

528. Proton Chemical Shifts in the Nuclear Magnetic Resonance Spectra of Transition-metal Hydrides: Octahedral Complexes.

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A theory is presented for the large high-field shifts in the nuclear magnetic resonance spectra of protons directly bonded to transition metals in diamagnetic complexes. Distortion of the partly-filled d -shell by the magnetic field, which causes the well-known temperature-independent paramagnetism and large anti-shielding of the metal nucleus, is the main contributor to the chemical shift of the proton. This effect depends on the inverse cube of the distance of the electrons from the proton, and is therefore sensitive to the metal-hydrogen bond-length R , and to the exponent k of the d -orbitals. Detailed calculations are carried out for d^8 low-spin octahedral complexes of O_h , D_{4h} , C_{4v} , and C_{2v} symmetries, the components of the proton shielding tensor being evaluated as functions of R and k . The data are discussed, and shifts of the observed magnitude are obtained for realistic values of R and k . The chemical shifts are very sensitive to anisotropy in the metal atom. Some minor discrepancies are attributed to inadequate stereochemical and spectral information and to uncertainty in the metal d -orbitals. A large anisotropy in the proton shielding ($\sigma_{\parallel} - \sigma_{\perp} \sim -500$ p.p.m.) is predicted.

DURING the last decade a number of transition-metal complexes have been prepared in which a hydrogen atom is attached directly to the metal atom.¹ Although the complexes vary widely in structure and properties, experiments show, in all cases where it has been measured, that the proton line in the n.m.r. spectrum is at higher field than is usual, τ varying between 10 and 50 p.p.m. This shift is now used as a criterion of the presence of a hydrogen atom attached to a transition-metal atom, especially in species obtainable only in solution, where no other method of comparable directness exists.^{1a}

A number of explanations for the shift have been put forward. In an early model for the hydrocarbonyls $\text{CoH}(\text{CO})_4$ and $\text{FeH}_2(\text{CO})_4$ the hydrogen atoms were embedded as protons in the metal atom, forming a "pseudo-atom," and the shift was attributed to high diamagnetic shielding by the metal electrons.² However, the model is now discredited and in any case would not apply to complexes where the hydrogen atom occupies a stereochemical position. Another suggestion was that the hydrogen atom is attached by "a rather ionic bond with hydride-like character,"³ the shift being due to local diamagnetic shielding. Although applied to $\text{CoH}(\text{CO})_4$, where the H atom is acidic in character, this idea seems more applicable to the neutral octahedral and square-planar complexes. However, τ for the free H^- ion⁴ is only 5, so even allowing for orbital contraction due to the neighbouring metal atom, τ values up to 50 p.p.m. cannot be entirely due to local shielding.

It was then suggested that the shifts are due to "paramagnetic circulation on the metal atom as well as diamagnetic shielding,"⁵ and Wilkinson^{1a} suggested a cause similar to that of the high-field shift in hydrogen iodide, *viz.*, paramagnetic anisotropy of the neighbouring atom. He further pointed out that since the large shift is not observed when the H atom is attached to a B-group heavy atom, *e.g.*, Sn or Ge, where $\tau = 5-8$ p.p.m.,⁶ it is probably connected with the d -electrons of the transition-metal atom. Since large paramagnetic screening effects occur when there are accessible low-lying excited electronic states and such states are known to exist in transition-metal complexes with unfilled d -electron shells, it seems reasonable to suggest that they may give rise to

¹ (a) Wilkinson, "Advances in the Chemistry of Coordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 50; (b) Chatt, *Proc. Chem. Soc.*, 1962, 318.

² Cotton and Wilkinson, *Chem. and Ind.*, 1956, 1305.

³ Friedel, Wender, Shufler, and Sternberg, *J. Amer. Chem. Soc.*, 1955, **77**, 3951.

⁴ Ormand and Matsen, *J. Chem. Phys.*, 1959, **30**, 368.

⁵ Bishop, Down, Emtage, Richards, and Wilkinson, *J.*, 1959, 2484.

⁶ Drake and Jolly, *J.*, 1962, 2807; Potter, Pratt, and Wilkinson, *J.*, 1964, 524.

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abnormal shielding of a neighbouring proton, as they do for the metal nucleus itself.⁷ The work presented here is an attempt to calculate the contribution of a transition-metal atom to the shielding of a neighbouring proton, using a simple ligand-field theoretical model for the complexes.

Before considering this in detail, we should note the recent calculation by Stevens, Kern, and Lipscomb⁸ of the proton shielding in $\text{CoH}(\text{CO})_4$, using a modification of the Ramsey theory developed in an attempt to eliminate the need for a knowledge of excited states.⁹ We discuss this calculation more fully later and show that it does not provide a general explanation of the observed shifts.

The complexes so far known can be grouped into (i) d^6 low-spin octahedral, (ii) d^8 low-spin square-planar, and (iii) others (mostly carbonyl and cyclopentadienyl hydrides). This Paper is restricted to octahedral complexes; d^8 planar complexes are considered in a later Paper.

GENERAL THEORY

The electronic shielding of a nucleus is described by the tensor $\sigma_{\alpha\beta}$, given by the Ramsey formula:¹⁰

$$\sigma_{zz} = \frac{e^2}{2mc^2} \langle 0 | \sum_j \left(\frac{x_j^2 + y_j^2}{r_j^3} \right) | 0 \rangle - \frac{e^2}{2m^2c^2} \sum_{n \neq 0} (E_n - E_0)^{-1} \left\{ \langle 0 | \sum_j l_{zj} | n \rangle \langle n | \sum_k r_k^{-3} l_{zk} | 0 \rangle + \langle 0 | \sum_k r_k^{-3} l_{zk} | n \rangle \langle n | \sum_j l_{zj} | 0 \rangle \right\} \quad (1)$$

where $|0\rangle$ and $|n\rangle$ are ground and excited molecular wave functions of energies E_0 and E_n , l_z is the one-electron orbital angular momentum operator, and the origin of the co-ordinate system is at the shielded nucleus. To evaluate the contribution to the shielding of a proton from the d -electrons of a neighbouring transition-metal atom it is convenient to modify equation (1) in the following way. Using the co-ordinate system of Fig. 1, the angular momentum about H can be related to that about M, giving

$$l_{Hx} = l_{Mx} - Ri\hbar(\partial/\partial y_H); \quad l_{Hy} = l_{My} + Ri\hbar(\partial/\partial x_H); \quad l_{Hz} = l_{Mz}.$$

Substituting for l_H , and using the relation,¹¹

$$\langle k | (\partial/\partial r_\alpha) | n \rangle = (-m/\hbar^2)(E_k - E_n) \langle k | r_\alpha | n \rangle,$$

the second term of equation (1) becomes:

$$\begin{aligned} \sigma_{xx}: & -\frac{e^2}{2m^2c^2} \sum_{n \neq 0} (E_n - E_0)^{-1} \left\{ \begin{aligned} & \langle 0 | \sum_j l_{Mxj} | n \rangle \langle n | \sum_k r_{Hk}^{-3} l_{Hxk} | 0 \rangle \\ & + \langle 0 | \sum_k r_{Hk}^{-3} l_{Hxk} | n \rangle \langle n | \sum_j l_{Mxj} | 0 \rangle \end{aligned} \right\} \\ & + \frac{e^2 Ri}{2mc^2 \hbar} \sum_{n \neq 0} \left\{ \begin{aligned} & \langle 0 | \sum_j y_{Hj} | n \rangle \langle n | \sum_k r_{Hk}^{-3} l_{Hxk} | 0 \rangle \\ & - \langle 0 | \sum_k r_{Hk}^{-3} l_{Hxk} | n \rangle \langle n | \sum_j y_{Hj} | 0 \rangle \end{aligned} \right\} \quad (2) \\ \sigma_{zz}: & -\frac{e^2}{2m^2c^2} \sum_{n \neq 0} (E_n - E_0)^{-1} \left\{ \begin{aligned} & \langle 0 | \sum_j l_{Mzj} | n \rangle \langle n | \sum_k r_{Hk}^{-3} l_{Hzk} | 0 \rangle \\ & + \langle 0 | \sum_k r_{Hk}^{-3} l_{Hzk} | n \rangle \langle n | \sum_j l_{Mzj} | 0 \rangle \end{aligned} \right\} \end{aligned}$$

⁷ Griffith and Orgel, *Trans. Faraday Soc.*, 1957, **53**, 601.

