1}, but Beach [40] reports a shoulder at 38 500 cm^{-1} which was not observed by other workers.

(b) $[Mn(CO)_5X]$ (X = Cl, Br, *or* I).—As mentioned previously, results of the present author (Table 2) for penta-

TABLE 2

Electronic spectra

Complex	Solvent	$\nu_{max.}$/cm^{-1} (ε/l mol^{-1} cm^{-1}) [a]	Assignment	Ref.
$[Mn(CO)_5H]$	*b*	34 500 [0·1], 46 730 [0·75], 51 300 [1·0]		23
$[Re(CO)_5H]$	*b*	37 000 [0·25] 47 280 [1·46], 50 630 [1·72]		23
$[Mn(CO)_5Me]$	*b*	36 500 [0·07], 45 660 [0·6], 52 000 [0·7]		23
$[Mn(CO)_5(CF_3)]$	*b*	37 000 [0·9], 47 170 [0·9], 52 600		23
$[Mn(CO)_5(SiH_3)]$	*b*	50 000		42
$[Mn(CO)_5Me]$	*c*	35 500 (3 000), 45 050 (28 000), 51 020 (36 000)		23
$[Mn(CO)_5Et]$	*c*	35 000 (2 800), 46 500 (22 000), 51 280 (50 000)		*d*
$[Mn(CO)_5(SiMe_3)]$	*c*	37 040sh (400), 47 620 (9 000)		*d*
$[Mn(CO)_5(GeMe_3)]$	*c*	36 360sh (300), 47 620 (8 000)		*d*
$[Mn(CO)_5(SnMe_3)]$	*c*	44 600sh (7 000), 50 000 (80 000)		*d*
$[Mn(CO)_5Cl]$	*e*	26 750 (650)	(A)	
		42 500sh (1 060)	(b′)	
		43 800 (12 000)	(B)	
		51 000 (14 000)	(C)	
		26 550 (675)	(A)	
		43 100sh (1 000)	(b′)	
		44 800 (13 200)	(B)	
		51 350 (15 000)	(C)	

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TABLE 2 (*Continued*)

Complex	Solvent	$\nu_{max.}$/cm^{-1} (ε/l mol^{-1} cm^{-1}) [a]	Assignment	Ref.
[$Mn(CO)_5Br$]	*e*	25 970 (400)	(A)	
		36 500 (1 800)	(A′)	
		41 670sh (1 000)	(b′)	
		43 100 (13 000)	(B)	
		50 500d (12 000)	(C)	
	f	26 100 (465)	(A)	
		37 040 (1 500)	(A′)	
		42 200sh (1 000)	(b′)	
		44 050 (12 600)	(B)	
		50 000 (10 000)	(C)	
	g	25 880 (420)	(A)	
	h	26 000 (400)	(A)	
	i	25 900 (340)	(A)	
[$Mn(CO)_5I$]	*e*	23 470 (320)	(A)	
		32 600 (3 140)	(A′)	
		42 000 (24 400)	(B)	
		50 250 (60 000)	(C)	
	f	25 130 (300)	(A)	
		33 100 (2 900)	(A′)	
		42 700 (19 900)	(B)	
		50 000 (45 000)	(C)	
	g	24 630 (330)	(A)	
[$Re(CO)_5Cl$]	*e*	28 700 (400)	(a)	
		30 770 (1 700)	(A)	
		33 000 (650)	(a′)	
		37 000 (1 500)	A′)	
		42 900 (20 000)	(B′)	
		47 170 (65 000)	(B)	
		52 600 (50 000)	(C)	
	f	29 070 (500)	(a)	
		31 130 (1 900)	(A)	
		33 000 (700)	(a′)	
		36 230 (1 300)	(A′)	
		44 150 (23 000)	(B′)	
		48 540 (70 000)	(B)	
		54 050 (100 000)	(C)	
	g	29 150 (800)	(a)	
		31 150 (1 800)	(A)	
		33 300 (700)	(a′)	
		37 040 (1 400)	(A′)	
[$Re(CO)_5Br$]	*e*	38 000 (500)	(a)	
		30 200 (1 500)	(A)	
		32 150 (600)	(a′)	
		36 900 (1 500)	(A′)	
		41 000sh (1 500)	(B′)	
		46 100 (35 000)	(B)	
		50 000 (32 000)	(C)	
	f	28 820 (618)	(a)	
		31 150 (1 670)	(A)	
		33 000 (300)	(a′)	
		37 310 (1 680)	(A′)	
		41 670 (2 000)	(B′)	
		45 450 (33 400)	(B)	
		50 000 (25 000)	(C)	
[$Re(CO)_5I$]	*e*	27 600 (200)	(a)	
		30 210 (2 100)	(A)	
		32 260sh (700)	(a′)	
		36 500 (2 600)	(A′)	
		45 000 (36 000)	(B)	
	f	27 320 (240)	(a)	
		30 000 (2 000)	(A)	
		31 950 (800)	(a′)	
		36 360 (2 450)	(A′)	
		45 450 (37 000)	(B)	
	g	29 670 (2 200)	(A)	
[$Cr(CO)_5Br$]$^-$	*f*	22 570 (840)	(A)	
		28 820sh (200)	(a)	
		40 320 (24 000)	(B)	
		45 450 (3 000)	(b)	
		50 510 (30 000)	(C)	
[$Cr(CO)_5I$]$^-$	*f*	22 830 (1 000)	(A)	
		28 740sh (200)	(a)	
		39 530 (18 000)	(B)	
		44 400sh (1 100)	(b)	
		45 870 (22 800)	(D)	
		50 250 (17 000)	(C)	
[$Mo(CO)_5Cl$]$^-$	*f*	24 570 (2 156)	(A)	
		28 570sh (250)	(a)	
		31 750sh (300)	(b)	
		39 220 (25 000)	(B)	
		43 670sh (1 000)	(c)	
		49 500 (15 000)	(C)	
[$Mo(CO)_5Br$]$^-$	*f*	24 630 (2 150)	(A)	
		32 050sh (300)	(b_1)	
		34 500sh (300)	(b)	
		39 700 (30 000)	(B)	
		46 300 (28 000)	(D)	
		50 510 (20 000)	(C)	
[$Mo(CO)_5I$]$^-$	*f*	24 500 (1 500)	(A)	
		32 050sh (150)	(b)	
		34 500sh (200)	(b)	
		39 700 (30 000)	(B)	
		46 300 (28 000)	(D)	
		50 510 (20 000)	(C)	
[$W(CO)_5Cl$]$^-$	*f*	24 000 (3 100)	(A)	
		26 040sh (900)	(a)	
		33 300sh (550)	(b)	
		40 650 (60 000)	(B)	
		46 950sh (2 000)	(c)	
		50 760 (10 000)	(C)	
	j	24 450 (3 000)	(A)	
		26 320sh (600)	(a)	
		33 300sh (300)	(b)	
		40 820 (55 000)	(B)	
		47 620sh (10 000)	(C)	
[$W(CO)_5Br$]$^-$	*f*	24 040 (3 500)	(A)	
		26 320sh (800)	(a)	
		33 100sh (300)	(b)	
		40 500 (70 000)	(B)	
		46 500sh (15 000)	(C)	
		50 760 (30 000)	(C)	
	j	24 450 (3 200)	(A)	
		26 320sh (600)	(a)	
		33 300sh (300)	(b)	
		40 650 (65 000)	(B)	
		46 510sh (12 000)	(c)	
[$W(CO)_5I$]$^-$	*f*	24 630 (2 750)	(A)	
		29 000 (270)	(a)	
		30 000 (1 400)	(b)	
		40 400 (47 000)	(B)	
		47 200 (75 000)	(D)	
		50 750 (60 000)	(C)	
[$Mn(CO)_3(py)_2Cl$]		25 900 (1 500)		
[$Mn(CO)_3(py)_2Br$]		25 900 (1 700)		
[$Mn(CO)_3(py)_2I$]		25 770 (1 800)		
[$Mn(CO)_3(bipy)Br$]		24 900 (2 500)		
[$Mn(CO)_3(bipy)I$]		24 210 (2 300)		
[$Mn(CO)_3$-{$(Ph_2PCH_2)_2$}Cl]		25 970 (1 000)		
[$Mn(CO)_3$-{$(Ph_2PCH_2)_2$}Br]		25 770 (1 100)		
[$Mn(CO)_3$-{$(Ph_2PCH_2)_2$}I]		25 190 (800)		
[$Mn(CO)_3$-{$(MeSCH_2)_2$}Cl]		26 040 (1 200)		
[$Mn(CO)_3$-{$(MeSCH_2)_2$}Br]		25 840 (750)		
[$Mn(CO)_3$-{$(MeSCH_2)_2$}I]		25 300 (650)		
[$Mn(CO)_3$-{$(MeSeCH_2)_2$}Cl]		25 840 (750)		
[$Mn(CO)_3$-{$(MeSeCH_2)_2$}Br]		25 710 (1 200)		
[$Mn(CO)_3(Me_2As\cdot$-$C_6H_4\cdot AsMe_2)Br$]		25 770 (780)		
[$Mn(CO)_3(Me_2As\cdot$-$C_6H_4\cdot AsMe_2)I$]		25 380 (935)		

