GENERAL DISCUSSION

Mr. A. F. Orchard (*Oxford University*) said: I have some additional comments on the interpretation of the $Mn(CO)_5CH_3$ photoelectron spectrum. It may be that Koopman's approximation is yielding misleading results here. However, one can identify a number of factors that may contribute to an ordering $b_2 > e$ for the highest occupied molecular orbitals. One possibility, given a particularly high electron density on the manganese atom, is an indirect stabilization of the mainly-$3d_\pi$ e level as a result of an increased $4p_\pi$-π^* interaction. Alternatively, there may be effects arising from a more positive potential of the bonded methyl group. This would lead to greater degree of $4p_\pi$-$3d_\pi$ mixing, since the off-diagonal Fock integral connecting these orbitals becomes more negative. A direct lowering of the e level would then result. In addition, direct interaction with a more positive potential should somewhat stabilize $3d_\pi$ relative to $3d_\delta$. None of these effects alone provides a compelling explanation of the problem: but, taken together, they present a credible picture.

We have also tentatively suggested that the bound methyl group might, in this particular situation, possess significant π-acceptor properties. This notion is, from a general chemical point of view, somewhat heretical. But it does provide the most straightforward explanation of the anomalous $Mn(CO)_5CH_3$ photoelectron spectrum.

Dr. M. G. Clark (*University of Cambridge*) said: I would like to say a few words about the correlation of quadrupole splitting with stereochemistry, as exemplified by the ratio,

$$QS(\text{trans-}MA_2B_4) : QS(\text{cis-}MA_2B_4) = -2 : 1$$

mentioned by Bancroft, Mays, and Prater.[1] My basic premise is that relations of this kind, which are observed in various Sn(IV) and low-spin Fe(II) systems,[2,3] reflect an underlying symmetry feature. Particular rationalizations, such as point-charge or molecular-orbital models, are then seen as manifestations of this symmetry property. Consider, for example, the electric field gradient (EFG) tensor at the nucleus of the central atom M in an octahedral system MA_2B_4, where A and B are monatomic ligands. Trans-MA_2B_4 has point symmetry D_{4h}, hence the asymmetry parameter η of the EFG tensor [4] must vanish ($\eta \equiv 0$). The C_{2v} symmetry of cis-MA_2B_4 does not demand $\eta \equiv 0$, but theoretical models of the $-2 : 1$ quadrupole splitting ratio give $\eta = 0$. Thus the relationship is associated with a situation in which the system has symmetries higher than those strictly required by its point group. This has been termed " intermediate symmetry ".[5]

Sufficient conditions for simple relationships between quadrupole splitting and stereochemistry are: (1) *additivity*: the total EFG tensor at the nucleus of the central

[1] Incidentally the minus sign, although demanded by theory, does not seem to have been verified experimentally.

[2] Sn(IV): B. W. Fitzsimmons, N. J. Seeley and A. W. Smith, *Chem. Comm.*, 1968, 390; B. W. Fitzsimmons, N. J. Seeley and A. W. Smith, *J. Chem. Soc. A*, 1969, 143; B. W. Fitzsimmons, *Chem. Comm.*, 1968, 1485.

[3] Low-spin Fe(II): R. R. Berrett and B. W. Fitzsimmons, *J. Chem. Soc. A*, 1967, 525; G. M. Bancroft, M. J. Mays and B. E. Prater, *Chem. Comm.*, 1968, 1374; G. M. Bancroft, M. J. Mays, and B. E. Prater, 1969, this discussion.

[4] For the theory of EFG tensors see M. H. Cohen and F. Reif, *Solid State Phys.*, 1957, **5**, 321.

[5] J. S. Griffith, *Mol. Phys.*, 1964, **8**, 217.

atom M is the sum of individual contributory EFG tensors, one for each ligand. This is also a necessary condition in any theory purporting to reasonable generality. The existence of a set of " partial quadrupole splittings " implies additivity. In general, additivity will require that contributions to the field gradient from distant parts of the solid be negligible. (2) *Axially symmetric bonds*: each individual contributory EFG tensor is axially symmetric about the relevant ligand-central atom axis, and thus may be characterized by a single parameter q.[1] This condition is not *necessary*; for example, consider $MA_2\beta_2$, where A is a monodentate ligand contributing an EFG tensor characterized by q_A, η_A, and β is a bidentate chelate with each point of ligation contributing an EFG tensor characterized by q_β, η_β. Denoting the monodentate ligand by a line to define its relative asymmetry, we consider isomers (I)