⁸ Stevens, Kern, and Lipscomb, *J. Chem. Phys.*, 1962, **37**, 279.

⁹ Kern and Lipscomb, *J. Chem. Phys.*, 1962, **37**, 260.

¹⁰ Pople, Schneider, and Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, Ch. 7.

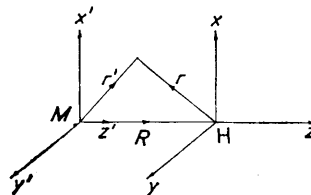
¹¹ Eyring, Walter, and Kimball, "Quantum Chemistry," Wiley, New York, 1944, p. 111.

(2) can be further simplified by contracting the summation over excited states in the second term of σ_{xx} and using the commutation relation $y l_x - l_x y = -i \hbar z$. The full expressions for σ_{xx} and σ_{zz} (σ_{yy} being analogous to σ_{xx}) are then:

$$\begin{aligned} \sigma_{xx} &= \frac{e^2}{2mc^2} \langle 0 | \sum_j \left(\frac{y_{Hj}^2 + z_{Hj}^2 + Rz_{Hj}}{r_{Hj}^3} \right) | 0 \rangle \\ &\quad - \frac{e^2}{2m^2c^2} \sum_{n \neq 0} (E_n - E_0)^{-1} \left\{ \langle 0 | \sum_j l_{Mxj} | n \rangle \langle n | \sum_k r_{Hk}^{-3} l_{Hxk} | 0 \rangle \right. \\ &\quad \left. + \langle 0 | \sum_k r_{Hk}^{-3} l_{Hxk} | n \rangle \langle n | \sum_j l_{Mxj} | 0 \rangle \right\} \\ \sigma_{zz} &= \frac{e^2}{2mc^2} \langle 0 | \sum_j \left(\frac{x_{Hj}^2 + y_{Hj}^2}{r_{Hj}^3} \right) | 0 \rangle \\ &\quad - \frac{e^2}{2m^2c^2} \sum_{n \neq 0} (E_n - E_0)^{-1} \left\{ \langle 0 | \sum_j l_{Mzj} | n \rangle \langle n | \sum_k r_{Hk}^{-3} l_{Hzk} | 0 \rangle \right. \\ &\quad \left. + \langle 0 | \sum_k r_{Hk}^{-3} l_{Hzk} | n \rangle \langle n | \sum_j l_{Mzj} | 0 \rangle \right\} \end{aligned} \quad (3)$$

These can be divided into "diamagnetic" and "paramagnetic" parts, the former

FIG. 1. The co-ordinate system.



depending only on $|0\rangle$, and the latter on both $|0\rangle$ and $|n\rangle$. The observed shielding constant $\sigma = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$ is then $\sigma = \sigma^d + \sigma^p$, where

$$\sigma^d = \frac{e^2}{3mc^2} \langle 0 | \sum_j \left(\frac{r_{Hj}^2 + Rz_{Hj}}{r_{Hj}^3} \right) | 0 \rangle. \quad (4)$$

It is appropriate here to point out that the expression used by Stevens, Kern, and Lipscomb⁸ to calculate σ_H in $\text{CoH}(\text{CO})_4$ is just our σ^d . (The apparent difference in sign is due to a difference in co-ordinate system at H.) It appears therefore that their essentially empirical procedure results in σ^p being neglected. We shall show later that, in complexes with unfilled d -electron shells, σ^p contributes substantially to σ_H , and their theory is therefore inadequate for such complexes. Their reasonable success with first-row hydrides⁹ and with $\text{CoH}(\text{CO})_4$ must be due to σ^p being small in these compounds.

We must now consider the wave functions $|0\rangle$ and $|n\rangle$ to be used. We are primarily concerned with the non-bonding d -electrons of the metal since there seems to be no reason why either the metal-hydrogen bonding electrons or the inner electrons of the metal should give rise to abnormal shielding. We therefore take $|0\rangle$ for a d^6 low-spin complex of O_h symmetry as $|t_{2g}^6\rangle$. The excited states $|n\rangle$ are restricted to states arising from the excitation of non-bonding d -electrons to antibonding orbitals of the same d -shell, these being the states of lowest energy and hence the principal contributors to σ^p . Since equation (3) only contains one-electron operators not acting on the spin co-ordinates this further restricts $|n\rangle$ to singlet states arising from the excitation of only one electron (*i.e.*, from the configuration $|t_{2g}^5 e_g\rangle$ in O_h symmetry). Using these states we neglect the possibility of shielding contributions due to excitation of d -electrons to ligand orbitals or of ligand electrons to metal orbitals. Such transitions seem unlikely for the H ligand, and it is reasonable to expect the contributions for other ligands to be small because of the r_H^{-3} factor in σ^p . (Wilkinson¹⁰ suggested that π -bonding between the metal and phosphine

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ligands *cis* to the H atom might give rise to long-range shielding of the proton; the small and anti-shielding effect of the C=O bond in aldehydes on the aldehydic proton¹² justifies the neglect of this contribution.)

We assume that the ligands are on the cartesian axes. This is not expected to be exactly true, since the H atom is small and distortion from octahedral symmetry has in fact been shown to occur in OsHBr(CO)(PPh₃)₃ by X-ray analysis;¹³ although the H atom was not located, the *cis*-bonds are bent by about 10° towards its expected position. Since we shall show later that the shielding of the proton is very sensitive to anisotropy in the metal atom, the neglect of this distortion could lead to appreciable error in the calculations, and this has to be remembered when comparing the theory with experiment.

THEORY FOR OCTAHEDRAL COMPLEXES

Complexes of the following types are considered: (i) *O_h*, MH₆; (ii) *D_{4h}*, *trans*-MX₄H₂; (iii) *C_{4v}*, MX₅H and *trans*-MX₄HY; (iv) *C_{2v}*, *cis*-MX₄H₂.

(i) *O_h Symmetry*.—The *d*-orbitals are split into two sets, *t_{2g}* and *e_g*. The ground state of the *d*⁶ low-spin ion is ¹A_{1g}(*t_{2g}*⁶). There are two singlet states corresponding to the configuration *t_{2g}*⁵*e_g*, of symmetries *T_{1g}* and *T_{2g}*, the former being lower in energy. The wave functions of these states are given in Appendix 1. Since the angular momentum operator *l_{Mz}* transforms as *T_{1g}* in the octahedral group, only the ¹*T_{1g}* states contribute to σ^p. This is also the case in the shielding of the metal nucleus.⁷ Substituting in equation (3), we obtain: †

$$\begin{aligned} \sigma^d &= \frac{2e^2}{3mc^2} \left[\langle d_{yz} \left| \frac{r_H^2 + Rz_H}{r_H^3} \right| d_{yz} \rangle + \langle d_{zx} \left| \frac{r_H^2 + Rz_H}{r_H^3} \right| d_{zx} \rangle + \langle d_{xy} \left| \frac{r_H^2 + Rz_H}{r_H^3} \right| d_{xy} \rangle \right] \\ \sigma_{xz^p} &= - \frac{e^2}{2m^2c^2\Delta E} \left[\sqrt{3} \langle d_{yz} | l_{Mz} | d_{z^2} \rangle + \langle d_{yz} | l_{Mz} | d_{x^2-y^2} \rangle \right] \times \\ &\quad \left[\sqrt{3} \langle d_{z^2} \left| \frac{l_{Hx}}{r_H^3} \right| d_{yz} \rangle + \langle d_{x^2-y^2} \left| \frac{l_{Hx}}{r_H^3} \right| d_{yz} \rangle \right] \quad (5) \\ \sigma_{xy^p} &= - \frac{2e^2}{m^2c^2\Delta E} \langle d_{xy} | l_{Mz} | d_{x^2-y^2} \rangle \langle d_{x^2-y^2} \left| \frac{l_{Hy}}{r_H^3} \right| d_{xy} \rangle \end{aligned}$$

where $\Delta E = E(^1T_{1g}) - E(^1A_{1g})$.