[a] Relative intensities in [ ] and ε in ( ). [b] Vapour phase. [c] Cyclohexane. [d] This work. [e] Iso-octane or cyclohexane. [f] Methanol. [g] Chloroform. [h] Benzene. [i] Diethyl ether. [j] Water.

carbonylhalogenomanganese complexes are in excellent accord, both with respect to band positions and intensities, with values given by Blakney and Allen.[23] The latter authors observed one additional high-energy band not observed here due to instrument limitations. However, the most interesting comparison between the two sets of data arises in the small, but significant, solvent shifts in the distinct maxima at 26 000 (A) and 45 000 cm^{-1} (B). On changing from a non-polar to a polar solvent (cyclohexane or iso-octane to methanol), the following shifts (in cm^{-1}) occurred where + indicates a high-energy shift (Other workers' [23] values are in parentheses):

$[Mn(CO)_5Cl]$	(A)	−200 (−150)
	(B)	+1 000 (+1 000)
$[Mn(CO)_5Br]$	(A)	+130 (+130)
	(B)	+950 (+940)
$[Mn(CO)_5I]$	(A)	+1680 (+1470)
	(B)	+700 (+700)

The remarkable agreement between the two sets of data suggests that the actual reproducibility of the present results is considerably better than the theoretical ± 50 cm^{-1} quoted in the Experimental section. Also it indicates that solvent shifts for bands (A) in the complexes $[Mn(CO)_5Cl]$ and $[Mn(CO)_5Br]$ are indeed significant.

Band (A) in the complex $[Mn(CO)_5Br]$ was investigated in five solvents (Table 2). Although the shifts observed are only just significant compared to the corresponding band in $[Mn(CO)_5I]$, the bathochromic shifts in chloroform and diethyl ether contrast with the hypsochromic shift in methanol. These shifts, obviously not proportional to solvent polarity, must be connected to some highly specific solvent–solute interactions. For the complex $[Mn(CO)_5I]$, band (A) has its maximum at lower energy in chloroform than in methanol, but it is much lower in iso-octane. The half-width of the band indicates that transitions to two excited states are involved.

(c) $[Re(CO)_5X]$ (X = Cl, Br, *or* I).—Pentacarbonylhalogenorhenium complexes have more bands in their spectra below 53 000 cm^{-1} than those of manganese (Table 2), and the high-energy shift of the lowest-energy bands results in colourless species. There is still a relatively intense, low-energy, band (A), now at 30 000 cm^{-1}, but it has weaker bands 2 000 cm^{-1} above and below it. A very intense band, which appears to correspond to band (B) for the $[Mn(CO)_5X]$ species, is also apparent at 45 000—48 000 cm^{-1}. In the $[Mn(CO)_5X]$ species there is one distinct band at *ca.* 35 000 cm^{-1} and a shoulder on band (B) between (A) and (B). In the $[Re(CO)_5X]$ complexes a similar distinct band (at *ca.* 36 000 cm^{-1}) and shoulder were observed.

The solvents shifts (in cm^{-1}) from a non-polar (cyclohexane) to a polar solvent (methanol) for bands (A) and (B) were as follows:

$[Re(CO)_5Cl]$	(A)	+380
	(B)	+1 370
$[Re(CO)_5Br]$	(A)	+640 (+800)
	(B)	−650
$[Re(CO)_5I]$	(A)	−210 (−106)

These results are quite different from those of the $[Mn(CO)_5X]$ complexes. In this case the iodide does not show a large bathochromic shift and in fact has a small hypsochromic shift. This confirms Schuh's [13] early results, although he also reported a shift of *ca.* +1 000 cm^{-1} for band (A) in $[Re(CO)_5Cl]$ compared to the present +380 cm^{-1}.

(d) $(Et_4N)[M(CO)_5X]$ (M = Cr, Mo, *or* W; X = Cl, Br, *or* I).—Spectra for all the $[M(CO)_5X]^-$ ions except $[Cr(CO)_5Cl]^-$ (which decomposed too rapidly) are reported in Table 2. The profiles of the spectra are very similar to those of the $[M(CO)_5X]$ species with a moderately intense band (A) *ca.* 15 000 cm^{-1} lower in energy than the first of two or three high-intensity bands. One or two weak shoulders at *ca.* 30 000 cm^{-1} appeared to increase slightly in intensity with time but they are included as they were always present in the original spectra. Bands of the ions $[Cr(CO)_5I]^-$ and $[Cr(CO)_5Br]^-$ are closer in energy than those of the corresponding manganese complexes. However, through the series X = Cl, Br, and I there is a shift to higher energy in contrast to the shift to lower energy in the manganese and rhenium complexes. This shift is extremely odd and has not been observed before to our knowledge, either for $d \rightarrow d$ or halide$\rightarrow$metal c.t. transitions. The first very intense band at 40 000 cm^{-1} is fairly constant throughout the series of eight ions, but the low-energy band is at much lower energy for $[Cr(CO)_5X]^-$ than for $[Mo(CO)_5X]^-$ and $[W(CO)_5X]^-$.

Unfortunately it was impossible to obtain spectra of these species in non-polar solvents. However spectra of the salts $(Et_4N)[W(CO)_5Cl]$ and $(Et_4N)[W(CO)_5Br]$ were measured in aqueous solution and only the first band showed a clear bathochromic shift compared to the methanol spectrum.

(e) $[Fe(CO)_5X]BCl_4$ (X = Cl *and* Br).—Spectra of the salts $[Fe(CO)_5Cl]BCl_4$ and $[Fe(CO)_5Br]BCl_4$ were measured by Iqbal and Waddington in carbon tetrachloride solution.[43]

(f) $[Mn(CO)_3(L_2)X]$ [L_2 = 2py,[25] bipy, $\{(Ph_2PCH_2)_2\}$, $\{(MeSCH_2)_2\}$, $\{(MeSeCH_2)_2\}$, *or* $Me_2As{\cdot}C_6H_4{\cdot}AsMe_2$;[44] X = Cl, Br, *or* I].—Only the lowest-energy bands are quoted for these complexes, as ligand absorptions complicate the spectra at higher energy.