I   II
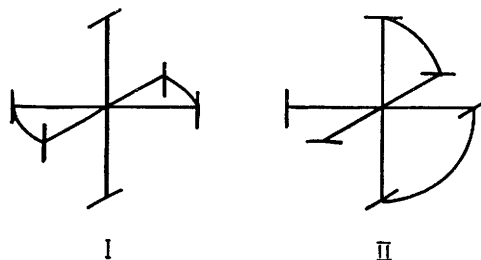
and (II). Summing over individual contributions, the EFG tensors at M are, for (I):

$$\begin{bmatrix} q_\beta(1-\eta_\beta)-q_A(1-\eta_A) & 0 & 0 \\ 0 & q_\beta(1-\eta_\beta)-q_A(1+\eta_A) & 0 \\ 0 & 0 & -2[q_\beta(1-\eta_\beta)-q_A] \end{bmatrix}$$

and for (II):

$$\begin{bmatrix} -\frac{1}{2}[q_\beta(1-\eta_\beta)-q_A(1-\eta_A)] & 0 & 0 \\ 0 & -\frac{1}{2}[q_\beta(1-\eta_\beta)-q_A(1+\eta_A)] & 0 \\ 0 & 0 & q_\beta(1-\eta_\beta)-q_A \end{bmatrix}.$$

For a $\frac{1}{2}\leftrightarrow\frac{3}{2}$ Mössbauer transition, such as ^{57}Fe or ^{119}Sn, the ratio $QS(I):QS(II) = -2:1$. Note that although the point symmetries of (I) and (II) are so low (C_{2h} and C_1, respectively) that the EFG tensors are no longer axially symmetric, the EFG tensor for (II) still has more symmetry than is strictly required by the point group.

Dr. M. J. Mays (*University of Cambridge*) said: Fig. 3 of the paper of Greatrex and Greenwood correlates the change in chemical isomer shift with the total charge on the species and with coordination number. It is not clear, however, whether there are two separate trends, since total charge and coordination number are both allowed to vary in each of the figures shown. Are there in fact two separate trends or are they interconnected?

Dr. M. G. Clark (*University of Cambridge*) said: One feature of Greatrex and Greenwood's paper is that it gives yet another example of a positive correlation between centre shift and coordination number. Such correlations arise in widely differing systems.[2] The existence of a set of partial centre shift values at least

[1] For the theory of EFG tensors see M. H. Cohen and F. Reif, *Solid State Phys.*, 1957, **5**, 321.

[1] e.g., G. M. Bancroft, A. G. Maddock, and R. G. Burns, *Geochim. Cosmochim Acta*, 1967, **31**, 2219, found such correlations in iron silicates.

approximately independent of coordination number would usually be a sufficient condition for such a correlation, although the converse is not necessarily true.

On the question of the range of validity of partial centre shift (PCS) and partial quadrupole splitting (PQS) values, such as those proposed by Bancroft, Mays, and Prater, it seems intuitively likely that, since the centre shift does not involve any explicitly angular-dependent factors, PCS values have the greater range of validity. This consideration points out a fundamental difficulty concerning theoretical investigation of the isomer shift, which is the main contributor to the centre shift. Because of the explicitly angular-dependent factors in the quadrupole coupling, symmetry arguments can play a major role in its study. This is not so with the isomer shift, and since the strongest points of any theory of bonding tend to be those which are symmetry-based, one is in an unfavourable position for theoretical analysis. Finally, with regard to PQS values, my previous remark suggests that both simple and elaborate parameterizations may sometimes give similar experimental consequences.

Prof. N. N. Greenwood (*Newcastle upon Tyne*) said: In answer to Mays and Clark; the right-hand side of fig. 3 includes the effects of both coordination number and charge, but the correlation of chemical isomer shift with coordination number is, in fact, independent of the effect of charge as can be seen from the vertical columns in the following data (δ in mm sec^{-1} relative to nitroprusside):

co-ord. no.	neutral species		mono-anions		di-anions	
4					$[Fe(CO)_4]^{2-}$	0.08
5	$Fe(CO)_5$	0.17	$[Fe(CO)_4H]^-$	0.09	$[Fe_2(CO)_8]^{2-}$	0.18
					$[Fe_3(CO)_{11}]^{2-}$	0.16
6	$Fe_3(CO)_{12}(b)$	0.31	$[Fe_2(CO)_8H]^-$	0.33	$[Fe_4(CO)_{13}]^{2-}$	0.28
			$[Fe_3(CO)_{11}H]^-(b)$	0.28		
7	$Fe_3(CO)_{12}(a)$	0.37	$[Fe_3(CO)_{11}H]^-(a)$	0.30		
	$Fe_2(CO)_9$	0.42				

The fact that an increase in coordination number increases δ and therefore implies a diminution is s electron density at the nucleus is not surprising. The effect is well established in both iron and tin Mössbauer spectroscopy.

