

# 1

## Theoretical, Physical, and Inorganic Aspects of Chemical Shifts

BY CYNTHIA J. JAMESON AND JOAN MASON

### 1 Introduction

As the convenience and availability of multinuclear n.m.r. spectrometers have increased, the number of papers dealing with applications of the chemical shift has increased to the point where it seems reasonable to separate the applications to organic systems from the inorganic systems. Thus, this Chapter is on the theoretical, physical, and inorganic aspects of chemical shifts, whereas applications to organic systems are treated in Chapter 2. This review covers papers published in the period June 1978 to May 1979. During this period reviews pertinent to the topics covered in this Chapter have appeared.<sup>1-3</sup>

### 2 Theoretical and Physical Aspects of Nuclear Shielding

**A. The Nuclear Shielding Tensor and the Question of Gauge Origin.**—The nuclear magnetic shielding of a nucleus in a molecule in a uniform magnetic field is described by a second rank tensor,  $\hat{\sigma}$ , whose components are defined by

$$\sigma_{\alpha\beta} = \left( \frac{\partial^2 E}{\partial \mu_\alpha \partial B_\beta} \right)_{\mu, \mathbf{B}=0} \quad (1)$$

where  $E$  is the total electronic energy in the presence of the nuclear magnetic moment,  $\hat{\mu}$ , and the uniform magnetic induction,  $\hat{B}$ .

The calculation of the components of the nuclear magnetic shielding involves the evaluation of the matrix elements of operators containing  $\hat{r}_i$  (the position vector of the  $i$ th electron with respect to the chosen origin of co-ordinates) and  $\hat{r}_i \times \hat{p}_i$  (the angular momentum of the  $i$ th electron with respect to the origin of co-ordinates). Of course, the nuclear magnetic shielding itself is independent of the choice of origin. Since approximate wavefunctions are used in numerical calculations, the calculated parts of  $\sigma_{\alpha\beta}$ , which may be denoted by  $\sigma_{\alpha\beta}^d$  and  $\sigma_{\alpha\beta}^p$  (the diamagnetic and paramagnetic terms), each of which is origin dependent, lead to a sum which is not invariant with respect to the choice of origin. In practical terms, the problem of gauge origin has led to alternative approaches to the calculation of nuclear magnetic shielding. These approaches have been discussed in previous reports and will not be repeated here.

- 1 R. K. Harris and B. E. Mann, ed. 'NMR and the Periodic Table', Academic Press, New York, 1979.
- 2 J. Mason, in 'Advances in Inorganic Chemistry and Radiochemistry', ed. H. J. Emeléus and A. G. Sharpe, Academic Press, New York, 1979, Vol. 22, p. 199.
- 3 R. W. Vaughan, in 'Annual Review of Physical Chemistry', ed. B. S. Rabinovitch, Annual Reviews Inc., Palo Alto, 1978, Vol. 29, p. 397.

**B. *Ab Initio* Calculations of the Shielding Tensor.**—There have been a great number of *ab initio* calculations of the magnetic shielding of various nuclei belonging to the first two rows of the Periodic Table from  $^1\text{H}$  to  $^{19}\text{F}$ , most of which have been reviewed in previous volumes. However, there have been no *ab initio* calculations of the full shielding (diamagnetic and paramagnetic terms) for heavier nuclei, probably because the large number of basis functions makes the costs prohibitive. An attempt to reduce the computational effort by separating the inner shells from the molecular calculation and the use of a pseudo-potential in the calculation of the valence shell to represent the overall repulsive effect of the inner shells have been reported by Ridard, Levy, and Millie.<sup>4</sup> Their method employs the following steps: (i) compute the all-electron wavefunction of the free atom and the contribution of the inner shells to  $\sigma^d$ , (ii) compute the valence shell of the molecular system by means of the pseudo-potential and the molecular two-electron repulsion integrals; then orthogonalize the valence orbitals with respect to the inner shells of the free atom and compute the molecular matrix elements of  $L_N$  and  $L_N/r_N^3$ , (iii) compute  $\sigma^d$  and  $\sigma^p$  for the valence shell and (iv) add to the  $\sigma^d$  of (iii) the contribution of the inner shells of the free atom calculated in (i). This computational method was applied to the magnetic shielding of  $^{29}\text{Si}$ ,  $^{31}\text{P}$ ,  $^{33}\text{S}$ , and  $^{35}\text{Cl}$  in  $\text{SiH}_4$ ,  $\text{PH}_3$ ,  $\text{H}_2\text{S}$ , and  $\text{HCl}$ . In their attempts to explore the method, the basis set used to describe the valence shell was not optimized (when the inner shells are not present it is possible to use a larger basis set for the valence shell). Nevertheless, the results are very encouraging. The error in the method relative to that of an all-electron molecular calculation for  $\sigma^d$  was less than half a percent. For  $\sigma^p$  the error is much larger (18% in  $\text{PH}_3$ ), which could easily be reduced to half by improving the basis set for the valence shell. With the increasing interest in shielding of heavy nuclei, it is worthwhile to explore this method of calculation further.