Molecular-orbital Picture of $[M(CO)_5X]$ *Molecules*.—Electronic spectra of hexacarbonyls of chromium, molybdenum, and tungsten were originally interpreted on the basis of a simple qualitative m.o. picture.[45] Semi-empirical m.o. calculations [2,20–22] and p.e. spectra have more recently confirmed this picture and better experimental work [20] is in agreement with the original assignments. In this light, it is expected that, with p.e. spectral results [10,46] and m.o. calculations [4–6] on complexes $[Mn(CO)_5X]$ (X = H, Me, CF_3, Cl, Br, and I) available, there should be a satisfactory m.o. picture for interpretation of electronic spectra of these species. This exercise has been carried out; [23] the m.o. picture is now briefly reviewed.

(a) $[M(CO)_5R]$ (R = H, Me, Et, CF_3, $SiMe_3$, $GeMe_3$, *and* $SnMe_3$).—For the simplest case, $[M(CO)_5H]$, the picture is quite clear and all but one author [40] have proposed the same energy order for the highest-filled metal d levels.[5,6,23] (Filled M–C, C–O σ, and C–O π levels have been shown to be at least 4 eV [7–10] lower in energy than the metal d levels and are neglected in this discussion.) On replacing one of the CO groups of an $[M(CO)_6]^+$ species with H^-, a ligand with no π-bonding capacity, the highest-filled d orbital of t_{2g} symmetry will be split into $e(d_{xz,yz})$ and $b_2(d_{xy})$. Neglecting all other effects, the b_2 level should be relatively unperturbed

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[43] Z. Iqbal and T. C. Waddington, *J. Chem. Soc.* (*A*), 1968, 2958.

[44] P. S. Braterman and R. A. N. McLean, unpublished work.

[45] H. B. Gray and N. A. Beach, *J. Amer. Chem. Soc.*, 1963, **85**, 702.

[46] S. Cradock, E. A. V. Ebsworth, and A. Robertson, *J.C.S. Dalton*, 1973, 22.

but as the $e(d_{xz,yz})$ orbital is now interacting ($d \rightarrow \pi^*$) with only three instead of four CO groups, it will be at higher energy. In fact, on a Koopman's theorem picture, for the complex [Mn(CO)$_5$H] the $7e$ level ($-8{\cdot}85$ eV) is 0·3 eV higher in energy than the $2b_2$ level[10] ($-9{\cdot}14$ eV). Because of the lower formal positive charge, it would be expected that the hypothetical unperturbed filled d level ($-8{\cdot}95$ eV) would be at higher energy than the t_{2g} level in the analogous [Mn(CO)$_6$]$^+$ complex ($-9{\cdot}85$ eV, estimated by Gray and Beach and calculated by Fenske and his co-workers[47]). This would also partly account for the greater interaction with the π^*(CO) levels in the complex [Mn(CO)$_5$H] as evidenced by the lower CO-stretching vibrational frequencies. The unfilled metal $d(\sigma^*)$ levels (e_g in O_h symmetry) are split into $10a_1$ (d_{z^2}) and $5b_1$ ($d_{x^2-y^2}$). Because of the lower central metal charge one would expect one or more $d \rightarrow d$ transitions to be at lower energy in the complex [Mn(CO)$_5$H] than those in [Mn(CO)$_6$]$^+$.

Neglecting ligand–ligand interactions, it would be expected that π^* CO levels which interact with metal d levels would be pushed to higher energy than those which do not. Considering the interaction with metal orbitals to be more important energetically than ligand–ligand interaction, the following energy order is obtained: $11a_1 < 8e_1$ (in-plane) $< 6b_1 < 2a_2 \ll 9e$(CO 5) $< 10e_2$(CO 1—4) $< 3b_2$. This is the same order as is obtained considering only interaction with the metal orbitals, and the second-order energies have been given on a simple Hückel basis.[17]

The only other orbitals which could possibly be involved in the electronic spectra in the region of interest are the σ and σ^* M–H orbitals. Calculations[4] indicate that corresponding σ orbitals in the complexes [MeMn(CO)$_5$] and [(CF$_3$)Mn(CO)$_5$] are close in energy to the filled metal 3d orbitals and cause the strange intensity ratios observed in p.e. spectra of these species.[10] The $9a_1$ M–H orbital is probably lower in energy than the $9a_1$ M–C(H$_3$) or M–C(F$_3$) orbitals and ionisation from it occurs at 10·55 eV compared to 8·85 and 9·14 eV for the metal d orbitals. The a_1 σ^*(M–H) orbital probably has a high d_{z^2} character and transitions to this orbital from mainly metal orbitals will be $d \rightarrow d$ transitions. For the complexes [Mn(CO)$_5$Me] and [Mn(CO)$_5$(CF$_3$)] the Me and CF$_3$ group orbitals (other than the $9a_1$ M–C orbital) are at least 3 eV lower in energy than the metal 3d orbitals. However, interaction between these group orbitals and the metal 3d orbitals has a considerable effect on the latter. For example, the highest-filled $7e$ orbital in [MeMn(CO)$_5$] has an ionisation energy of 8·46 eV.[10] Despite this, the order of the highest-filled 3d levels is calculated to be the same in the complex [Mn(CO)$_5$Me] as in [Mn(CO)$_5$H].

(b) [Mn(CO)$_5$X] (X = Cl, Br, *or* I). As discussed in the Introduction section, the presently accepted m.o. picture for pentacarbonylhalogenomanganese complexes, deduced from p.e. and electronic spectra of [Mn(CO)$_5$I] and two sets of m.o. calculations, indicates that the highest-filled orbital (of e symmetry) is mainly halogen p_π in character. Otherwise the picture can be assumed to be the same as in the complex [Mn(CO)$_5$H] with the mainly halogen p_π orbital above the mainly metal 3d orbital of e symmetry. Metal–halogen σ-bonding orbitals will be somewhat more stable than the metal d orbitals.

Although this picture seems quite satisfactory for the complex [Mn(CO)$_5$I], the calculations indicate certain discrepancies for [Mn(CO)$_5$Cl] and [Mn(CO)$_5$Br]. Assuming Koopman's theorem to be true for most series of halides, there is an energy difference of 2 eV between the chloride and the iodide for any orbitals in which these atoms are involved.[48] In the [Mn(CO)$_5$X] species[10] the difference is 0·3 eV and is smaller than that between any other two isostructural chlorides and iodides, whose ionisation energies have been measured. Also in most metal complexes, c.t. transitions are usually at least 1 eV lower in energy when an iodine atom is involved rather than a chlorine atom. {There is one other exception to this rule, [(R$_3$P)$_2$PtX$_2$], in molecules[49] with possibly similar bonding characteristics to these studied here.} The almost constant value through the series of pentacarbonylhalogeno-complexes was explained by a high negative charge on the halogen atom which increases from iodide to chloride.[5] The total p_π electron density is calculated to be equal to[5] or close to[6] that in a free halide ion, but the halide $p\sigma$ electron density decreases from chloride to iodide producing the greater negative charge on the chloride.