The wave functions used to derive equation (5) neglect spin-orbit coupling and configuration interaction. The former is only important in the third transition series and even there can probably be neglected without serious error. The latter is most important in the first transition series, and it is known to influence strongly the ¹*T_{2g}* state in Co³⁺ complexes but not the ¹*T_{1g}* state;¹⁴ however, since σ^p involves only the ¹*T_{1g}* state, configuration interaction can reasonably be neglected.

To evaluate equation (5) numerically we assume that the *d*-orbitals can be represented by Slater orbitals of the form:¹⁵

$$\psi(n^*, k, l, m) = \left\{ \frac{(2k)^{2n^*+1}}{(2n^*)!} \right\}^{\frac{1}{2}} r^{n^*-1} e^{-kr} Y_{l,m}(\theta, \phi).$$

We further assume that *k* is the same for all *d*-orbitals of the same shell. Matrix elements of the types $\langle \psi_M | r_H^{-1} | \psi_M \rangle$, $\langle \psi_M | z_H r_H^{-3} | \psi_M \rangle$, and $\langle \psi_M | l_{Hx} r_H^{-3} | \psi'_M \rangle$ can be obtained from the

† σ^d and σ^p henceforth refer to the metal *d*-electron contribution to the shielding.

¹² Pople, *Proc. Roy. Soc.*, 1957, *A*, **239**, 550.

¹³ Orioli and Vaska, *Proc. Chem. Soc.*, 1962, **333**.

¹⁴ Griffith, "The Theory of Transition-Metal Ions," Cambridge University Press, 1961, section 11.6.1.

¹⁵ Ref. 14, p. 104.

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general expressions of Pitzer, Kern, and Lipscomb,¹⁶ and $\langle \psi_M | L_{M\alpha} | \psi'_M \rangle$ is easily calculated directly. The general results are given in Appendix 2 as functions of k , the M-H internuclear distance R , and ΔE , and for $n^* = 3$ and 4, *i.e.*, for principal quantum number $n = 3$ and 5. (The expressions of Pitzer, Kern, and Lipscomb only allow calculation of

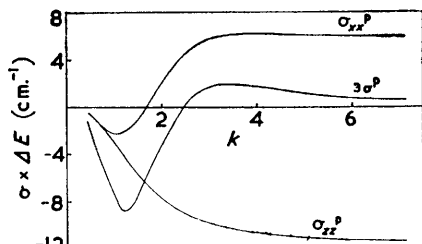


FIG. 2. σ_{xx}^p , σ_{zz}^p , and $3\sigma^p$ for $n = 3$; $R = 2$ a.u.

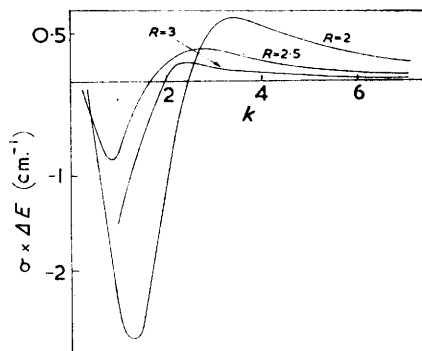


FIG. 3. σ^p for $n = 3$; $R = 2, 2.5, 3$ a.u.

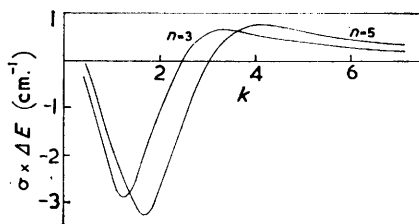


FIG. 4. σ^p for $n = 3, 5$; $R = 2$ a.u.

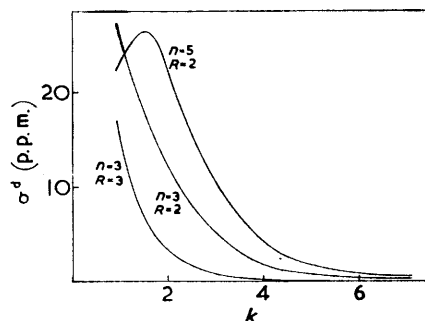


FIG. 5. σ^d for $n = 3$; $R = 2, 3$ a.u.; and $n = 5$, $R = 2$ a.u.

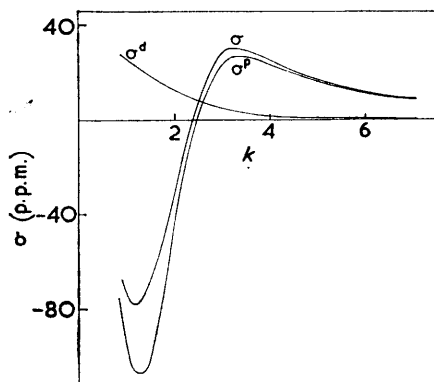


FIG. 6. σ^d , σ^p , and σ for $n = 3$; $R = 2$ a.u., $\Delta E = 25,000$ cm.⁻¹.

matrix elements for integral values of n^* ; results for $n = 4$ must therefore be interpolated between those for $n = 3$ and 5.) Figs. 2—5 illustrate the main features of the results for R values of 2, 2.5, and 3 a.u. (1 a.u. = 0.5292 Å).

The only complexes of O_h symmetry containing a hydride ligand are MH_6 , and no complexes of this type have been made; however, some of types MX_5H and *trans*- MX_4HY

¹⁶ Pitzer, Kern, and Lipscomb, *J. Chem. Phys.*, 1962, **37**, 267.

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approximate to O_h symmetry, and it is worth seeing if and when our theory predicts high-field shifts of the right order of magnitude. Fig. 6 shows σ^d, σ^p , and σ calculated for $n = 3$; $R = 2$ a.u., and $\Delta E = 25,000$ cm.⁻¹. The graph for $R = 3$ a.u. is qualitatively similar, the maximum value of σ being ~ 10 p.p.m. Thus, shifts of ~ 30 p.p.m. are obtained in a symmetrical complex, for $R \sim 2$ a.u. and $k \sim 3$, σ^p being the principal contributor to σ ; a large change in k or increase in R causes an appreciable reduction in σ .

The Magnitudes of R and k .—The metal-hydrogen internuclear distance has so far been determined in two complexes, $\text{FeH}_2(\text{CO})_4$ (from the broad-line proton magnetic resonance spectrum of the solid⁵) and $\text{MoH}_2(\pi\text{-C}_5\text{H}_5)_2$ (by X-ray analysis¹⁷). In both cases R was found to be $\sim 1.1 \text{ \AA} = 2.1$ a.u. While it is unlikely that R is the same in all complexes, in the absence of more data it appears justifiable to take the bond distance as ~ 2 a.u. There seems no reason to reject this as improbably short, as do Stevens, Kern, and Lipscomb,⁸ on the basis of Pauling's atomic radii, since it is doubtful whether these are applicable to the complexes being considered.