Dr. G. M. Bancroft (*Oxford University*) said: Are Greatrex and Greenwood not relying more on chemical insight than Mössbauer spectra in distinguishing between structures (a) and (b) of $[(CO)_3FePMe_2Ph]_3$? The only Mössbauer parameter which changes significantly is the Q.S. of the apical iron atom.

Prof. N. N. Greenwood (*Newcastle upon Tyne*) said: In reply to Bancroft and Mays, more than chemical intuition is involved in deciding in favour of fig. 5(b) as the structure of the compound $[(CO)_3FePMe_2Ph]_3$. The paper indicates the Mössbauer evidence in favour of a trimer, rather than a dimer or tetramer, and also suggests reasons for placing the three phosphines on separate iron atoms rather than on one. There is also mass spectrometric evidence which indicates that each iron atom is associated tith one phosphine ligand only (J. Moss and B. L. Shaw, unpublished results).

Dr. A. J. Rest (*Cambridge*) said: I am particularly interested in $(HFe(CO)_4)^-$ (structure 8 in fig. 1 of paper by Greatrex and Greenwood) because we have recently prepared $HMn(CO)_4$ in an argon matrix at 15°K by photolyzing $HMn(CO)_5$.[1]

[1] A. J. Rest and J. J. Turner, *Chem. Comm.*, 1969, **375**.

The intermediate value of the quadrupole splitting for $(HFe(CO)_4)^-$ was taken by Greatrex and Greenwood as evidence for a heavily distorted five co-ordinated species with C_{3v} symmetry. We find that $HMn(CO)_4$ has an infra-red spectrum consistent with C_{3v} symmetry analogous to $HCo(CO)_4$ with little distortion of the equatorial carbonyl groups in the trigonal bipyramid towards the hydride ligand. The photolytic production of $HMn(CO)_4$ is quantitative and can be reversed using a different photolytic source.

Prof. N. N. Greenwood (*Newcastle upon Tyne*) said: In connection with Rest's remarks, we agree that it is difficult to decide whether or not the three non-axial carbonyl groups in $[Fe(CO)_4H]^-$ are planar or distorted towards the hydrogen atom (as shown in fig. 1.8 in our paper). We postulated the distorted structure partly because of the low value of the quadrupole split and partly because virtually all known carbonyl complexes for which accurate structural data are known are distorted in this way. The structure is also consistent with the vibrational spectroscopic evidence quoted in ref. (20) of our paper.

Dr. M. G. Clark (*University of Cambridge*) said: In connection with the paper by Greatrex and Greenwood, I wonder if Greenwood would like to comment further on the correlation of isomer shift with total charge on species? Whereas the correlation of isomer shift with coordination number has been observed in a variety of systems, its correlation with total charge on the species seems to have been less well explored.

Prof. N. N. Greenwood (*Newcastle upon Tyne*) said: In reply to Clark, there seems to be no problem in understanding how an increase in charge on the carbonyl species can, in principle, influence the chemical isomer shift. The experimental evidence on this point is unequivocal; the theoretical interpretation must consider the 5 effects listed in our paper, though it is not possible to decide on a detailed allocation of the changes in chemical isomer shift to each individual mechanism separately. The results imply that an increase in anionic charge increases the s electron density at the iron nucleus and this seems reasonable.