These arguments would be quite satisfactory if no indication of the ionisation energy of the halide ions themselves was available. The value of 7·9 eV for the first ionisation energy of CsI[50] is probably as near to that of the pure iodide ion as one can get in the gas phase. The explanation given above for the first ionisation process for the complex [Mn(CO)$_5$I] is then quite satisfactory, *i.e.* the iodine atom has a higher negative charge than that in, say, MeI (first i.p. = 9·54 eV).[48] However, the lowest ionisation energy available for Br$^-$ is 9·4 eV in LiBr, and for Cl$^-$ is 10·1 eV in LiCl.[51] These values are then somewhat higher than first ionisation energies in the complexes [Mn(CO)$_5$Br] (8·76 eV) and [Mn(CO)$_5$Cl] (8·80 eV) respectively. It then seems impossible for the ionisation process to involve an orbital which is mainly halogen in character. The earlier conclusion,[52] from mass-spectrometric ionisation potentials, that the highest-filled orbital has 80% metal character and 20% halogen character should also be considered.

We therefore prefer to consider that the highest two orbitals both have considerable halogen p_π and metal d_π ($d_{xz,yz}$) character (and probably more of the latter than m.o. calculations have indicated). The highest level has more halogen p_π character in the iodide and probably in the bromide, but more metal d_π character in the chloride. Further support for our m.o. picture can be obtained by comparison of the highest-energy levels in the complex [Mn(CO)$_5$Cl] with [Mn(CO)$_6$]$^+$. Although the p.e. spectrum of the latter is not available, a semi-empirical calculation,[20] which gives a satisfactory value for the first i.p. of the complex Cr(CO)$_6$, predicts the first i.p. of [Mn(CO)$_6$]$^+$ to be 9·8 eV. Now, if the highest orbital in the complex [Mn(CO)$_5$Cl] is almost purely chlorine p_π as has been suggested (86%), then the next-highest orbital ($7e$) at $-10{\cdot}48$ eV will be mainly metal as is the $2b_2$ orbital at $-11{\cdot}00$ eV. The average d-orbital energy would then be *ca.* $-10{\cdot}6$ eV in [Mn(CO)$_5$Cl], which in comparison with [Mn(CO)$_6$]$^+$ seems impossible.

(c) [Re(CO)$_5$X] (X = Cl, Br, *or* I). Comparison of

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[47] R. L. DeKock, A. C. Sarapu, and R. F. Fenske, *Inorg. Chem.*, 1971, **10**, 38.

[48] See, for example, A. W. Potts, H. J. Lempka, D. G. Streets, and W. C. Price, *Phil. Trans.*, 1970, **268**, 59.

[49] R. M. Canadine, unpublished work, cited in C. K. Jørgensen, *Progr. Inorg. Chem.*, 1970, **12**, 101.

[50] G. Platel, *J. Chim. phys.*, 1965, **62**, 1176.

[51] J. Berkowitz, H. A. Tasman, and W. Chupka, *J. Chem. Phys.*, 1962, **36**, 2170.

[52] G. A. Junk, H. J. Svec, and R. J. Angelici, *J. Amer. Chem. Soc.*, 1968, **90**, 5758.

[M(CO)$_5$X] species down a periodic Group should involve consideration of the corresponding hexacarbonyl species. In contrast to most metal complexes there is little shift in electronic spectral bands, in the first i.p., and in calculated one-electron energy levels on descending a periodic Group.[20] In fact, the d_{z^2,x^2-y^2} level (e_g) is calculated to become more stable on descending a periodic Group, but this is compensated by a corresponding decrease in energy of the $d_\pi(t_{2g})$ level {except for [Re(CO)$_6$]$^+$ compared to [Mn(CO)$_6$]$^+$}. However, there are considerable shifts to higher energy in electronic spectra of third-row metal hexahalides compared to first-row complexes.[53] This is partly due to lower shielding of 4d and 5d orbitals in the higher oxidation states involved, thus causing greater interaction of halide σ-donor orbitals with the metal and subsequent increase in energy of the antibonding d_{σ^*} levels. There will also be some slight stabilisation of the d_π orbitals on the metal with increased nuclear charge. For [M(CO)$_5$X] species, the $b_2(d_{xy})$ and $b_1(d_{x^2-y^2})$ orbitals will be relatively unaffected by change in the central metal atom, but the $e(d_{xz,yz})$ orbital should be stabilised and have less interaction with the $e(p_\pi\ \mathrm{X})$ orbital, and the $a_1(d_{z^2})$ orbital should be stabilised much more on going from 3d to 4d and 5d metals. Therefore, although there may not be a significant change in metal→ligand c.t. transitions between, say, [Mn(CO)$_5$X] and [Re(CO)$_5$X] species, there should be a considerable increase in energy in the $e,\mathrm{X}(p_\pi,d) \rightarrow a_1,d_{\sigma^*}$ transition in the latter.

(d) [Cr(CO)$_5$X]$^-$ (X = Cl, Br, *or* I). The effect of varying the central metal charge can also be considered in terms of hexa-carbonyl and -halide complexes. For the hexacarbonyls, t_{2g} orbitals are greatly affected by changing the charge, and d_π energy decreases by 7 000—11 000 cm^{-1} for each unit increase of nuclear charge.[20,21] The e_g,d_{σ^*} orbital is stabilised slightly for species with an overall positive charge. Because of the major shift in the t_{2g} orbital, all electronic transitions move to higher energy as the nuclear charge is increased. Provided most of the effect of changing the nuclear charge is felt by the metal atom rather than by the halide ligand, the same results are expected for the pentacarbonylhalogenometal complexes. Two pieces of evidence support this when going from a [Mn(CO)$_5$X] to a [Cr(CO)$_5$X]$^-$ species. First, CO-stretching vibrations or non-rigorous CO force constants[1,54] shift by about the same amount as the charge is changed for both M(CO)$_6$ and [M(CO)$_5$X] species, *e.g.* f = 16·46 mdyn Å^{-1} for Cr(CO)$_6$, 14·55 for V(CO)$_6^-$,[55] and f_{eq} = 17·29 for Mn(CO)$_5$I, and 15·45 for [Cr(CO)$_5$I]$^-$.[56] This indicates that the negative charge has about the same effect on the bonding in M(CO)$_6$ and [M(CO)$_5$X] species. This should mean that metal d_π orbitals in [M(CO)$_5$X]$^-$ ions are raised in energy with respect to the halide p_π orbitals. Then although we consider the highest-filled orbital in the complex [Mn(CO)$_5$I] to be mainly iodine p_π in character, it could be that the effect of the negative charge raises the energy of the metal 3$d_\pi(e)$ orbital in [Cr(CO)$_5$I]$^-$ enough for it to be dominant in the highest-filled orbital. The second piece of supporting evidence comes from an unpublished e.s.r. study.[57] When the ion [Cr(CO)$_5$I]$^-$ is oxidised to [Cr(CO)$_5$I] the unpaired electron is found to be mainly situated on the metal. It seems highly probable that the highest-filled orbital (e) in [Cr(CO)$_5$I]$^-$ is in fact mainly metal 3d_π.

These qualitative arguments have found support in improved calculations[3] on pentacarbonylhalogeno-species, which indicated a higher metal 3d_π population in the highest-filled orbital than in earlier calculations.[5] Through the series [Fe(CO)$_5$Br]$^+$, [Mn(CO)$_5$Br], and [Cr(CO)$_5$Br]$^-$ a very large rise in the 3d levels takes place, with the result that in [Cr(CO)$_5$Br]$^-$ the highest-filled level is mainly 3d_π.

For hexahalides[53] an increase in nuclear charge again stabilises d_π more than d_{σ^*} orbitals and thus makes all d→d transitions move to higher energy. However the effect on the halide is even less than on the d_{σ^*} orbitals as halide→metal c.t. transitions move to lower energy. The same effects should be observed with the [M(CO)$_5$X] species if there is no large decrease in charge on the halide with overall nuclear charge on the complex.