**C. Semi-empirical Calculations.**—The ring-current concept has been used extensively to calculate  $^1\text{H}$  chemical shifts of cyclic conjugated hydrocarbons (see also Chapter 2, Section 2D). It has been shown, however, that the ring currents contribute only about half of the observed deshielding in benzene. The remaining part has been attributed to local anisotropic shielding effects. The combination of these effects appears to provide an explanation of the observed chemical shifts. During this review period, special attention has been paid to systems containing triple bonds. Vogler calculates the sigma core and pi contributions to the shielding separately, using the mean excitation energy approximation, and compares the calculated values with experimental proton shifts in acetylene, ethylene, and benzene.<sup>5</sup> Calculated and experimental results for 42 different hydrocarbons are available as supplementary material. Agarwal and McGlinchey continue their calculations of local anisotropic contributions to proton shielding in pi systems by using the classical analogy of a current circulating in a loop of wire and incorporating the experimental  $^{13}\text{C}$  shielding components.<sup>6</sup> Their recent application of this approximate method to an alkyne is displayed in the form of an isoshielding contour map. It is not possible to assess agreement with experiment since the rest of the contribu-

<sup>4</sup> J. Ridard, B. Levy, and Ph. Millie, *Mol. Phys.*, 1978, **36**, 1025.

<sup>5</sup> H. Vogler, *J. Amer. Chem. Soc.*, 1978, **100**, 7464.

<sup>6</sup> A. Agarwal and M. J. McGlinchey, *Canad. J. Chem.*, 1978, **56**, 959.

tions to the chemical shielding (due to the sigma framework) were not calculated.

The semi-empirical method used by Ellis and co-workers has been reformulated, in large part to use a new set of empirical molecular-orbital parameters chosen in a least-squares procedure so as to fit a set of experimental  $^{13}\text{C}$  shifts of some model compounds.<sup>7</sup> The parameters were tested on a wide variety of hydrocarbons. Other semi-empirical calculations using extended Huckel, INDO, CNDO/S, and MINDO/3 have been reported.<sup>8–10</sup>

**D. Anisotropy of the Shielding Tensor.**—Components of the shielding tensor have become more easily available since the development of high-resolution solid-state n.m.r. techniques.<sup>11</sup> Using the cross-polarization technique of Pines, Gibby, and Waugh, all the  $^{13}\text{C}$  chemical shielding tensors in acetophenone and in *p*-xylene have been determined relative to an external reference of liquid benzene.<sup>12, 13</sup> Two studies which are of special interest are the first applications of n.m.r. to the study of matrix-isolated molecules reported simultaneously by Kohl, Semack, and White and by Zilm, Conlin, Grant, and Michl.<sup>14, 15</sup> In the former case, the proton spectrum of HCl monomer and HCl dimer were observed and the geometry of the HCl dimer was found to be in agreement with the infrared data, but the anisotropy of the argon environment was found to be greater than anticipated from the i.r. line-widths. In the second experiment the components of the  $^{13}\text{C}$  shielding tensor were obtained for matrix isolated ethylene,  $\sigma_{11} = 238 \pm 2$ ,  $\sigma_{22} = 126 \pm 2$ ,  $\sigma_{33} = 29 \pm 2$  p.p.m. to high frequency of  $\text{CH}_4$ , in fairly good agreement with the *ab initio* results using a large basis set. These experiments demonstrate that solid-state n.m.r. spectra of matrix-isolated species offer a means of acquiring chemical shielding anisotropies in small molecules for which the most accurate calculations can be done.

