Paramagnetic Transition-metal Carbonyls and Cyanides. Part III.[1] Electron Spin Resonance Studies of Manganese Pentacarbonyl Halides after High-energy Irradiation

By **Oren P. Anderson, Stephen A. Fieldhouse, Charles E. Forbes,** and **Martyn C. R. Symons,*** Department of Chemistry, The University, Leicester LE1 7RH

Exposure of the manganese pentacarbonyl halides $[Mn(CO)_5X]$ (X = Cl, Br or I), to ^{60}Co γ-rays at 77 K gives an $S = \frac{1}{2}$ centre having a g *ca.* 2 and a large hyperfine coupling to ^{55}Mn and the halogen nuclei. The results are interpreted in terms of electron addition into a σ^* orbital involving mainly the metal d_{z^2} and halide p_z orbitals. A second centre having two apparent g values in the $g = 6$ region is also formed for all the three complexes. These again exhibit hyperfine coupling to ^{55}M and to the halogen nuclei. Various structures are considered, and it is concluded that the most reasonable are cations formed by loss of an electron and one or more carbonyl groups with unpairing of the remaining electrons to give $S = \frac{5}{2}$.

BECAUSE the majority of transition-metal carbonyl complexes are diamagnetic, e.s.r. spectroscopy has not been widely applied to the study of their electronic structures. In order to overcome this we have exposed a range of compounds to ionizing radiation in the hope of forming electron-gain and electron-loss species amenable to study by e.s.r. spectroscopy.[1,2] Our studies are, in some ways, complimentary to the extensive and informative studies by Turner and his co-workers [3] of metal carbonyl photolysis using matrix isolation coupled with infrared and ultraviolet spectroscopy.

In Part II we reported an e.s.r. study of radiation-produced centres in thallium(I) tetracarbonylcobaltate which included a centre thought to be $[Co(CO)_4]^{2-}$.[1] Here we give full details of our work on $[MnBr(CO)_5]$, mentioned in a preliminary report,[2] together with our results for the chloro- and iodo-analogues.

EXPERIMENTAL

Pentacarbonyliodomanganese(I) [4] and pentacarbonylchloromanganese(I) [5] were prepared by standard literature procedures. The bromo-complex was purchased from Strem Chemicals and purified by vacuum sublimation. The purity of the complexes was established by i.r. spectroscopy. Single crystals of $[MnBr(CO)_5]$ were obtained by slow vacuum sublimation at room temperature over a period of *ca.* 2 weeks. Suitable crystals of the pentacarbonyl bromide having dimensions of *ca.* 2 × 2 × 3 mm were obtained.

All the samples were irradiated at 77 K with a Vickrad ^{60}Co source (1.7 Mrad h^{-1}) for periods between 2 and 4 h. E.s.r. spectra were obtained on Varian E3 or 4500 spectrometers at 77 K using a quartz liquid-nitrogen Dewar. For the single-crystal e.s.r. study of $[MnBr(CO)_5]$, crystals were chosen using the criterion that irradiated crystals should show only two magnetically equivalent sites. A suitable

---

[1] Part II, M. C. R. Symons and D. N. Zimmerman, *J.C.S. Dalton*, 1975, 2545.

[2] O. P. Anderson and M. C. R. Symons, *J.C.S. Chem. Comm.*, 1972, 1020.

[3] See, for example, M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc.* (*A*), 1971, 2939; M. Poliakoff and J. J. Turner, *J.C.S. Dalton*, 1974, 2276.

[4] W. Hieber and K. Wollmann, *Chem. Ber.*, 1961, **94**, 305.

[5] E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1959, 1501.