Further evidence in support of this bonding picture is sought in the Discussion section. It should be stated again that the present m.o. scheme is similar to that deduced from p.e. spectra and m.o. calculations, except that the highest-filled level in all [M(CO)$_5$X] species is not considered to be mainly halogen p_π. In fact, in all anionic and some neutral species {*e.g.* [Mn(CO)$_5$Cl]} it is believed to be mainly metal d. The order of the lowest-energy virtual orbitals in the [M(CO)$_5$X] species is also in some doubt. In the neutral hexacarbonyls[20] the e_g (mainly d_{σ^*}) level is somewhat lower in energy than the lowest-energy π(CO) orbital (t_{1u}). Although in the lower C_{4v} symmetry these orbitals would not have such distinct characters, it might be thought that replacement of CO by a weaker-field ligand would allow at least the lowest-energy virtual orbital to maintain much of its d_{σ^*} character. Since the weak-field ligand is being placed on the z axis, one would expect that the $a_1(d_{\sigma^*})$ orbital would be lower in energy than $b_1(d_{\sigma^*})$.

The π^*(CO) orbitals will be much less affected by the change in halide than the metal orbitals since the (CO) orbitals are at the same energy in the complexes [Mn(CO)$_5$X] (X = Cl, Br, or I) as shown in the p.e. spectra. What effect the change in halide will have on energies of transitions involving metal d_{σ^*} and π^*(CO) orbitals, as opposed to the actual orbital energies, is difficult to predict because of the very different electron-repulsion terms involved. However the simple one-electron picture used here will underestimate the difference for d→d as against d→π^*(CO) transitions.

DISCUSSION

The assignment of bands in the electronic spectra to particular transitions is based on a number of considerations. These include solvent shifts, absorption coefficients, band widths, comparison of a related series of complexes, and comparison with other types, *e.g.* M(CO)$_6$, and other [ML$_5$X] complexes. Finally, p.e. spectra of the manganese pentacarbonyl species, m.o. calculations, and the simple m.o. picture discussed above are used.

It should be clearly pointed out that prediction of transitions from a one-electron m.o. scheme neglecting electronic repulsions and configuration interaction is not a very satisfactory basis for discussing electronic spectra. However some idea of the order of electronic transitions can be obtained and successes have already been re-

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[53] C. K. Jørgensen, 'Orbitals in Atoms and Molecules,' Academic Press, New York, 1962, ch. 8.

[54] J. R. Miller, *J. Chem. Soc.* (*A*), 1971, 1885.

[55] E. W. Abel, R. A. N. McLean, S. P. Tyfield, P. S. Braterman, A. P. Walker, and P. J. Hendra, *J. Mol. Spectroscopy*, 1969, **30**, 29.

[56] E. W. Abel and I. S. Butler, *Trans. Faraday Soc.*, 1967, **63**, 45.

[57] R. A. N. McLean and J. P. Maher, unpublished work.

corded with systems related to those at present under discussion {*e.g.* $M(CO)_6$ [20] and $[Co(NH_3)_5X]^{2+}$ (ref. 58)}. Four broad types of transitions are considered as coming within the range of this study ($<52\,000$ cm^{-1}): *viz.* (A), $d\rightarrow d$; (B), $p_\pi(X)\rightarrow d_{\sigma*}(M)$; (C), $d_{\pi*}(M)\rightarrow\pi(CO)$; and (D), $p_\pi(X)\rightarrow\pi^*(CO)$. Following the discussion of the bonding above it can be seen that there will be little to distinguish type (A) from (B) and (C) from (D). This is also indicated by the symmetry-allowed one-electron transitions in each group: *i.e.* (A), $e\rightarrow b_1$, $e\rightarrow a_1$; (B), $e\rightarrow b_1$, $e\rightarrow a_1$; (C), $e\rightarrow a_1$, $e_{(1)}(\pi^*CO\ 1\text{—}4)$, b_1, a_2, $e_{(5)}(\pi^*CO\ 5)$, $e_{(2)}$ and $b_2\rightarrow e_{(1)}$, $e_{(5)}$, $e_{(2)}$; and (D), $e\rightarrow a_1$, $e_{(1)}$, b_1, a_2, $e_{(5)}$, $e_{(2)}$.

(a) $[Mn(CO)_5R]$ (R = H, Me, Et, CF_3, $SiMe_3$, $GeMe_3$, *and* $SnMe_3$).—The first assignment [40] of the electronic spectrum of the complex $[Mn(CO)_5H]$ attributed the weak shoulder at *ca.* 34 000 cm^{-1} to a $d\rightarrow d$ transition [though considering the $b_2(d_\pi)$ orbital as the highest-filled one] and the intense band at *ca.* 46 000 cm^{-1} to several $M\rightarrow\pi^*(CO)$ c.t. transitions (though not the first which was assigned to a shoulder at 38 500 cm^{-1}). However, more recently [23] the first transition has been reassigned as a $M\rightarrow\pi^*(CO)$ charge transfer, excited levels involved being classified as $\pi(CO)$ non-interacting (e, a_1, a_2, and b_1); *i.e.* non-interacting with metal d orbitals. In this case it was thought that the intensity of the band was too great for it to be a $d\rightarrow d$ transition. However, it had earlier been shown that $d\rightarrow d$ transitions in the hexacarbonyl are quite intense.[20] Secondly, c.t. transitions from metal to non-interacting carbonyl orbitals generally produce very high intensity bands. Also, based on the presently accepted assignment of the electronic spectra of the hexacarbonyl,[20,55] there appears to be quite a separation between two sets of c.t. transitions to orbitals which, under the present discussion, would be considered to be non-interacting.

Therefore, we propose that the first weak resolved band in the electronic spectrum of the complex $[Mn(CO)_5H]$ is due to a transition from the metal $d_\pi(e)$ to an a_1 orbital which has mainly M–Hσ^* character, but part COπ^* character. Essentially this orbital can be considered to be the antibonding orbital corresponding to the orbital involved in Fenske and DeKock's 'direct-donation' effect for transferring electronic charge from the ligand X in a $[M(CO)_5X]$ system to the *cis*-carbonyl ligands (see Figure 2 of ref. 5). This orbital was mainly situated on the ligand X and it seems reasonable that the corresponding antibonding orbital will have mainly metal character. This assignment satisfactorily explains the low intensity of the band ($d\rightarrow d$ character) and the large energy difference between it and the next intense band at 46 700 cm^{-1}. The latter must contain a number of allowed $M(d)\rightarrow\pi^*(CO)$ transitions, probably $e(M\ d_{xz,yz})\rightarrow e$, a_2, $b_1(\pi^*CO\ 1\text{—}4$ non-interacting). This is in agreement with the assignment of the hexacarbonyls, as the most intense band in their spectra was assigned to a transition involving non-interacting $\pi^*(CO)$ orbitals. The third observed band at 51 300 cm^{-1} would then be assigned to transitions involving $\pi^*(CO)$ orbitals which have symmetry interactions with $d_{xz,yz}$ and d_{xy} orbitals. Other mainly $d\rightarrow d$ transitions will probably be masked by c.t. transitions. However, because of the presence of many orbitals of the same symmetry, excited states except for that involving the a_2 $\pi^*(CO)$ orbital will involve considerable mixing between metal and ligand orbitals. The main justification for the tentative assignments proposed for the second and third bands is that the small number of resolvable bands seems to indicate that excited states can be related to those of the hexacarbonyls with little effect of reduction in symmetry.