The variation in R in series of similar complexes can be roughly estimated from the infrared M-H stretching frequencies, which are known for many complexes and generally lie in the range 1600–2200 cm.⁻¹, since these depend only on the M-H bond. For example, in the series $\text{trans-M}(\text{diphosphine})_2\text{HX}$ ¹⁸ ($\text{M} = \text{Fe, Ru, Os}$) $\nu_{\text{H-M}}$ varies between 1600 and 2000 cm.⁻¹. Using some relation between ν and R , such as the Douglas-Clark rule ($\nu R^3 = \text{const.}$),¹⁹ and taking $R \sim 2$ a.u., the variation in R is ~ 0.2 a.u. Crystallographic data²⁰ also suggest changes in R of this order of magnitude.

Although determination of R is a difficult problem, accurate information could be gained from the effect of partial molecular orientation on the high-resolution n.m.r. spectrum,²¹ and it is hoped in the near future to apply this to complexes of the type $\text{trans-PtHX}(\text{PEt}_3)_2$.

The estimation of k is even more problematic since it cannot be directly measured. It is usual to apply Slater's rules,¹⁵ which for Fe^{2+} and Co^{3+} give 2.08 and 2.42, respectively. However, the recent Hartree-Fock calculations of Watson,²² for a range of first-series transition-metal atoms and ions using Roothaan's method, show that Slater's rules underestimate k for 3d-orbitals. The wave functions are obtained analytically as sums of Slater functions but these are best fitted^{22c} by single Slater functions with k from 3 to 4. The smallness of the Slater rule k is further seen by its prediction of $r_{\text{max.}} = 1.4$ a.u. for Fe^{2+} whereas Watson's calculations give ~ 0.8 a.u.^{22a} It therefore seems reasonable to take free-atom k values between 3 and 4 for Fe^{2+} and Co^{3+} .

However, k will not be the same in a complex as in the free atom, and much evidence from spectral and magnetic data has been advanced that k is reduced in the complex.²³ Brown²⁴ attempted to calculate values of the Racah parameter B , using Slater orbitals, and estimated that decreases of up to 0.8 in k occur due to bonding effects, causing decreases in B . However, Watson's calculations indicate that B cannot be directly calculated by Slater's first-order theory. All that can at present be done is to take k as somewhat less than the free-atom value; values about 3 for Fe^{2+} and Co^{3+} are reasonable. In the absence of calculations for the second and third series transition-metals we take k to be about the same.

Thus, the most probable values of R and k approximate to those giving σ values of

¹⁷ Bennett, Gerloch, McCleverty, and Mason, *Proc. Chem. Soc.*, 1962, 357.

¹⁸ Chatt and Hayter, *J.*, (a) 1961, 5507; (b) 1961, 2605.

¹⁹ Linnett, *Trans. Faraday Soc.*, 1945, **41**, 223; Heath, Linnett, and Wheatley, *Trans. Faraday Soc.*, 1950, **46**, 137.

²⁰ Basolo and Pearson, *Progr. Inorg. Chem.*, 1962, **4**, 381.

²¹ Buckingham and Lovering, *Trans. Faraday Soc.*, 1962, **58**, 2077.

²² (a) Watson, *Phys. Rev.*, 1960, **118**, 1036; (b) 1960, **119**, 1934; (c) Richardson, Nieuwpoort, Powell, and Edgell, *J. Chem. Phys.*, 1962, **36**, 1057.

²³ Owen, *Proc. Roy. Soc.*, 1955, *A*, **227**, 183; Figgis, *Trans. Faraday Soc.*, 1961, **57**, 204; Schäffer and Jørgensen, *J. Inorg. Nuclear Chem.*, 1958, **8**, 143.

²⁴ Brown, *J. Chem. Phys.*, 1958, **28**, 67.

the correct order of magnitude. Henceforth, in making predictions of σ in complexes, we take R and k to be around these optimum values.

σ^p is not very sensitive to changes in ΔE , a variation from 20,000 to 30,000 cm^{-1} causing a change in σ^p_{max} at $R = 2$ a.u. of only ~ 10 p.p.m. Changes in ΔE are therefore not able to account for the much larger changes in τ occurring, for example, in series of complexes of the type *trans*- MX_4HY .

Going from the first to third transition series, ΔE increases, and, although σ^d and σ^p also increase for given R , σ is expected to decrease somewhat, the maximum value for $\Delta E = 44,000 \text{ cm}^{-1}$ being ~ 20 p.p.m.

An interesting feature of the results is that, in certain ranges of k , σ^d and σ^p differ substantially from zero, the value predicted by the near-neighbour dipole approximation (NNA) for an isotropic near-neighbour.¹⁰ In fact, it can be shown that the NNA (using the same approach and wave functions as above) gives expressions for σ^d and σ^p identical with those in Appendix 2 in the limit of $k \rightarrow \infty$, *i.e.*, when the orbitals are contracted to a point at a distance R from the proton. The NNA is inadequate because it treats the neighbouring metal atom as a point; this is obviously not a good approximation for a separation of 2 a.u. Another interesting point is that the equations for σ_{xx}^p and σ_{zz}^p in Appendix 2 reduce to $\sigma_{xx}^p = \sigma_{zz}^p = -8e^2\hbar^2\langle r^{-3} \rangle / m^2c^2\Delta E$ when $R = 0$, and this is precisely the expression for the paramagnetic shielding of the M nucleus.⁷

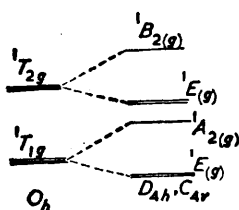


FIG. 7. The splitting of ${}^1T_{1g}$ and ${}^1T_{2g}$ in D_{4h} and C_{4v} .

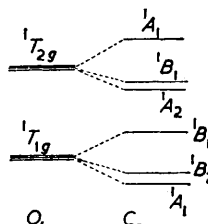


FIG. 8. The splitting of ${}^1T_{1g}$ and ${}^1T_{2g}$ in C_{2v} .

(ii) and (iii) D_{4h} and C_{4v} Symmetries.—The tetragonal perturbation from O_h symmetry splits the degeneracy of the ${}^1T_{1g}$ and ${}^1T_{2g}$ states as shown in Fig. 7. The wave functions of the ground and excited states are given in Appendix 1. It can again be shown that only the states arising from ${}^1T_{1g}$ contribute to σ^p , and, further, that only the 1E state contributes to $\sigma_{xx}^p (= \sigma_{yy}^p)$ and the 1A_2 state to σ_{zz}^p . Substituting in equation (3) we then obtain results identical with equation (5) except that the energy denominators in σ_{xx}^p and σ_{zz}^p become $\Delta E_E = E({}^1E) - E({}^1A_1)$ and $\Delta E_A = E({}^1A_2) - E({}^1A_1)$, respectively. Figs. 2–5 for σ^d , σ_{xx}^p , and σ_{zz}^p therefore apply if these changes in the meaning of ΔE are made. σ^p is the sum of two quantities, $\frac{2}{3}\sigma_{xx}^p$ and $\frac{1}{3}\sigma_{zz}^p$, which are opposite in sign and both much larger than σ^p in the region where σ^p is positive, so σ^p is very sensitive to relative changes in ΔE_E and ΔE_A , *i.e.*, to the anisotropy of the complex. A further general result can be obtained by using expressions for ΔE_E and ΔE_A in terms of ligand parameters, δ , discussed elsewhere.²⁵ δ_X is a measure of the ligand-field strength of ligand X bonded to a metal M, and $= \frac{1}{4}\Delta_X$, where Δ_X is the splitting of the t_{2g} and e_g orbitals in MX_6 . In a complex of type *trans*- MX_4HY , $\Delta E_E = 2\delta_X + \delta_H + \delta_Y - C$, and $\Delta E_A = 4\delta_X - C$, so that in a series of complexes in which Y varies, σ_{zz}^p should be constant while σ_{xx}^p increases as δ_Y decreases (assuming R and k remain constant). σ^p should therefore increase regularly as the ligand-field strength of Y decreases. For example, for $n = 3$ and $R = 2$ a.u., if ΔE_A is constant at 22,000 cm^{-1} and ΔE_E varies from 18,000 to 26,000 cm^{-1} [which is representative of complexes of the type *trans*- FeX_4HY (X = amine or phosphine, Y

²⁵ Stephens, Oxford University D.Phil. Thesis, 1964.