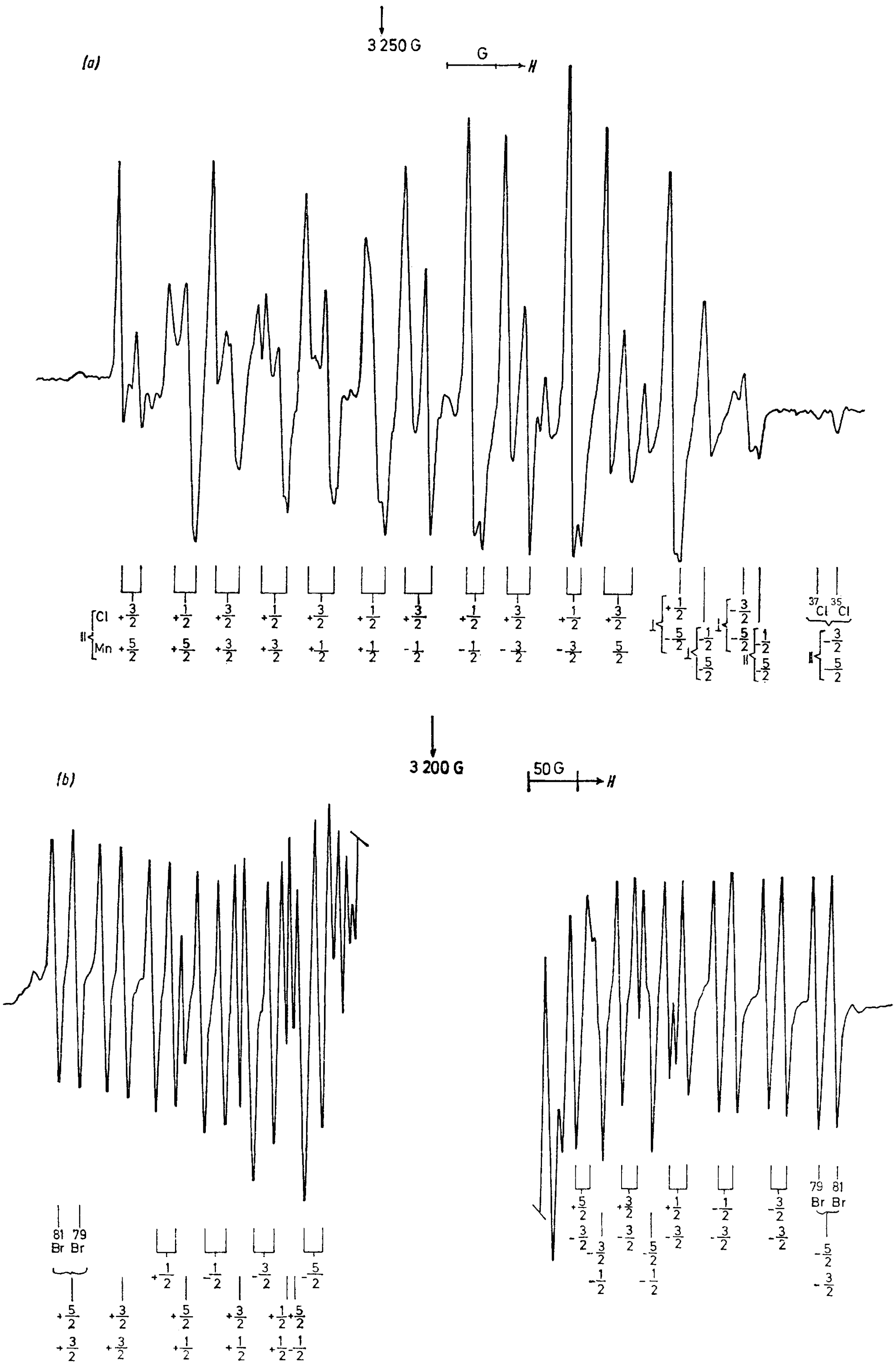

FIGURE 1 (*a*) and (*b*)