The assignment of the first band to a transition from a $M(d_{xz,yz})$ to a mainly σ^* orbital gains some support from a comparison of the spectrum of the complex $[Mn(CO)_5H]$ with both $[Mn(CO)_5Me]$ and $[Re(CO)_5H]$. Although the second bands in $[Mn(CO)_5H]$ and $[Re(CO)_5H]$ (46 700 and 47 300 cm^{-1} respectively) are fairly close in energy, the energy of the first transition in $[Re(CO)_5H]$ is 2 500 cm^{-1} greater. This is in accord with the greater σ-bonding interaction, but similar π-bonding interaction in rhenium carbonyl complexes compared to those of manganese.[59] This would cause greater destabilisation of σ^* orbitals in the former. In contrast the electron-releasing effect of the Me group will raise all the energy levels in the complex $[MeMn(CO)_5]$ but with a greater effect on the filled levels. This should and does reduce the energy for a transition to mainly non-interacting π levels (second band). However, the first band shows an increase in energy and with the present assignment this is explained by the greater σ-donor effect increasing the energy of the σ^* orbital in $[MeMn(CO)_5]$ more than the d_π levels.

The energy of the band (50 000 cm^{-1}) observed [42] in the complex $[(SiH_3)Mn(CO)_5]$ is considerably higher than the corresponding band in $[MeMn(CO)_5]$. This would be expected if the Mn $e(d_\pi)$ orbitals were stabilised in the former complex by interaction with the Si d orbitals. It would be expected that, as with other silyl molecules, the first-ionisation energy would be considerably higher than that of the carbon analogue. This has been found by Cradock *et al.*: [46] $[MeMn(CO)_5]$, 8·46; $[(SiH_3)Mn(CO)_5]$, 8·99 eV. Blakney and Allen [23] have already commented on similarities of the $[(CF_3)Mn(CO)_5]$ and $[MeMn(CO)_5]$ spectra. Following calculations of Hall and Fenske,[4] it is quite clear that the difference in bonding is not due to any π interaction between the metal atom and the CF_3 group. The slight increase in energy of the transitions in the complex $[(CF_3)Mn(CO)_5]$ is due to the greater inductive-stabilising effect of the CF_3 group, and this group seems to have a similar effect on all orbitals involved in transitions in the $Mn(CO)_5$ moiety.

Spectra of the $[Mn(CO)_5(MMe_3)]$ species (M = Si and Ge) show a shift to higher energy compared to $[Mn(CO)_5Me]$ and $[Mn(CO)_5Et]$, which could be interpreted as stabilisation of the manganese orbitals by interaction with the empty silicon and germanium d_π orbitals,

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[58] H. Yamatera, *J. Inorg. Nuclear Chem.*, 1960, **15**, 50 and references therein.

[59] R. A. N. McLean, *Canad. J. Chem.*, 1974, **52**, 213.

assuming that virtual orbitals are less affected by the change of substituent atom. Because of the electron-releasing influence of the methyl groups this effect is not as great as with [$Mn(CO)_5(SiH_3)$]. The complex [$Mn(CO)_5(SnMe_3)$] does not seem to fall into the same category as the first strong band is at even lower energy than those of the carbon derivatives. If anything, the Me_3Sn group destabilises the metal d_π orbital.

(b) [$Mn(CO)_5X$] (X = Cl, Br, *or* I).—The unique feature which distinguishes the pentacarbonylhalogenometal complexes from the corresponding hydrides, the low-energy band (A), will be discussed first. The width of this band, and its solvent dependence in [$Mn(CO)_5I$], are in accord with its assignment to a transition from a mainly halogen p_π orbital (e). However, in line with earlier discussion, it is believed that the antibonding orbital involved, of a_1 symmetry, has mainly σ^* character with a smaller percentage of π^*(CO) character. The low energy of this transition is due partly to the high energy of the e orbital, the low energy of the a_1 σ^* orbital caused by weaker σ-bonding along the z axis, and interaction with the a_1 π^*(CO) orbital. The first two effects will influence electronic spectra of all the halogeno-complexes, and trends through a series of metal carbonyl halides would be expected to be the same if the halide ligand dominates the highest-filled and lowest-unfilled orbitals.

The increase in energy in band (A) in the order [$Mn(CO)_5I$] < [$Mn(CO)_5Br$] < [$Mn(CO)_5Cl$] is in agreement with the expected trends but the differences are somewhat smaller than in other monohalogeno-complexes {*e.g.* [$Co(NH_3)_5X]^{2+}$}.[60] As with earlier workers,[5,10] it is believed that this indicates that metal $d_{xz,yz}$ contribution to the highest-filled orbital increases through this series becoming dominant with the chloride. This argument is supported by the solvent shifts. If the highest-filled orbital in the complex [$Mn(CO)_5I$] is mainly halide in character, one would expect the observed blue shift in the first band in a polar solvent. As the transition becomes less X→M charge transfer and more $d \rightarrow d$, one expects less solvent effect as is observed with [$Mn(CO)_5Br$]. The reproducible red shift in the first band of the complex [$Mn(CO)_5Cl$] in a polar solvent appears to indicate that, as in neutral hexacarbonyls,[20] the transition has some M→π^*(CO) character. This is in accord with the m.o. picture presented above.

At first sight, the intensity pattern for band (A), *i.e.* [$Mn(CO)_5I$] < [$Mn(CO)_5Br$] < [$Mn(CO)_5Cl$], is rather strange, if it is considered that [$Mn(CO)_5Br$] has more $d \rightarrow d$ and less X→M c.t. character than [$Mn(CO)_5I$]. However, it is noted that in many first row monohalogeno-complexes [ML_5X] {*e.g.* [$Co(NH_3)_5X]^{2+}$} the $p_\pi \rightarrow$M charge transfer is relatively weak (ε 600—2 500 l mol^{-1} cm^{-1}). In the neutral hexacarbonyl[20] spin-allowed $d \rightarrow d$ transitions have similar intensity and bands with M→π^*(CO) character are somewhat stronger. Therefore, there is no conflict between the observed intensity order and the present assignment. Observations on the metal carbonyl halide anions below add weight to this assignment.

For higher-energy bands, there is less certainty about the assignment partly due to the large number of possible transitions and because some weak bands are hidden by the intense band at *ca.* 43 000 cm^{-1}. The second band (A′) at *ca.* 35 000 cm^{-1}, by comparison with the third-ionisation energy in the p.e. spectrum, can be assigned to a transition from the second highest e level to the a_1 (σ^*) level. [The energy separation between the (A) and (A′) bands is fairly close to the difference in the two ionisation energies.] This assignment could also account for the fact that of all the bands below 50 000 cm^{-1} this band shows the greatest shift from [$Mn(CO)_5I$] (32 600 cm^{-1}) to [$Mn(CO)_5Br$] (36 500 cm^{-1}). This compares well with the difference in third-ionisation energies of 3 800 cm^{-1}. However it is possible that the e(highest-filled)$\rightarrow b_1(d_{\sigma^*})$ transition is also present especially in the complex [$Mn(CO)_5I$] where the band is more intense.

The very intense band (B) at *ca.* 42 000 cm^{-1} and shoulders on it, in comparison with [$Mn(CO)_6]^+$ and [$Mn(CO)_5H$], must involve π^*(CO) excited states, but any attempt at a more accurate assignment would not be worthwhile. However, the nearly constant energy value through the series of halides seems to indicate that the same states are involved and that the parent orbital is the highest filled {which varies by less than 3 000 cm^{-1} from [$Mn(CO)_5Cl$] to [$Mn(CO)_5I$]}. Previous workers[23] suggested the energy order of the π^* levels was π^* (non-interacting with d orbitals) $b_1, e, a_1, a_2 < \pi^*\ e, e < \pi^*\ b_2$. This is obtained purely on an overlap basis and there are many other factors which could alter parts of this order. As indicated already, it is believed, as Fenske and DeKock,[5] that the a_1 π^* level has significant interaction with σ orbitals in the M–X band. M.o. calculations[20] on metal carbonyls also indicate that the order of π^* levels bears little resemblance to that obtained using overlap criteria only.