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ranges from I to CN)], $\sigma_{\text{max}}^{\text{p}}$ varies from 70 to 0 p.p.m. This is much larger than the variations caused by average ΔE changes.

(iv) C_{2v} Symmetry.—The splitting of the ${}^1T_{1g}$ and ${}^1T_{2g}$ states in C_{2v} symmetry is shown in Fig. 8. In practice, it is usual to treat the 1A_1 and 1B_2 states from ${}^1T_{1g}$, and the 1A_2 and 1B_1 states from ${}^1T_{2g}$, as degenerate, forming pseudo 1E levels, since simple ligand-field calculations give this result and no splitting is normally observed in the spectrum. The wave functions of the ground and excited states are given in Appendix 1. It is again found that only the states arising from ${}^1T_{1g}$ contribute to σ^{p} , the 1B_1 state contributing to σ_{xx}^{p} and the 1E state to σ_{yy}^{p} and σ_{zz}^{p} . Equation (5) is then unchanged except that the energy denominators in σ_{xx}^{p} , σ_{yy}^{p} , and σ_{zz}^{p} are replaced by ΔE_B , $\Delta E_{E'}$, and $\Delta E_{E''}$, respectively, where $\Delta E_B = E({}^1B_1) - E({}^1A_1)$ and $\Delta E_{E'} = E({}^1E) - E({}^1A_1)$. We again expect σ^{p} to be sensitive to anisotropy.

Using the ligand parameter scheme in which $\Delta E_B = 2\delta_x + 2\delta_{\text{H}} - C$ and $\Delta E_{E'} = 3\delta_x + \delta_{\text{H}} - C$, it can be shown that increasing δ_{H} or decreasing δ_x decreases σ^{p} , but the changes are much less than in the corresponding *trans*- MX_4H_2 complex; this is to be expected since the anisotropy is less. σ^{p} for *cis*- MX_4H_2 should then be greater than σ^{p} for *trans*- MX_4H_2 if $\delta_x < \delta_{\text{H}}$, and *vice versa*.

These results allow us to make a general prediction about the effect on σ^{p} of changes in the ligands, assuming that R and k remain constant; increases in ligand-field strength along the z -axis, *i.e.*, the M-H bond, decrease σ^{p} while increases along the x and y axes increase σ^{p} , the latter changes being smaller per ligand than the former. This has already been demonstrated in complexes of type *trans*- MX_4HY and *cis*- and *trans*- MX_4H_2 , and is also true for less symmetrical complexes; for example, in *cis*- and *trans*- RhX_4HCl , where $\text{X} = \frac{1}{2}\text{en}$ or $\frac{1}{2}\text{trien}$, and, assuming $\delta_{\text{H}} > \delta_x > \delta_{\text{Cl}}$, we predict that σ^{p} is larger for the *trans*- than for the *cis*-complex since the latter is obtained from the former by substituting X for Cl on the z -axis and Cl for X on the x -axis. Similarly, σ^{p} for *cis*- RhX_4H_2 should be greater than for *cis*- RhX_4HCl and smaller for the *trans*-complexes. The magnitude of these changes depends on δ for the particular ligands.

It can be seen that if our theory is correct, and if σ^{d} and other shielding contributions are roughly constant, τ can provide useful stereochemical information on related complexes. We now consider the available τ values to see to what extent these conditions appear to be satisfied.

DISCUSSION

The comparison of the theory with the data is made difficult by two factors. First, there is no experimental way of separating the metal-atom contribution to the observed τ from other contributions; it is reasonable, however, to take the other contributions as giving $\tau \sim 5$ p.p.m. and to compare our predicted metal-atom contributions with the shifts from this value. Secondly, the calculated σ depends on several parameters, R , k , and ΔE , none of which is known with any accuracy for our complexes. We therefore first make a survey of the data to test our general predictions; we then calculate σ using estimates of ΔE and $R = 2$ a.u. for a range of k values. We finally consider the effects of variations in R and ΔE .

To estimate ΔE we have used the δ parameter scheme discussed elsewhere.²⁵ The δ values used in this Paper are given in Table I. δ_{H} for Co^{3+} is derived from the spectrum of $\text{Co}(\text{CN})_5\text{H}^{3-}$; ²⁶ δ_{P} for Ru^{2+} is derived from the spectrum of *trans*- $\text{RuX}_2\{\text{C}_2\text{H}_4(\text{PEt}_2)_2\}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).²⁷ Both are very approximate. The majority of the other δ values are obtained by extrapolation. The uncertainty in δ_{H} ²⁵ should be emphasised since σ^{p} is very sensitive to this.

²⁵ Griffith and Wilkinson, *J.*, 1959, 2757.

²⁷ Chatt and Hayter, *J.*, 1961, 772.

The n.m.r. data at present available for octahedral complexes are assembled in Table 2, giving ($\tau-5$). The complexes range from stable solids with certain stereochemistry [as *trans*-M(diph)₂HX (M = Ru, Os; diph = diphosphine)] to species only detected in solution and where even the formula is uncertain, as with some of the rhodium complexes.

TABLE 1.

δ_X (cm.⁻¹); en = ethylenediamine, trien = triethylenetetramine, P = any phosphine (different phosphines are not distinguished).

Ligand	I	Br	Cl	NH ₃	$\frac{1}{2}$ en	$\frac{1}{4}$ trien	P	H	CN
Metal { Fe ²⁺	1700	—	2700	—	—	—	6100	7700	—
Ru ²⁺	3100	4400	5000	—	—	—	9000	11,400	—
Os ²⁺	3800	—	6100	—	—	—	10,800	13,600	—
Co ³⁺	—	—	—	—	—	—	—	8200	8400
Rh ³⁺	—	—	5100	8500	8700	8700	—	12,100	12,400

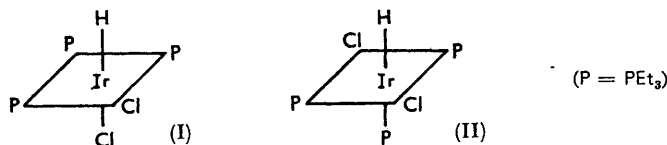
TABLE 2.

N.m.r. data for octahedral complexes.