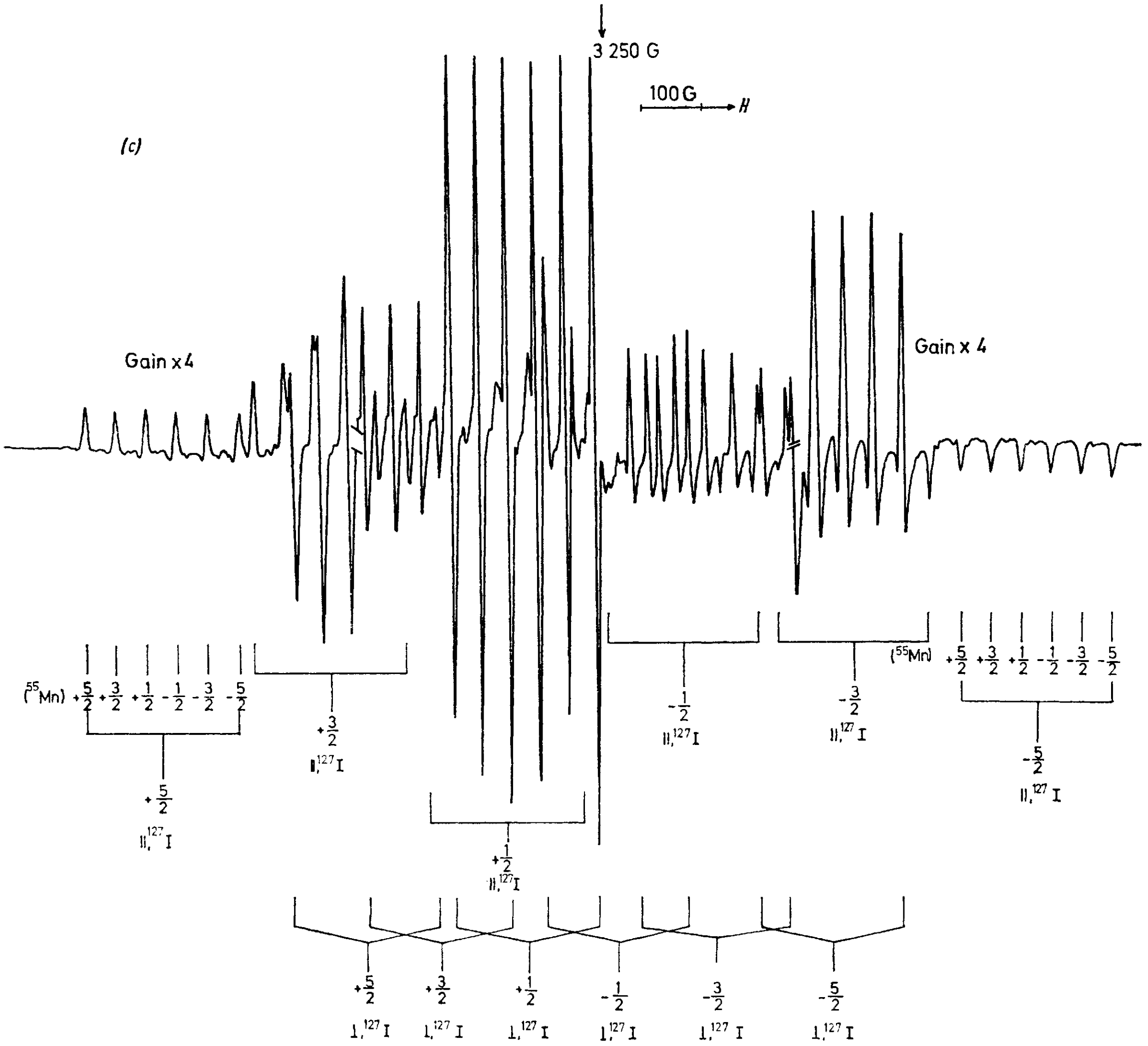

FIGURE 1 First-derivative *X*-band e.s.r. spectra for pentacarbonylmanganese halides after exposure to ^{60}Co γ-rays at 77 K showing features for centre A, thought to be the anion: (*a*) [Mn(CO)$_5$Cl] powder; (*b*) [MnBr(CO)$_5$] single crystal spectrum for an orientation in which spectra for the two inequivalent sites in the unit cell coincide; and (*c*) [Mn(CO)$_5$I] powder

crystal was mounted and aligned visually on a Perspex rod. After irradiation, the rod was attached to a protractor and placed in a quartz liquid-nitrogen Dewar. Crystals were rotated perpendicular to the magnetic field through 180° and measurements were taken at 15° intervals. Samples were annealed above 77 K by decanting the liquid nitrogen from the insert Dewar flask and continuously monitoring the e.s.r. spectra. Whenever significant changes were observed, the samples were recooled to 77 K for thorough study.

RESULTS AND DISCUSSION

Two distinct paramagnetic centres (A and B) were obtained at 77 K. These were lost almost simultaneously on annealing and no further paramagnetic species were then detectable. Solutions in methyltetrahydrofuran also gave A and B in addition to the normal solvent radicals. Absence of a blue colour and a narrow central e.s.r. feature indicated that e_t^- centres were not formed, which establishes that one or both of the centres A or B must be formed by electron capture. Since the relative concentration of centre A was far higher than B in these solutions compared with the pure materials we favour A as the electron-gain centre.

Typical e.s.r. spectra for centres A and B are shown in Figures 1 and 2, and the e.s.r. parameters derived therefrom are given in Table 1.

Centre A.—These centres behave as $S = \frac{1}{2}$ species containing one manganese and one halogen atom. Unfortunately, and in contrast with the i.r. technique,[3] our results give no direct information relating to the presence of the carbonyl ligands. Searches for possible ^{13}C satellite features were inconclusive because of lack of signal strength. When analysing the data, the components of the ^{55}Mn hyperfine coupling were considered with all the sign combinations. However, the only physically meaningful results are for $A_{\parallel}$ positive and $A_{\perp}$ negative. The resulting isotropic coupling constants ($A_{\text{iso.}}$, Table 1) are small negative numbers, and the parallel components of the dipolar coupling ($2B$) are positive. The latter result can only occur for an orbital involving the $3d_{z^2}$ atomic orbital on manganese. This is supported by the low values of $A_{\text{iso.}}$ (^{55}Mn) which are very much less in magnitude than the usual values of *ca.* −80 to −100 G found for manganese in many complexes.* This low value reflects partly the relatively low spin densities on manganese but, mainly, the admixture of 4*s* with $3d_{z^2}$ which adds a positive component to $A_{\text{iso.}}$. The 2*B* values, divided by $2B^0$, the calculated dipolar coupling for unit occupancy of $3d_{z^2}$ (109 G), suggest an orbital population close to 0.60 for $3d_{z^2}$ in these radicals (Table

---

* 1 G = 10^{-4} T.