The π^*(CO) level would be expected to be much less affected by change in halogen than the metal-atom orbitals. Therefore, it is not surprising that transitions from the two highest-filled orbitals (which from the p.e. results[10] are within 3 000 cm^{-1}) to the π^*(CO) levels remain fairly constant (within 3 000 cm^{-1}) for all the pentacarbonylhalogeno-complexes. The constant energy of this band through the series adds further support to the deduction of Evans *et al.*[10a] from p.e. spectra that halogen p_π–metal d_π interaction increases in the order I < Br < Cl. This can be seen in the energy increase in the $6e$–$7e$ separation through this series. A corollary to this effect will be increased polarisation of electron density towards the *trans*-CO group. This argument can explain an anomalous observation in CO-stretching vibrations of [$Mn(CO)_5X$] species {and almost all other [$M(CO)_5X$] species, [$Cr(CO)_5X]^-$ being the exception} which has received little comment. Although the energy of CO vibrations of the equatorial group is consistent with the electronegativity, *i.e.* [$Mn(CO)_5I$] < [$Mn(CO)_5Br$] <

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[60] M. Linhard and M. Weigel, *Z. phys. Chem.* (*Frankfurt*), 1957, **11**, 308.

$[Mn(CO)_5Cl]$ (and Fenske and DeKock's direct ligand-to-ligand donation), that of the axial CO group shows a small but significant reversal of this order. We believe that greater polarisation of *d* orbitals in the chloride causes larger d–π^*(CO) interaction and this lowers the energy of the axial CO-stretching vibration by weakening the bond. This effect was not observed in the calculations (see ref. 5, p. 1058), but it is believed that this may have been caused by the assumption that all Mn–C bond lengths are equal.

There is no implication in these arguments that there is any significant transfer of electron density from the halogen to the metal atom through the p_π orbital. In fact, it seems quite reasonable that the net charge on the halogen should be near zero [5] in these complexes. It is suggested that the presence of halide p_π electrons causes polarisation of the metal $d_{xz,yz}$ electrons towards the *trans*-carbonyl group.

(c) $[Re(CO)_5X]$ (X = Cl, Br, *or* I).—In these complexes, band (A), on the basis of the bonding arguments above, can be assigned in the same way as the corresponding band in the $[Mn(CO)_5X]$ species, *i.e.* $e(p_\pi X, \mathrm{M}\ d_{xz,yz}) \rightarrow a_1[\sigma^*, \pi^*(CO)]$. Comparison with neutral hexacarbonyls again gives some evidence for the $d \rightarrow d$ nature of this band. Although $Cr(CO)_6$ does not clearly show vibrational structure on the first $d \rightarrow d$ band, in $W(CO)_6$ [20] this is quite distinct and component peaks are separated by *ca.* 2 000 cm^{-1}. Similarly, in $[Re(CO)_5X]$ species there are weak peaks [(a), (a′)] *ca.* 2 000 cm^{-1} above and below peak (A) so that (a), (A), and (a′) can be assigned as excitations to 0, 1, and 2 vibrational levels of the first $d \rightarrow d$ transition. Alternatively (a) could involve a triplet excited state and (A) would be the 0—0 component of the first singlet–singlet transition, or (A) and (a′) could be components of spin–orbit splitting.

Ionisation energies obtained for the $[Re(CO)_5X]$ species from electron-impact studies [52] are slightly higher than, but within 0·1 eV of, values for corresponding $[Mn(CO)_5X]$ species. Although the electron-impact i.p.s have a greater range than p.e. values for the $[Mn(CO)_5X]$ species, the values are equal within the experimental errors quoted. Therefore, the electron-impact i.p.s for $[Re(CO)_5X]$ species are reasonably reliable. The first excited state for $[Re(CO)_5X]$ is somewhat higher in energy than that for $[Mn(CO)_5X]$, which can be explained by the higher energy of the σ^* level in the former

In non-polar solvents, band (A) is almost at the same position in all three $[Re(CO)_5X]$ species, which indicates (other things being equal) that the energy order of the excited state is $[Re(CO)_5Cl] < [Re(CO)_5Br] < [Re(CO)_5I]$. This would be predicted by electronegativity considerations. Bands (A′) and (B) can be assigned in the same way as those in the $[Mn(CO)_5X]$ species. Band (B) shifts to lower energy through the series X = Cl, Br, and I as in the $[Mn(CO)_5X]$ species but by a greater amount. The position of band (B′) probably indicates greater separation of the π^* (CO) levels in $[Re(CO)_5X]$ species.

(d) $[M(CO)_5X]^-$ (M = Cr, Mo, *or* W; X = Cl, Br, *or* I).—In the $[M(CO)_5X]^-$ species, on the basis of the m.o. arguments given above, the highest-filled orbital is considered to be mainly metal *d*. Further evidence for this can be obtained from the half-width of the lowest-energy band (A) in $[Cr(CO)_5I]^-$, which is the same as that for the ion $[Cr(CO)_5Br]^-$. This contrasts with the much broader band in $[Mn(CO)_5I]$ as compared to that in $[Mn(CO)_5Br]$. The broad band in the complex $[Mn(CO)_5I]$ is caused by the presence of two spin–orbit states due to the high proportion of I character in the highest-filled orbital. Obviously, this is not so for the ion $[Cr(CO)_5I]^-$.

The negative charge effectively raises the metal *d* levels with respect to the halide p_π levels in $[M(CO)_5X]^-$ compared with $[M(CO)_5X]$ species. Also interaction between halide p_π and metal d_π levels increases in the order I < Br < Cl.[5,10] Therefore, it is possible that the stability order of the highest-filled orbitals in $[M(CO)_5X]^-$ species is the unique $[M(CO)_5I]^- > [M(CO)_5Br]^- > [M(CO)_5Cl]^-$. This would then partly explain the increase in energy of band (A) through $[M(CO)_5Cl]^- < [M(CO)_5Br]^- < [M(CO)_5I]^-$. Generally in halogeno-complexes, one expects the a_1 (σ^*) level to be in the energy order I < Br < Cl. However, because of the possibility of a large amount of π^* character in this orbital, which would increase in the order Cl < Br < I, there may be little difference in the energies of this level through the series of halides. Increased π^* character in the $a_1\ \sigma^*$ orbital may also explain why band (A) in the $[Cr(CO)_5X]^-$ species is closer in energy to band (A) in $[W(CO)_5X]^-$ than corresponding bands in $[Mn(CO)_5X]$ and $[Re(CO)_5X]$ [see (c) above]. The increased intensity of band (A) in the $[M(CO)_5X]^-$ compared with the $[M(CO)_5X]$ species is also explained by the $M \rightarrow \pi^*$(CO) character of the transition.

As before, band (B) is assigned to a mainly $M \rightarrow \pi^*$(CO) (non-interacting) transition and this corresponds to the second $^1A_{1g} \rightarrow {}^1T_{1u}$ transition of neutral hexacarbonyls. It is interesting to note that this band, although only showing a slight shift through the series of eight complexes studied, is in the order Mo < Cr < W. This is the accepted order for $d_\pi \rightarrow \pi^*$(CO) interaction [8] and it seems reasonable that for complexes with the smallest interaction there should be smallest separation between the mainly metal *d* and π^*(CO) orbitals. Further evidence for the $X(p_\pi) \rightarrow M(d_\pi)$ interaction which destabilises the highest-energy level, increasing as I < Br < Cl,[10] is the small increase in energy of band (B) through this series even compared with neutral species. This could also be interpreted [3] in terms of generally greater metal character in the highest-filled orbital of $[M(CO)_5X]^-$ species which results in changing halogen having less effect than in the neutral species.