On the question of the influence of varying charge whilst keeping the structure constant, there is some evidence to show that the resultant changes in chemical isomer shift depend entirely on the nature of the ligands surrounding the central atom and on the spin-state of this atom. Thus, octahedral complexes of high-spin iron(III) have chemical isomer shifts in the region of $0 \cdot 7$ mm sec^{-1} with respect to hydrated sodium nitroprusside and addition of an electron to give the corresponding octahedral complexes of high-spin iron(II) increases this by nearly 1 mm sec^{-1} to about $1 \cdot 6$ mm sec^{-1} because of increased screening of the $3s$ electrons from the nucleus by the added $3d$ electron. By contrast, reduction of the low-spin complex $[Fe^{III}(CN)_6]^{3-}$ to $[Fe^{II}(CN)_6]^{4-}$ leaves the chemical isomer shift virtually unaltered (to within $\sim 0 \cdot 02$ mm sec^{-1}) because the shielding effect of the added $3d$ electron (which makes the complex diamagnetic) is almost exactly counterbalanced by the delocalization of d electron density on to the ligands. Intermediate cases are also known between these extremes of complete localization of the added electron and complete delocalization of equivalent electron density via d_π-p_π interactions on to ligand-based orbitals. For example,[1] reduction of the trismaleonitriledithiolate complex $[Fe^{IV}\{S_2C_2(CN)_2\}_3]^{2-}$ to $[Fe^{III}\{S_2C_2(CN)_2\}_3]^{3-}$ increases the chemical isomer shift from $0 \cdot 50$ to $0 \cdot 65$ mm sec^{-1} indicating that the added electron has entered

[1] T. Birchall and N. N. Greenwood, *J. Chem. Soc. A*, 1969, 286.

an orbital which has both metal and ligand character. Such examples illustrate the care which must be exercised in interpreting formal oxidation states of metal and in classifying ligands as stabilizing either high or low oxidation states—frequently the total electron density at the central atom remains unaltered.

Dr. H. A. O. Hill (*Oxford University*) said: With regard to the paper by Bancroft *et al.*, how sensitive to the anion is the quadrupole splitting in those compounds containing a complex Fe(II) cation? A dependence on the anion would obviously make difficult an estimation of the $q_{lattice}$ contribution to the electric field gradient and hence the partial QS in these complexes.

Dr. G. M. Bancroft (*Cambridge University*) said : In reply to Hill, we have assumed that the contribution to the QS from parts of the lattice other than the nearest neighbour ligands can be neglected. This assumption is most likely to break down for the cationic and anionic compounds. Indeed, the agreement between the predicted and observed values is the poorest for $[Fe(SnCl_3)(ArNC)_5]ClO_4$.

Prof. N. N. Greenwood (*Newcastle upon Tyne*) said: The concept of partial centre shifts is undoubtedly valuable in certain restricted ranges of compounds and it is important to try to establish the range of validity of the concept. The compounds discussed by Bancroft are all 6-coordinate complexes of low-spin iron(II) and as such the range of centre shifts is small. In such cases the temperature of comparison may be important if the compounds have significantly different values for the temperature coefficient of δ. The similarity in centre shifts also requires a restricted range of partial centre shifts and most of the ligands listed in table 3 fall in the range 0-0·1 mm sec^{-1}; agreement between observed and calculated values is therefore not too surprising.

The concept certainly does not work for complexes in which the ligand is πC_5H_5, nor does it work when the spin-state of Fe(II) changes, or when the coordination number of the iron atom alters. For example, it is not applicable to the carbonyl complexes discussed in the preceding paper. Is it possible, therefore, to define conditions when the concept is applicable and when it is not?

Dr. G. M. Bancroft (*Cambridge University*) said: With regard to Greenwood's question on the sensitivity of the C.S., the C.S., as seen in table 1, is surprisingly sensitive to the nature of the ligands. The range of C.S. values for these compounds is almost 0·7 mm/sec—about 40 % of the total range for all iron compounds. The temperature coefficient of the C.S. for all these compounds is similar from 80 to 295°K; perhaps more important are the possible variations in the Z.P.M. shift. However, these variations in the S.O.D. shift should lead to variations in P.C.S. values of one ligand from compound to compound of only about 0·01 mm/sec— and the total range of P.C.S. values is 0·29 mm/sec. The good agreement between predicted and observed values for such a large number of compounds containing ligands having such widely varying P.C.S. values, strongly supports the concept for six-coordinate Fe(II) low-spin compounds.

The concept also applies for Fe(II) six coordinate high spin compounds studied by Hazony *et al.*[1] Although it is difficult to generalize at this stage, it seems likely that the concept of P.C.S. values will usually work for a given coordination number, valency and spin state of iron or any other Mössbauer isotope.

[1] Y. Hazony, R. C. Axtmann and J. W. Hurley, Jr. *Chem. Phys. Lett.*, 1968, **2**, 440.