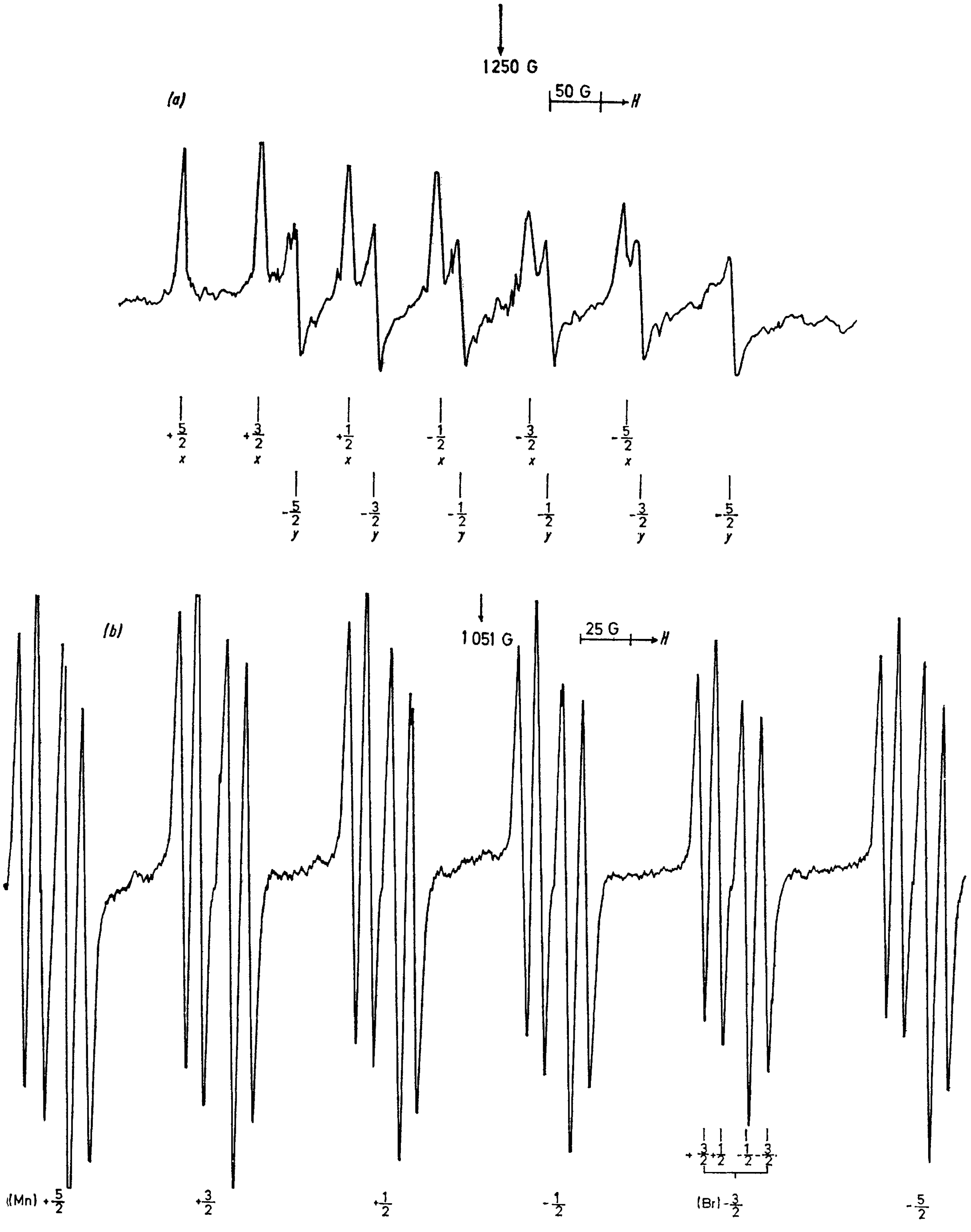

FIGURE 2 (*a*) and (*b*)

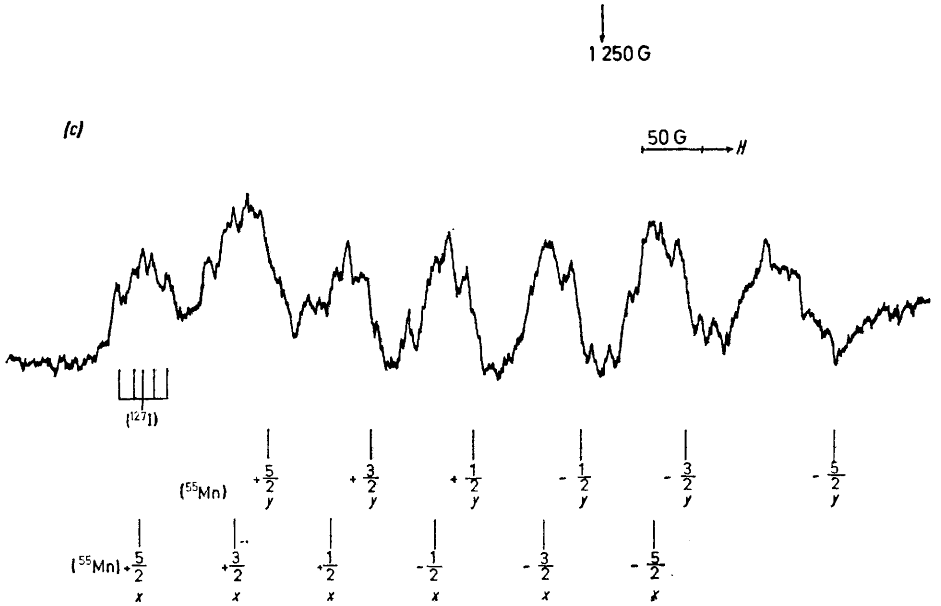

FIGURE 2 First-derivative X-band e.s.r. spectra for pentacarbonylmanganese halides after exposure to ^{60}Co γ-rays at 77 K showing features for centre B, thought to be the cation: (*a*) $[Mn(CO)_5Cl]$ powder (scale expansion revealed a poorly resolved quartet splitting on each feature); (*b*) $[MnBr(CO)_5]$ single crystal spectrum for the orientation in Figure 1(*b*) (the uneven spacing between the ^{81}Br and ^{79}Br features is a quadrupole effect); and (*c*) $[Mn(CO)_5I]$ powder (the ^{127}I features are poorly defined and unevenly spaced because of a strong quadrupole effect)