Complex type	Complex *	Ref.	$\tau - 5$ † (p.p.m.)	ΔE_A ‡ (cm. ⁻¹)	ΔE_B ‡ (cm. ⁻¹)	σ^P (p.p.m.) at $h =$	2.5	3.0	3.5	4.0	4.5
MX ₅ H	Co(CN) ₅ H ³⁻	26	17.1	32,400 §	32,200 §	3.2	18.5	21.1	19.0	—	—
	Rh(CN) ₅ H ³⁻	26	15.3	48,400	48,100	—	5.9	14.2	15.6	13.9	—
<i>trans</i> -MX ₄ HY	Fe[C ₂ H ₄ (PET ₂) ₂] ₂ HCl	18a	38.8	22,000	20,200	16.0	41.6	46.4	43.4	—	—
	Fe[C ₂ H ₄ (PET ₂) ₂] ₂ HI	18a	33.6	22,000	19,200	24.2	51.5	56.9	54.0	—	—
	Fe[<i>o</i> -C ₆ H ₄ (PET ₂) ₂] ₂ HCl	18a	35.7	22,000	20,200	16.0	41.6	46.4	43.4	—	—
	Fe[<i>o</i> -C ₆ H ₄ (PET ₂) ₂] ₂ H ₂	18a, 28	18.1	22,000	25,200	-13.9	4.0	6.0	3.0	—	—
	Ru[C ₂ H ₄ (PET ₂) ₂] ₂ HCl	18b	26.8	34,800	33,200	—	12.2	24.4	26.5	24.5	—
	Ru[C ₂ H ₄ (PET ₂) ₂] ₂ HBr	18b	26.0	34,800	32,600	—	14.0	26.6	28.9	26.6	—
	Ru[C ₂ H ₄ (PET ₂) ₂] ₂ HI	18b	24.3	34,800	31,300	—	18.2	31.6	34.1	31.9	—
	Os[C ₂ H ₄ (PET ₂) ₂] ₂ HCl	18b	31.0	42,300	40,400	—	2.5	17.8	22.3	21.7	—
	Os[C ₂ H ₄ (PET ₂) ₂] ₂ HI	18b	25.8	42,300	38,100	—	6.7	23.4	28.3	27.9	—
<i>cis</i> -MX ₄ H ₂	Rh trien H ₂ ⁺	30	22.1	40,400	37,000	3.5	13.5	15.0	12.8	—	—
	Rh en ₂ H ₂ ⁺	30	26.0	40,400	37,000	3.5	13.5	15.0	12.8	—	—
	RuHCl(CO)(PET ₂ Ph) ₃	29	12.1	—	—	—	—	—	—	—	—
Less symmetrical	<i>cis</i> -Rh trien HCl ⁺	30	23.5	—	—	—	—	—	—	—	—
	IrHCl ₂ (PET ₃) ₃ (I)	1b, 29	26.7	—	—	—	—	—	—	—	—
	(II)	1b, 29	17.6	—	—	—	—	—	—	—	—

* trien = triethylenetetramine; en = ethylenediamine. † The σ values relative to H₂O of Chatt *et al.* have been converted into τ values using $\sigma + 4.7 = \tau$.^{18b} ‡ C is taken to be 2400, 1200, and 900 cm.⁻¹ in the 1st, 2nd, and 3rd transition series, respectively. § From the measured spectrum.²⁰

In accord with our general predictions are the following: (i) in *trans*-Fe(diph)₂HX, τ decreases from X = halogen to X = H; (ii) in *trans*-M(diph)₂HX (X = halogen), τ decreases from M = Fe to M = Ru; (iii) in M(CN)₅H³⁻, τ decreases from M = Co to M = Rh; (iv) τ decreases from (I) to (II) (P = PET₃), the latter being obtainable from the former by replacing Cl on the *z*-axis by P, and P by Cl on the *x*-axis.



Contradicting the predictions are: (i) in *trans*-M(diph)₂HX (M = Fe, Ru, Os), τ decreases in order X = Cl, Br, I, *i.e.*, in reverse order of the ligand-field strengths;

²⁰ Chatt, Hart, and Rosevear, *J.*, 1961, 5504.

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(ii) in *trans*-M(diph)₂HX, τ increases from M = Ru to M = Os; (iii) τ for *cis*-Rh trien HCl⁺ is greater than for *cis*-Rh trien H₂⁺.

For the complexes of *D*_{4h}, *C*_{4v}, or *C*_{2v} symmetry estimated energy levels are given in Table 2; σ^p has been calculated for a range of *k* values and the results are also given in Table 2. The results for 4*d*-complexes are derived by interpolation between those for 3*d* and 5*d*. All calculations are for *R* = 2 a.u. In all cases, in the *k* range where σ^p best fits ($\tau - 5$), σ^d is less than 5 p.p.m.

The results show that the decrease in τ in *trans*-M(diph)₂HX (M = Fe, Ru, Os) in order X = Cl, Br, I can be fitted with constant *R* if *k* decreases in the same order. This is consistent with the order of these ligands in the nephelauxetic series. The observed τ values correspond to $2.5 < k < 3$ for the first transition series, which is reasonable. Apparently *k* increases from the first to the third transition series, and this seems to be the cause of the increase in τ from M = Ru to M = Os in *trans*-M(diph)₂HX. Although this is contrary to Slater's rules,¹⁵ it does not seem unreasonable; *k* values of 3.5–4 are required in the second and third transition series.

Although the calculated σ values can in most cases be made to fit ($\tau - 5$), the maximum calculated σ^p in *trans*-Fe(diph)₂H₂, *cis*-Rh trien H₂⁺, *cis*-Rh en₂ H₂⁺, and *trans*-Os(diph)₂HCl are ~10 p.p.m. below ($\tau - 5$). This could be due to errors in ΔE or *R*; the former is more likely, as δ_H may be smaller than assumed,²⁵ and a decrease in δ_H would increase σ^p , especially in the dihydrido-complexes. Thus, if δ_H for Fe²⁺ were 7000 cm.⁻¹, σ^p would be (corresponding values of *k* in parentheses) 6.7 (2.5), 13.0 (3.0), 15.9 (3.5), 12.6 (4.0) p.p.m. for *trans*-Fe(diph)₂H₂. A decrease in δ_H would also cause a somewhat smaller increase in σ^p for all the monohydrido-complexes, and hence a general decrease in the values of *k* required to fit τ .

It is worth considering whether changes in *R* can provide a more satisfactory explanation of any of the τ variations, but it is difficult to do this reliably since the results are so sensitive to *k*, as shown in Figs. 3 and 5. At *k* = 3, for *n* = 3, a change in *R* from 2 to 2.5 a.u. reduces σ^p by about $\frac{1}{3}$ and σ^d by 1–2 p.p.m. The reduction in σ^p increases with increase in *k*. Changes in *R* ~0.1 Å could therefore give rise to changes in σ of several p.p.m. Changes of this order of magnitude may occur between different metal atoms and contribute to the change in τ . However, infrared data on complexes of the same metal suggest that changes in *R* are only large enough to affect τ significantly in *trans*-Fe(diph)₂HX,^{18a} from X = halogen to X = H, and in the IrHCl₂(PETe)₃ isomers,²⁹ and in neither of these cases are likely to be the predominant cause of the large shift. In *trans*-M(diph)₂HX,¹⁸ ν_{M-H} changes very little with change in X = halogen, and in the opposite direction to that required to explain the observed τ variation.

The major cause of chemical shifts between similar complexes is apparently the change in anisotropy of the metal atom, changes in *k* causing smaller, but in some cases appreciable, variations. Changes in *R* may in some cases contribute to the shifts, but are unlikely to be predominant.

It should be emphasised that the above calculations apply only to right-angular complexes, and that σ is sensitive to the distortion that is almost certainly present in these complexes. This could be the cause of the variations of 3–4 p.p.m. in the pairs *trans*-Fe[L(PETe)₂]₂HCl (L = C₂H₄ and *o*-C₆H₄) and *cis*-Rh(L)H₂⁺ (L = trien and en₂), which are larger than expected from the differences in ligand-field strengths, the presence of bi- and quadri-dentate ligands possibly being responsible for the distortion. Steric effects may also contribute to the shifts in *trans*-M(diph)₂HX (M = Fe, Ru, Os; X = halogen). An investigation of the structure, and optical and n.m.r. spectra, of a series of complexes in which steric differences between the ligands are greater than electronic differences might provide useful insight into this problem.