The largest  $^1\text{H}$  shielding anisotropy ever found has been reported for zirconium chloride monohydride; 102.6 p.p.m.<sup>16</sup> Since the hydrogen is believed to insert into the metal-metal double layer, the observed anisotropy may be considered a Knight shift anisotropy. In  $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$ ,  $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ , and  $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ , the bridging protons were found to have a chemical shift anisotropy of less than 30 p.p.m.<sup>17a</sup> As expected, the  $^1\text{H}$  anisotropy of  $\text{CaH}_2$ ,  $\text{SrH}_2$ , and  $\text{BaH}_2$  was found to be small.<sup>17b</sup> The relative orientation of the  $^1\text{H}$  chemical shift tensor principal axes in  $\text{CCl}_3\text{COOH}$  dimer with respect to the molecular frame has been determined.<sup>18</sup> The components of the  $^{31}\text{P}$  chemical shift tensors in single crystals of barium diethylphosphate and in the urea-phosphoric acid complex<sup>19</sup> as well as the anisotropy of the  $^{113}\text{Cd}$  shielding

<sup>7</sup> A. R. Garger, P. D. Ellis, K. Seidman, and K. Schade, *J. Magn. Resonance*, 1979, **34**, 1.

<sup>8</sup> R. M. Aminova, *Mol. Phys.*, 1979, **37**, 319.

<sup>9</sup> R. M. Aminova, H. I. Zoroatskaya, and Y. Y. Samitov, *J. Magn. Resonance*, 1979, **33**, 497.

<sup>10</sup> M. Jallali-Heravi and G. A. Webb, *Org. Magn. Resonance*, 1979, **12**, 174.

<sup>11</sup> A. Pines, M. G. Gibby, and J. S. Waugh, *Chem. Phys. Letters*, 1972, **15**, 373.

<sup>12</sup> J. V. D. Torman, W. S. Veeman, and E. DeBoer, *J. Magn. Resonance*, 1978, **32**, 49.

<sup>13</sup> J. V. D. Torman and W. S. Veeman, *J. Chem. Phys.*, 1978, **68**, 3233.

<sup>14</sup> J. E. Kohl, M. G. Semack, and D. White, *J. Chem. Phys.*, 1978, **69**, 5378.

<sup>15</sup> K. W. Zilm, R. T. Conlin, D. M. Grant, and J. Michl, *J. Amer. Chem. Soc.*, 1978, **100**, 8038.

<sup>16</sup> P. D. Murphy and B. C. Gerstein, *J. Magn. Resonance*, 1979, **34**, 333.

<sup>17</sup> A. T. Nicol and R. W. Vaughan, (a) *J. Amer. Chem. Soc.*, 1979, **101**, 583; (b) *J. Chem. Phys.*, 1978, **69**, 5211.

<sup>18</sup> M. E. Stoll, A. J. Vega, and R. W. Vaughan, *J. Chem. Phys.*, 1978, **69**, 5458.

<sup>19</sup> J. Herzfeld, R. G. Griffin, and R. A. Haberkorn, *Biochemistry*, 1978, **17**, 2711.

in powder samples of  $\text{CdCl}_2$ ,  $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{CdS}$ , and  $\text{CdSe}$  have been determined.<sup>20</sup>

When studies are carried out on partially oriented molecules in a liquid crystal, there is always some uncertainty associated with the results, apart from the difficulties associated with determining the order parameter. The anisotropy measured in a liquid-crystal environment is not necessarily the intrinsic anisotropy in the isolated molecule. It includes some contributions induced by the local fields generated by the liquid-crystal environment. To some extent this is true of measurements in solids and in matrix-isolated species too. An experiment to demonstrate just how large the anisotropy induced by a liquid-crystal environment might be was carried out by Fujiwara and Reeves.<sup>21</sup> Spherically symmetric as an isolated ion,  $^{133}\text{Cs}^+$  ion when placed in lyophilic mesophase showed an induced anisotropy in the Cs shielding, varying from  $-1$  to  $2$  p.p.m. (relative to zero for the isotropic part) with the expected  $3 \cos^2 \theta - 1$  dependence (where  $\theta$  = the angle between the mesophase director and the magnetic field direction).

**E. Magnetic and Electric Field Effects.**—The electric-field and magnetic-field dependence of nuclear shielding has been discussed previously.<sup>22</sup> For electric fields of small magnitude, it is convenient to expand the component  $\sigma_{\alpha\beta}$  of the shielding tensor as a power series in the electric field  $F$