TABLE 1

E.s.r. data for centres A and B in γ-irradiated pentacarbonylmanganese halides

	g-Tensor components		^{55}Mn Hyperfine tensor components (G)		Halogen hyperfine tensor components (G)		
Host	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$		$A_{\parallel}$	$A_{\perp}$
(*a*) Centre A							
$[Mn(CO)_5Cl]$	2.000	2.001	52.5	−51.3	(^{35}Cl)	38.8	19.4
$[MnBr(CO)_5]$	2.003	2.003	48	−50	(^{81}Br)	240	119
$[Mn(CO)_5I]$	2.000	2.004	51	−48	(^{127}I)	292	155
(*b*) Centre B							
$[Mn(CO)_5Cl]$	5.61 [a]	6.01 [a]	85	86		*ca.* 2	
$[MnBr(CO)_5]$	5.65 [a]	6.82 [a,b]	83	83		*ca.* 12	
$[Mn(CO)_5I]$	5.89 [a]	6.58 [a]	85	85		*ca.* 10	

[a] Effective g values only. [b] $g_z \approx 2.0$.

2). The $A_{iso.}$ values can be accommodated satisfactorily if the 4*s* population is *ca.* 0.02, using A^0 (4*s*) = 1 128 G.

TABLE 2

Estimated orbital populations for centre A *

Species	Manganese				Halogen			
$[Mn(CO)_5Cl]^-$	3*d*	0.63	4*s*	*ca.* 0.02	3*p*	0.13	3*s*	0.015
$[MnBr(CO)_5]^-$		0.59		*ca.* 0.02	4*p*	0.16	4*s*	0.02
$[Mn(CO)_5I^-]$		0.60		*ca.* 0.02	5*p*	0.20	5*s*	0.03

* Using A^0 and $2B^0$ values based on the wavefunctions of C. Froese (*J. Chem. Phys.*, 1966, **45**, 1417).

The hyperfine coupling to the halogen nuclei again present a sign ambiguity. If, by analogy with the V_K centres $[Cl_2]^-$, $[Br_2]^-$, and $[I_2]^-$, we take both $A_{\parallel}$ and $A_{\perp}$ as positive, we obtain the $A_{iso.}$ and $2B^0$ values listed in Table 1. The resulting *ns* and np_z orbital populations given in Table 2 are *ca.* 0.02 and 0.16 respectively for all the three complexes. These values are reasonable for an unpaired electron in a σ^* orbital centred on manganese and halogen. It is not necessary for this to be the lowest vacant orbital of the parent complexes since, as we have shown for the structurally similar complex $[Fe(CN)_5(NO)]^{2-}$, electron capture by the metal may proceed *via* the ligand orbitals.[6] However, in this case, theoretical calculations suggest that the lowest unfilled molecular orbital for these complexes is $10a_1$ (see Figure 3), composed mainly of $3d_{z^2}$ (Mn) and p_z (halogen) orbitals.[7] The $9a_1$ level was calculated [7] to have *ca.* 70% *p*-halogen character. This fits well with our results for the $10a_1$ level, and strongly supports our assignment.

We conclude that centre A is the radical anion, $[Mn(CO)_5X]^-$ (X = halogeno) with the extra electron in the σ_z^* orbital. Loss of the axial carbonyl group is not ruled out.

---

[6] M. C. R. Symons, D. X. West, and J. G. Wilkinson, *J.C.S. Chem. Comm.*, 1973, 917.

[7] R. F. Fenske and R. L. DeKock, *Inorg. Chem.*, 1970, **9**, 1053, and personal communication from R. F. Fenske.

Centre B.—These centres are characterized by low-field multiplets that we have designated as x and y features (Figure 2). (The $g_{x,y}$ values quoted in Table 1 are only effective values determined using $h\nu = g_{\text{eff.}}\beta H$. They are not fundamental spectroscopic values.) We were not able to obtain the z features from the powder spectra, but the form of the powder spectra requires that there is another feature at high field, probably in the $g = 2$ region. This was confirmed by the single-crystal results for the bromide, which showed, for certain rotations, the set of lines moving rapidly into the free-spin region. Unfortunately, the lines also lost intensity, and once they reached the central features (A) they were completely hidden. They did not appear on the high-field side of the A features after further rotation of the crystal. The spectra were studied at 4.2 K in the hope of sharpening the z features, but no significant changes were observed.