Weak bands around 28 500, 32 000, and 34 500 cm^{-1} in the $[Cr(CO)_5X]^-$ and $[Mo(CO)_5X]^-$ and 26 000 and 33 000 cm^{-1} in the $[W(CO)_5X]^-$ species are probably due to spin-forbidden transitions and for the bands above 30 000 cm^{-1} symmetry-forbidden transitions (both from the $b_2 d_\pi$ level and to the $b_1 d_{\sigma^*}$ level). All $[M(CO)_5X]^-$

species have a strong band (C) at 50 000 cm^{-1} which could be assigned as a transition from the highest-filled level to an interacting set of π^*(CO) orbitals (e or b_2). However, although all species have a weaker band between bands (B) and (C), the iodides have the strongest band (D) here. As this is absent in the other halides, it is probably due to a transition from the a_1 (M–X) σ orbital, which is the most halide-dependent filled orbital in these species,[3] to the a_1 σ^* orbital. This is usually the most intense transition in spectra of metal halide complexes.

(e) [Fe(CO)$_5$X]$^+$ (X = Cl *and* Br).—As carbon tetrachloride was used as solvent for measurement of the spectra of the [Fe(CO)$_5$X]$^+$ species,[43] only one of the reported bands is relevant to this discussion, that at 30 300 cm^{-1} (ε 580 l mol^{-1} cm^{-1}) in [Fe(CO)$_5$Br]$^+$. This band corresponds to (A) in [Mn(CO)$_5$Br] and [Cr(CO)$_5$Br]$^-$ and shows a shift to higher energy of the expected size compared to these species. The positive charge will have a much greater effect on the metal 3d orbitals than on the bromine 4p orbital, and as a result the highest-filled orbital is almost pure Br p_π.[3]

(f) [M(CO)$_3$(L$_2$)X] *and Other Metal Carbonyl Halide Complexes.*—Through a series of mono- and di-substituted Group VI hexacarbonyls, [M(CO)$_5$L] or [M(CO)$_4$(L$_2$)], there is a significant shift in the lowest-energy band with changing L: *e.g.* [Mo(CO)$_5$L] 30 960 (L = CO), 29 890 [P(OEt)$_3$], 29 200 (PPh$_3$), and 25 970 cm^{-1} (py); [Mo(CO)$_4$(L$_2$)] 29 239 [(L$_2$) = 2P(OPh)$_3$], 26 666 (2PPh$_3$), 25 300 (en), and 21 600 cm^{-1} (bipy). (Data from refs. 19, 61, and 62; en = ethylenediamine, bipy = 2,2′-bipyridine, and py = pyridine.) However, as seen in Table 2, the lowest-energy band in *cis*-disubstituted carbonyl halides [M(CO)$_3$(L$_2$)X] shows little shift from [M(CO)$_5$X] with ligand for (L$_2$) = 2py, {(MeSCH$_2$)$_2$}, {(MeSeCH$_2$)$_2$}, and {(Ph$_2$PCH$_2$)$_2$} and even with bipy the shift to lower energy is only 1 500 compared to 9 000 cm^{-1} in the hexacarbonyl series. This also seems to support the assignment $e(p_\pi\text{X},d_{xz,yz}\ \text{M}) \rightarrow a_1(\sigma^*)$ as this transition should be little affected by changes in radial ligands since it mainly involves the axial X–M–C–O system. For bipy the preferred conformation (for $d_\pi \rightarrow$ ligand overlap), with the plane of the ligand perpendicular to the X–M–C–O axis, allows the strongest possible interaction between the ligand π^* orbitals and the σ^*(M–X) orbital.

Assignment of the lowest-energy band in octahedral carbonyl halides should also be applicable to other carbonyl halide species.[26-29] In fact it is believed, on examining spectral data for other metal monohalogeno-complexes which obey the 18-electron rule, that the first c.t. transition can be assigned in an analogous way {*e.g.* [Co(CN)$_5$X]$^{3-}$ (ref. 63) and [NiL$_4$X]$^+$ (ref. 64)}. The example of the [Co(CN)$_5$X]$^{3-}$ complexes is pertinent to the present discussion as they are isoelectronic with the [Mn(CO)$_3$X] and [Cr(CO)$_5$X]$^-$ species. In the [Co(CN)$_5$X]$^{3-}$ species[63] there are unique low-energy bands, as in the carbonyls, at 25 800 cm^{-1} in [Co(CN)$_5$Cl]$^{3-}$, 25 300 cm^{-1} in [Co(CN)$_5$Br]$^{3-}$, and 20 100 cm^{-1} in [Co(CN)$_5$I]$^{3-}$. Now in the ion [Co(CN)$_6$]$^{3-}$, isoelectronic with Cr(CO)$_6$, the M$\rightarrow\pi^*$(CN) lowest-energy c.t. transition is at 49 000 cm^{-1} which is much higher than in Cr(CO)$_6$ (36 000 cm^{-1}), mainly because the π^*(CN) levels are relatively much higher in energy than π^*(CO). Therefore any assignment of the lowest-energy band in the monohalides to a M$\rightarrow\pi^*$(CN) charge transfer appears to be out of the question, and the present assignment of the pentacarbonylhalogeno-complexes seems to be appropriate here also. However in this case the transition probably has almost total $d_{xz,yz} \rightarrow d_{z^2}$ character with only the iodide having any significant contribution from the halide p_π orbital.

The conclusion that the lowest-energy band in [M(CO)$_5$X] species (X is a weak-field ligand) has a considerable amount of $d \rightarrow d$ character supports Saito's assignment[61] of the corresponding band in amine (am) carbonyl complexes, [M(CO)$_4$(am)], where for example am = en. However, where L is a stronger-field ligand, the lowest-energy transition may have more M$\rightarrow a_1$ π^*(CO) character as suggested by Braterman and Walker[16,17] and Darensbourg and Brown.[62] The work of Beach and Gray[20] and the present arguments, however, provide evidence against such an assignment.

Other spectra of substituted Group VI hexacarbonyls which have been recorded, but not previously assigned, can be used as evidence for the present assignments. In the neutral hexacarbonyls c.t. bands occur at about the same energy for all three metal atoms. However in classical metal complexes with ligands which stabilise intermediate oxidation states, $d \rightarrow d$ transitions occur at lower energy for first-row than second- and third-row complexes. This behaviour was observed in the low-energy band of the following complexes: [M(CO)$_5$(piperidine)];[65] [M(CO)$_5$(NCR)];[66] and [M(CO)$_5$(solvent)][6] [where M(CO)$_5$ was produced by photolysis and observed in solution or in a solid matrix]. In all these complexes the transition would be assigned as e, $d_{(xy,yz)} \rightarrow a_1(\sigma^*)$. This would also account for the very low energy of this band in Cr(CO)$_5$ trapped in argon,[67] compared to Cr(CO)$_5$ trapped in organic solvents which have the possibility of interaction with the ' hole ' on the Z axis.

I thank Professor F. G. A. Stone, University of Bristol, for providing spectral facilities, Dr. P. S. Braterman for initially bringing this problem to my attention, Professor E. W. Abel for helpful advice and encouragement, and the Salters Company and the Research Committee of the University of Ife for financial support.

[3/1953 *Received, 24th September,* 1973]

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