There remain the data on complexes of symmetry lower than *C*_{2v}; we have already

²⁹ Chatt and Shaw, *Chem. and Ind.*, 1960, 931.

remarked that the shifts in the iridium isomers fit the theory if R and k are the same in both. $\text{RuHCl}(\text{CO})(\text{PEt}_2\text{Ph})_3$ is interesting in that it has a much lower τ than the other ruthenium complexes. Since CO has a high ligand-field strength, the Cl atom should be *cis* to the H atom, and CO is probably *trans*, though this is less certain. It is interesting that this predicted configuration is that found by X-ray analysis for the analogous complex $\text{OsHBr}(\text{CO})(\text{PPh}_3)_3$.¹³

The remaining complex, Rh trien HCl^+ , is, however, not so easy to reconcile with the theory if it is *cis*, as suggested by Gillard and Wilkinson.³⁰ It is unlikely that the *cis*-complex could have τ as high as 28.5 p.p.m. unless $R < 2$ a.u. or there is a considerable reduction in δ_{H} from 12,100 cm^{-1} . Further, if R and k are the same, it should have a higher τ than *cis*-Rh trien H_2^+ . We suspect that the configuration of Rh trien HCl^+ may

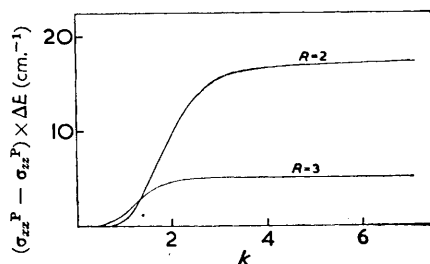


FIG. 9. $(\sigma_{zz}^p - \sigma_{xx}^p)$ for $n = 3$; $R = 2$, 3 a.u.

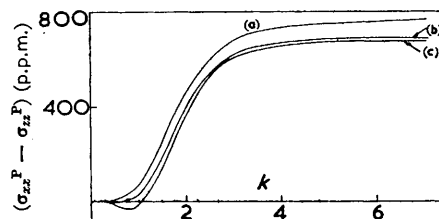


FIG. 10. $(\sigma_{zz}^p - \sigma_{xx}^p)$ for $n = 3$; $R = 2$ a.u.
 ΔE_E (a) 30,000; (b) 25,000; (c) 20,000 cm^{-1} .
 ΔE_A (a) 20,000; (b) 25,000; (c) 30,000 cm^{-1} .

be *trans*, especially as τ for the *trans*-complex should be less than for *trans*- $\text{Ru}(\text{diph})_2\text{HCl}$. The optical spectrum might help to distinguish the two configurations, as in the analogous case of $\text{Co en}_2(\text{NO}_2)\text{Cl}^+$.³¹

The anisotropy in the shielding, $(\sigma_{zz} - \sigma_{xx})$, can be measured through the effect of molecular electric field on the n.m.r. spectrum.²¹ $(\sigma_{zz} - \sigma_{xx})$ can be divided into the local and metal-atom contributions, giving $(\sigma_{zz} - \sigma_{xx}) = (\sigma_{zz}^{\text{local}} - \sigma_{xx}^{\text{local}}) + (\sigma_{zz}^{\text{d}} - \sigma_{xx}^{\text{d}}) + (\sigma_{zz}^{\text{p}} - \sigma_{xx}^{\text{p}})$. $(\sigma_{zz}^{\text{p}} - \sigma_{xx}^{\text{p}})$ has been calculated for a D_{4h} or C_{4v} complex for $n = 3$ and various R , ΔE_E , and ΔE_A combinations; the results are illustrated in Figs. 9 and 10. These show that, at $R = 2$ a.u. and $k > 2.5$, $(\sigma_{zz}^{\text{p}} - \sigma_{xx}^{\text{p}})$ lies in the range -500 — -1000 p.p.m. and therefore swamps the other contributions. Further, while sensitive to R and k , $(\sigma_{zz}^{\text{p}} - \sigma_{xx}^{\text{p}})$ is not sensitive to anisotropy in ΔE since the two large quantities $|\sigma_{xx}^{\text{p}}|$ and $|\sigma_{zz}^{\text{p}}|$ are now being added instead of subtracted. Hence, measurement of $(\sigma_{zz} - \sigma_{xx})$ would provide a valuable check of the theory.

[*Added in proof (May 8th, 1964)*: The theory can adequately account for many of the observed shifts, but more experiments are required to find R and to clarify the importance of changes in R , ΔE , k , and of distortion. Further calculations should be carried out with improved wave-functions for the outer d -orbitals, since these are not accurately represented by a single Slater function,^{22c} which decreases too rapidly in the outer reaches, to which σ_{H} is very sensitive. Probably, our calculations underestimate σ_{H} , so $R > 3$ a.u. (as found in the gaseous transition-metal hydrides MH ³²) could be tolerated.]

(i) The ligand-field strength of the hydride ligand has been shown to be slightly greater than that of CN in $\text{Co}(\text{CN})_5\text{H}_3^-$ from the ultraviolet spectrum.³³ However, the spectra of

³⁰ Gillard and Wilkinson, *J.*, 1963, 3594.

³¹ Basolo, Ballhausen, and Bjerrum, *Acta Chem. Scand.*, 1955, 9, 810.

³² Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York, 1950.

³³ J. M. Pratt, personal communication, May 1964.

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Rh(III) en_2HX complexes show that $\delta_{\text{H}_2\text{O}} < \delta_{\text{H}} < \delta_{\text{H}_3}$,³⁴ indicating that our detailed calculations need modification.

(ii) The decrease in τ for *trans*-Ru(diph) $_2\text{HX}$ from 29—32 for X = halogen to 18—24 for X = alkyl or aryl³⁵ is consistent with the increasing field-strength of X. *cis*- and *trans*-Ru[C $_2\text{H}_4(\text{PPh}_2)_2$] $_2\text{HMe}$ have approximately the same τ , indicating the $\delta_{\text{H}} \sim \delta_{\text{Me}} \sim \delta_{\text{P}}$.

(iii) M-H bond lengths have recently been measured in RhH(CO)(PPh $_3$) $_3$ by X-ray analysis, giving $1.72 \pm 0.15 \text{ \AA}$,³⁶ and in K $_2\text{ReH}_9$ by neutron diffraction, giving $1.68 \pm 0.01 \text{ \AA}$.³⁷

(iv) The comparatively small shifts of the protons in [ReH $_9$] $^{2-}$ ³⁸ and in the hydrocarbonyl (= 16—20 p.p.m.)³⁹ support our view that the larger shifts arise from the partly-filled *d*-shells.

One of us (P. J. S.) thanks the D.S.I.R. for a Research Studentship.

APPENDIX I.

Wave Functions.