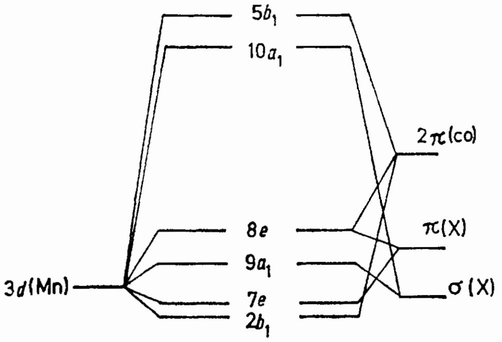

FIGURE 3 Approximate energy-level diagram for the neutral [$Mn(CO)_5X$] molecules. The highest filled molecular orbital is 8e

Although it is most reasonable to identify centre B as the electron-loss centre, since there must be one and it is bound to be paramagnetic under our conditions, it is just possible that both A and B are electron-gain centres, with the loss centres giving features too broad to detect. However, the absence of any new features at 4.2 K seems to rule this out, and B will be taken to be an electron-loss centre for the rest of this discussion.

The observations of e.s.r. transitions centred at *ca.* $g = 6$ are in marked contrast to those expected for a radical cation of the [$Mn(CO)_5X$]$^+$ type. The photoelectron (p.e.) spectra of the parent halides show that, assuming Frank–Condon conditions, the first transition corresponds to electron loss from the 8e level comprising a high proportion of halide $p_{x,y}$ π-atomic orbitals and relatively little $3d_{xz,yz}$ from manganese.[8] The e.s.r. halide hyperfine results at the $g = 6$ region are quite incompatible with a hole in the 8e level, as are the unusual g values found for these signals. We conclude that manganese 3d orbitals are primarily involved, and consider in turn the possibilities of one, three, or five unpaired electrons.

S = $\frac{1}{2}$. As will be demonstrated later, the two sets of signals observed in the $g = 6$ region are due to small deviations from tetragonal symmetry and can be considered collectively as 'perpendicular' transitions. Using models of the type presented by Abragam and Bleaney[9] and McGarvey,[10] we conclude that the observations of perpendicular transitions at $g = 6$ are incompatible with an $S = \frac{1}{2}$ system. It has been shown, by diagonalizing the basis set $|e^4>|b_2{}^1>$ with respect to spin–orbit coupling (λ) and the energy separation between the $|e>$ and $|b_2>$ levels (Δ), that three Kramers doublets are generated.

By allowing Δ and λ to remain as empirical parameters, the maximum value that can be obtained for $g_\perp$ is 2.73 ($g_\parallel$ 1.54). These values correspond to the energy configuration $\Delta = \lambda/2$ and are applicable for pure 3d metal functions. Including augmented orbitals (covalent bonding), as is likely in the present situation, only causes the g values (both $g_\perp$ and $g_\parallel$) to shift closer to the free-spin values. Similar calculations using as the basis set $|e^4>|a_1{}^1>$ lead to the conclusion that the maximum value obtainable for $g_\perp$ within any of the three Kramers doublets corresponds to the value of $g_\perp = 3.643$ ($g_\parallel$ 1.46), which corresponds to the energy configuration $\Delta = 3/2\lambda$. Again, these values are for a basis set of pure metal d functions. The effects of covalency should modify the above arguments, but in such a way as to shift g values towards the free-spin value.[9,11]

From these simplified calculations, together with more sophisticated calculations based upon the Hamiltonian (1) and using completely augmented orbitals, we conclude

$$\mathscr{H}(\text{spin–orbit}) = \xi_{\text{Mn}}\mathbf{l}\cdot s + \xi_X\mathbf{l}\cdot s \qquad (1)$$

that perpendicular transitions in the $g = 6$ region are not compatible with a doublet ground state.[12]

S = $\frac{3}{2}$. That these centres are of a high-spin nature is indicated by the complicated intensity relations found for their spectra as a function of the angle of rotation for the single-crystal studies of the bromo-complex. For a spin-quartet state we would expect for the ground state a configuration of the type ($|d_{xz}{}^2>|d_{xz}, d_{yz}{}^2>|d_{z^2}{}^2, d_{x^2-y^2}{}^2$). Since the ground state associated with this configuration $^4A_2$ is not orbitally degenerate, under conditions of tetragonal symmetry we would expect the lowest Kramers doublet to be $S_z = \pm\frac{1}{2}$ which gives rise to effective g values of $g_\parallel = 2$ and $g_\perp = 4.0$.[13]

Since these values are not in agreement with those observed, we conclude that either a different ground state for $S = \frac{3}{2}$ is present with considerable angular momentum, or that the systems under investigation are characteristic of an $S = \frac{5}{2}$ system. The latter possibility seems more feasible since all three of the halides show similar behaviour in the $g = 6$ region, indicating that

---

[8] D. L. Lichtenberg, A. C. Sarapu, and R. F. Fenske, *Inorg. Chem.*, 1973, **12**, 702.

[9] A. Abragam and D. Bleaney, 'Electron Paramagnetic Resonance of Transition Metal Ions,' Oxford University Press, Oxford, 1970.

[10] B. R. McGarvey, *Transition Metal Chem.*, 1966, **3**, 89.

[11] J. Owen and J. H. M. Thornley, *Reports Progr. Phys.*, 1966, **29**, 675.

[12] J. S. Griffith, *Discuss. Faraday Soc.*, 1958, **26**, 81.

[13] D. Bleaney and K. W. H. Stevens, *Reports Progr. Phys.*, 1953, **16**, 108.

spin–orbit coupling is not the deciding factor in generating the signals at $g = 6$.

$S = \frac{5}{2}$. A sextet ground state can be shown to give the simplest and most feasible explanation for the e.s.r. features observed for species B. Dowsing and Gibson [14] have recently extended the understanding of powder e.s.r. spectra for systems of $S = \frac{5}{2}$. Using the simplified spin Hamiltonian (2) originally suggested by Bleaney and Stevens [13] for sextet states, it has been shown that when

$$\mathscr{H} = \beta\bar{H}\cdot g\cdot\bar{S} + D[S_z^2 - S(S + 1)] + E(S_x^2 - S_y^2) \quad (2)$$

D is quite large in comparison to $g\beta H$ and E is small, one can expect, for the lowest Kramers doublet, effective g values of $g_{\parallel} = 2$ and $g_{\perp} = 6$.[14]

This interpretation is quite compatible with our results (Table 1). Averaging the two g values found for the Cl, Br, and I complexes by use of formula (3) gives values of

$$g_{\perp} = \frac{2}{g_x^{-1} + g_y^{-1}} \quad (3)$$

5.80, 6.18, and 6.22 respectively. Under no conditions was it possible to observe directly the third g component from analysis of powder spectra since these transitions are expected to be weak and are completely obscured by signals from the radical anion.

Confirmation that there is a parallel component in the $g = 2$ region was obtained from three single-crystal rotations for $[\mathrm{MnBr(CO)_5}]$ about approximately mutually orthogonal directions. A complete and accurate rotation study was not felt to be necessary, since the powder spectra give the essential details for describing the electronic structure of both centres A and B. The rotation studies indicate that, at least for the z direction, corresponding to the Mn–Br bond, the orientation of the tensors of both radical sites are nearly identical. For example, θ [g, species B] and θ [$A(\mathrm{Br})_{\mathrm{max.}}$, species A] for any of the three rotations studied correspond to within ±3°. Utilizing the single-crystal data in conjunction with parameters deduced from powder spectra, we can confidently predict that there is a third component close to $g = 2$. Although these results were only obtained from examination of irradiated $[\mathrm{MnBr(CO)_5}]$, it is reasonable to assume that the spectral parameters for all the three complexes studied are close to $g_{\perp} = 6$ and $g_{\parallel} = 2$, as required for a sextet ground state where the zero-field parameter, D, is large in comparison to $g\beta H$.

Structure for the B Centres.—A useful feature of the e.s.r. spectra of $S = \frac{5}{2}$ systems is the ability to measure deviations from O_h symmetry. This can be done using the parameters D and $\lambda = E/D$; D stems from tetragonal distortions from O_h symmetry, and λ is a useful parameter for describing rhombic distortions and has meaningful values between 0 and $\frac{1}{3}$.[15]

Utilization of the figures supplied by Dowsing and Gibson [14] for e.s.r. powder spectra of $S = \frac{5}{2}$ systems as functions of D and λ, the following values for λ have been obtained: $\lambda = 0.008$, 0.02, and 0.01 for the chloro-, bromo-, and iodo-complex respectively. In all three cases, the extent of rhombic distortion is small and is judged to be a reflection of the crystallographic site symmetry. The structure of solid $[\mathrm{Mn(CO)_5Cl}]$ has been determined by X-ray crystallography to be C_s, but the deviations from C_{4v} are small.[16] Small deviations from tetragonal symmetry have also been detected from single-crystal broad-line n.m.r. studies of the parent sets of complexes where asymmetry parameters were found to be small but not negligible in comparison to the $^{55}\mathrm{Mn}$ quadrupole coupling constants.[17] We conclude that the effective symmetry of species B is C_{4v}.

A useful parameter to define tetragonal deviations from O_h symmetry is D. In the case of the chloro-complex, very weak e.s.r. signals exhibiting $^{55}\mathrm{Mn}$ hyperfine splitting were found centred at 3 593 and 3 900 G (Figure 4). If these signals are associated with the $g = 6$ signals, as seems probable, then an assignment of the parameter D can be made of $0.32 \pm 0.03\ \mathrm{cm^{-1}}$. Attempts were made to find similar transitions in the case of the bromo-complex, up to 11 000 G, but were unsuccessful. Whether this is a natural feature of the bromide radical or due to low sensitivity is not known. In any case, it is reasonable to assume that for the Br and I complexes, $D \geqslant 0.4\ \mathrm{cm^{-1}}$. This assignment is also reasonable from simplified ligand-field models where the well established spectrochemical series is Cl > Br > I, which should give rise to increasing D values. This trend has also been observed for the dihalogenotetrakis(4-methylpyridine)manganese(II) complexes.[18] Our e.s.r. results do not exclusively predict a distorted O_h (tetragonal) symmetry, and loss of the axial carbonyl group could conceivably have occurred and still be compatible with our observations. However, there is no evidence to support this suggestion.