In O_h symmetry:

$$\begin{aligned} {}^1A_{1g}a_1 &= |d_{yz}^2d_{zx}^2d_{xy}^2\rangle \\ {}^1T_{1g}x &= (-\sqrt{3/2}\sqrt{2}) |d_{yz}d_{zx}^2d_{xy}^2d_x^2\rangle - (1/2\sqrt{2}) |d_{yz}d_{zx}^2d_{xy}^2d_x^2 - y^2\rangle \\ {}^1T_{1g}y &= (\sqrt{3/2}\sqrt{2}) |d_{yz}^2d_{zx}d_{xy}^2d_x^2\rangle - (1/2\sqrt{2}) |d_{yz}^2d_{zx}d_{xy}^2d_x^2 - y^2\rangle \\ {}^1T_{1g}z &= (1\sqrt{2}) |d_{yz}^2d_{zx}^2d_{xy}d_x^2 - y^2\rangle \\ {}^1T_{2g}\xi &= (-1/2\sqrt{2}) |d_{yz}d_{zx}^2d_{xy}^2d_x^2\rangle + (\sqrt{3/2}\sqrt{2}) |d_{yz}d_{zx}^2d_{xy}^2d_x^2 - y^2\rangle \\ {}^1T_{2g}\eta &= (-1/2\sqrt{2}) |d_{yz}^2d_{zx}d_{xy}^2d_x^2\rangle - (\sqrt{3/2}\sqrt{2}) |d_{yz}^2d_{zx}d_{xy}^2d_x^2 - y^2\rangle \\ {}^1T_{2g}\zeta &= (1/\sqrt{2}) |d_{yz}^2d_{zx}^2d_{xy}d_x^2\rangle \end{aligned}$$

The symmetry notation is as given by Griffith;¹⁴ $|d_{yz}d_{zx}^2d_{xy}^2d_x^2\rangle$ is short for $[|d_{yz}^+d_{zx}^2d_{xy}^2d_x^2\rangle - |d_{yz}^-d_{zx}^2d_{xy}^2d_x^2\rangle]$ and ϕ^2 means $\phi^+\phi^-$, where + and - denote α - and β -spins, respectively. $|>$ indicates an antisymmetrised normalised determinantal wave function.

Assuming the perturbation from O_h to be small, the wave functions in complexes of lower symmetry can be related to those in O_h symmetry. In D_{4h} and C_{4v} symmetries, the 4-fold axis being along the *z*-axis:

$$\begin{array}{ll} {}^1A_{1g}a_1 \longrightarrow & {}^1A_{1g}a_1 \\ {}^1T_{1g}x \longrightarrow & {}^1E_x \quad \quad {}^1T_{2g}\xi \longrightarrow {}^1E_x \\ {}^1T_{1g}y \longrightarrow & {}^1E_y \quad \quad {}^1T_{2g}\eta \longrightarrow -{}^1E_y \\ {}^1T_{1g}z \longrightarrow & {}^1A_{2g}a_2 \quad \quad {}^1T_{2g}\zeta \longrightarrow {}^1B_{2g}b_2 \end{array}$$

where the notation and phases again follow Griffith.¹⁴

In C_{2v} symmetry, with the 2-fold axis in the *xy*-plane and equidistant from the *x*- and *y*-axes:

$$\begin{array}{ll} {}^1A_{1g}a_1 \longrightarrow & {}^1A_1a_1 \\ (1/\sqrt{2})({}^1T_{1g}x + {}^1T_{1g}y) \longrightarrow & {}^1A_1a_1 \quad \quad (1/\sqrt{2})({}^1T_{2g}\xi + {}^1T_{2g}\eta) \longrightarrow {}^1B_1b_1 \\ (1/\sqrt{2})({}^1T_{1g}x - {}^1T_{1g}y) \longrightarrow & {}^1B_2b_2 \quad \quad (1/\sqrt{2})({}^1T_{2g}\xi - {}^1T_{2g}\eta) \longrightarrow {}^1A_2a_2 \\ {}^1T_{1g}z \longrightarrow & {}^1B_1b_1 \quad \quad {}^1T_{2g}\zeta \longrightarrow {}^1A_1a_1 \end{array}$$

³⁴ R. D. Gillard, personal communication, January 1964.

³⁵ Chatt and Hayter, *J.*, 1963, 6017.

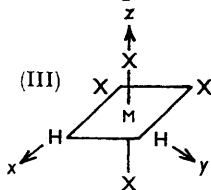
³⁶ LaPlaca and Ibers, *J. Amer. Chem. Soc.*, 1963, **85**, 3501.

³⁷ Abrahams, Ginsberg, and Knox, *Inorg. Chem.*, 1964, **3**, 558.

³⁸ Ginsberg, Miller, Cavanaugh, and Dailey, *Nature*, 1960, **185**, 528.

³⁹ Chatt and Shaw, Proc. XVIIth Internat. Congr. Pure Appl. Chem., 1959, Butterworths, London, 1961, p. 147.

We should point out here that the calculation of σ^p is slightly more difficult in C_{2v} symmetry since, to use the matrix elements of Pitzer, Kern, and Lipscomb, the H atom must be on the z -axis relative to the metal atom, whereas the above functions apply to the orientation (III). It is therefore necessary to rotate the co-ordinate system through 90° , the d -orbitals in the old system being re-expressed as linear combinations of d -orbitals in the new system. All σ -components above refer to the new system.



APPENDIX 2.

General Expressions for σ^d , σ_{xx}^p , and σ_{zz}^p . $\rho = 2kR$.

$$n = 3$$

$$\sigma^d = \frac{2e^2}{3mc^2R} \left[\frac{6720}{\rho^4} - e^{-\rho} \left(\frac{\rho^4}{12} + \frac{13\rho^3}{12} + \frac{53\rho^2}{6} + \frac{111\rho}{2} + 280 + \frac{1120}{\rho} + \frac{3360}{\rho^2} + \frac{6720}{\rho^3} + \frac{6720}{\rho^4} \right) \right]$$

$$\sigma_{xx}^p = \frac{2e^2\hbar^2}{m^2c^2R^3\Delta E} \left[2 + \frac{36}{\rho^2} - e^{-\rho} \left(\frac{\rho^6}{96} + \frac{\rho^5}{24} + \frac{\rho^4}{6} + \frac{2\rho^3}{3} + \frac{5\rho^2}{2} + 8\rho + 20 + \frac{36}{\rho} + \frac{36}{\rho^2} \right) \right]$$

$$\sigma_{zz}^p = -\frac{8e^2\hbar^2}{m^2c^2R^3\Delta E} \left[1 - \frac{24}{\rho^2} + e^{-\rho} \left(\frac{\rho^3}{24} + \frac{\rho^2}{2} + 3\rho + 11 + \frac{24}{\rho} + \frac{24}{\rho^2} \right) \right]$$

$$n = 5$$

$$\sigma^d = \frac{2e^2}{3mc^2R} \left[\frac{15840}{\rho^4} - e^{-\rho} \left(\frac{\rho^6}{672} + \frac{19\rho^5}{672} + \frac{37\rho^4}{112} + \frac{331\rho^3}{112} + \frac{173\rho^2}{8} + \frac{1053\rho}{8} + 660 + \frac{2640}{\rho} + \frac{7920}{\rho^2} + \frac{15840}{\rho^3} + \frac{15840}{\rho^4} \right) \right]$$

$$\sigma_{xx}^p = \frac{2e^2\hbar^2}{m^2c^2R^3\Delta E} \left[2 + \frac{405}{7\rho^2} - e^{-\rho} \left(\frac{\rho^8}{5376} + \frac{\rho^7}{896} + \frac{17\rho^6}{2688} + \frac{23\rho^5}{672} + \frac{59\rho^4}{336} + \frac{139\rho^3}{168} + \frac{191\rho^2}{56} + \frac{163\rho}{14} + \frac{433}{14} + \frac{405}{7\rho} + \frac{405}{7\rho^2} \right) \right]$$

$$\sigma_{zz}^p = -\frac{8e^2\hbar^2}{m^2c^2R^3\Delta E} \left[1 - \frac{270}{7\rho^2} + e^{-\rho} \left(\frac{\rho^5}{1344} + \frac{5\rho^4}{336} + \frac{53\rho^3}{336} + \frac{31\rho^2}{28} + \frac{38\rho}{7} + \frac{128}{7} + \frac{270}{7\rho} + \frac{270}{7\rho^2} \right) \right]$$

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