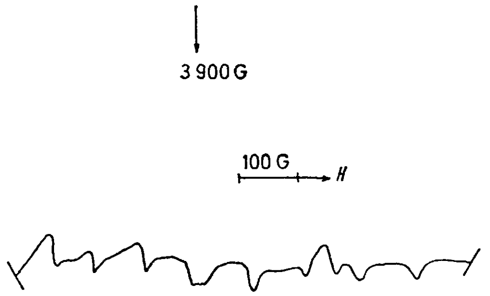

FIGURE 4 First-derivative X-band e.s.r. spectrum for $[\mathrm{Mn(CO)_5Cl}]$ after exposure to $^{60}\mathrm{Co}$ γ-rays at 77 K, showing weak high-field features thought to be associated with centre B

The observation of a high-spin carbonyl complex is, we believe, unique. For the few complexes containing an odd electron, an $S = \frac{1}{2}$ ground state is found. To explain

---

[14] R. D. Dowsing and J. F. Gibson, *J. Chem. Phys.*, 1969, **50**, 294.

[15] H. H. Wickman, M. P. Klein, and D. A. Shirley, *J. Chem. Phys.*, 1965, **42**, 2113.

[16] P. T. Green and R. F. Bryan, *J. Chem. Soc.* (*A*), 1971, 1559.

[17] H. W. Spiess and R. K. Sheline, *J. Chem. Phys.*, 1971, **54**, 1099.

[18] R. D. Dowsing, J. F. Gibson, M. Goodgame, and R. J. Hayward, *J. Chem. Soc.* (*A*), 1969, 1133.

the present results, several factors must be taken into account. Manganese(II) is known to have an extremely high mean electron-pairing energy of 25 000 cm^{-1}. Also, back bonding of the CO ligand may decrease with increasing metal oxidation state.[19] In conjunction with the presence of a weak donor of the halogen type, this may result in the observed high spin behaviour of all three $[Mn(CO)_5X]^+$ centres. It must also be taken into account that radical B is not a stable entity. Our results indicate that on electron loss from the parent molecule the cation relaxes in such a way as to give the configuration $|2b_2^1> |8e^2> |10a_1^1> |5b_1^1>$ for the ground state where the orbitals concerned are primarily metal in character. Since the p.e. spectra and molecular-orbital calculations combine to establish that before relaxation the electron must have come from the orbital which is largely on the halide ligand, we need to postulate a very large change to give this new configuration. This may involve loss of the axial carbonyl group, but we cannot understand why this should occur.

Pentacarbonylmanganese(I).—We have endeavoured to detect the e.s.r. spectrum for $[Mn(CO)_5]$, to no avail. We showed previously that when $[Mn_2(CO)_{10}]$ was sublimed in the absence of oxygen no e.s.r. spectrum was detected,[20] and that the spectrum previously assigned to $[Mn(CO)_5]$ [21] was only obtained with oxygen present and was better assigned to $[Mn(CO)_5(O_2)]$. Another claim to have studied $[Mn(CO)_5]$ by e.s.r. spectroscopy [22] is also doubtful, in our view. A species having $A_{iso.}(^{55}Mn) = 93$ G in tetrahydrofuran had a solid-state spectrum indicative of an $S = \frac{5}{2}$ species. The results in no way resemble those expected for $[Mn(CO)_5]$ and we agree with Hudson *et al.*[23] that the species must be some form of Mn^{II}.

In the present work, loss of the signal assigned to the anions, which might have been due to reaction (4), re-

$$[Mn(CO)_5X]^- \longrightarrow [Mn(CO)_5] + X^- \qquad (4)$$

sulted in the appearance of an extremely broad line which was unresolved even at 4.2 K. If this is due to $[Mn(CO)_5]$, it implies an efficient spin-relaxation process. If $[Mn(CO)_5]$ has the slightly distorted C_{4v} structure ($^2A_1$) predicted by Burdett [24] and proposed for the isoelectronic anion $[Co(CO)_5]^-$,[25] we would expect a well defined e.s.r. spectrum with narrow features. However, the alternative D_{3h} structure should have a degenerate ground state ($^2E'$) [24] and if this structure is thermally available then efficient spin relaxation might well occur.

We thank the University of Leicester for a grant (to O. P. A.), and the S.R.C. for grants (to S. A. F. and C. E. F.).

[5/2201 *Received, 12th November, 1975*]

---

[19] K. G. Cauton and R. F. Fenske, *Inorg. Chem.*, 1968, **7**, 1273.

[20] S. A. Fieldhouse, B. W. Fullam, G. W. Neilson, and M. C. R. Symons, *J.C.S. Dalton*, 1974, 567.

[21] E. O. Fischer, E. Offhaus, J. Muller, and D. Nothe, *Chem. Ber.*, 1972, **105**, 3027.

[22] S. A. Hallock and A. Wojeiki, *J. Organometallic Chem.*, 1973, **54**, C27.

[23] A. Hudson, M. F. Lappert, P. W. Lednor, and B. K. Nicholson, *J.C.S. Chem. Comm.*, 1974, 966.

[24] J. K. Burdett, *J.C.S. Faraday II*, 1974, 1599.

[25] P. A. Breeze and J. J. Turner, *J. Organometallic Chem.*, 1972, **44**, C7.