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{(0)} + \sigma_{\alpha\beta\gamma}^{(1)} F_{\gamma} + \frac{1}{2} \sigma_{\alpha\beta\gamma\delta}^{(2)} F_{\gamma} F_{\delta} + \dots \quad (2)$$

where  $\sigma_{\alpha\beta}^{(0)}$  is the value of the component in the absence of the field and the coefficients  $\sigma_{\alpha\beta\gamma}^{(1)}$  and  $\sigma_{\alpha\beta\gamma\delta}^{(2)}$  belong to tensors  $\sigma^{(1)}$  and  $\sigma^{(2)}$  which determine respectively the linear and quadratic field dependence of the shielding. In general there are nine components  $\sigma_{\alpha\beta}$ . The nuclear site symmetry determines the number of independent non-vanishing components. These have been previously tabulated by Buckingham and Malm.<sup>23</sup> If a molecule is placed in a uniform electric field, the site symmetry of some or all of the nuclei may be reduced so that the non-vanishing independent components  $\sigma_{\alpha\beta\gamma}^{(1)}$  for a given  $\gamma$  are not necessarily the same set as the  $\sigma_{\alpha\beta}^{(0)}$ . Raynes and Ratcliffe tabulate the non-vanishing components of the tensors  $\sigma^{(1)}$  and  $\sigma^{(2)}$  for various nuclear site symmetries.<sup>24</sup>

The effects of strong external fields on n.m.r. spectra are two-fold: an alignment effect and the effects due to the dependence of the n.m.r. parameters  $\sigma$  and  $J$  on the field. We are concerned here primarily with the dependence of  $\sigma$  on external electric and magnetic fields. However, it is noteworthy to mention the observation in high-resolution n.m.r. of a magnetic-field-induced alignment of molecules. The effect on n.m.r. spectra of the partial alignment of polar molecules in an electric field is well known.<sup>25</sup> Recently the effect on the  $^2\text{H}$  n.m.r. of partial alignment of the molecules pyrene and naphthalene in solution, induced by the interaction of the anisotropy in the molecular susceptibility  $\Delta\chi$  and the applied magnetic field, has

<sup>20</sup> A. Nolle, *Z. Naturforsch.*, 1978, **33a**, 666.

<sup>21</sup> F. Y. Fujiwara and L. W. Reeves, *Mol. Phys.*, 1978, **36**, 1897.

<sup>22</sup> J. P. Riley and W. T. Raynes, *Mol. Phys.*, 1977, **33**, 619.

<sup>23</sup> A. D. Buckingham and S. M. Malm, *Mol. Phys.*, 1971, **22**, 1127.

<sup>24</sup> W. T. Raynes and R. Ratcliffe, *Mol. Phys.*, 1979, **37**, 571.

<sup>25</sup> C. W. Hilbers and C. MacLean, *Mol. Phys.*, 1969, **16**, 275.

*Theoretical, Physical, and Inorganic Aspects of Chemical Shifts*

been detected.<sup>26, 27</sup> The incomplete averaging of  $(3 \cos^2 \theta - 1)$  over all orientations leads to splitting of the peaks by the quadrupole coupling constant. The splitting is expected to be proportional to  $\Delta\chi B_0^2$  although this could not be verified. The splittings were observed at 9.3 T with a 400 MHz spectrometer.

The possibility that the magnetic-field dependence of the nuclear magnetic shielding for some substances could be observed by high-precision n.m.r. experiments in very strong magnetic fields was first pointed out by Ramsey in 1970.<sup>28</sup> The magnetic field dependence of  $\sigma$  can be expressed as

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{(0)} + \frac{1}{6} \tau_{\alpha\beta\gamma\delta}^{(2)} B_\gamma B_\delta + \dots \quad (3)$$

The odd powers of  $B$  vanish because the magnitude of the shielding must be independent of the direction of the magnetic field. Ramsey estimated the magnitude of  $\tau/\sigma$  and suggested the experimental verification of the magnetic-field dependence of the shielding in cobalt compounds. Since that time n.m.r. spectrometers have shown a trend to higher field strengths and currently spectrometers operating at 600 MHz for protons are in use. An approximate calculation of  $\tau$  for diamagnetic cobalt(III) complexes using only the excited states arising from the  $(t_{2g})^3(e_g)^1$  configuration was carried out by Doddrell, Pegg, and Bendall.<sup>29</sup> They obtain  $\tau B_0^2$  values of  $-0.01$  to  $-0.09$  p.p.m. for a magnetic field corresponding to a  $^1\text{H}$  frequency of 720 MHz. In other words, they estimate an effect which is opposite in sign to  $\sigma^{(0)}$ . In a footnote they report having observed experimentally a field-dependent chemical shift for  $^{59}\text{Co}$  of the order of 1–3 p.p.m. in the same direction as  $\sigma^{(0)}$  upon changing the  $^{59}\text{Co}$  resonance frequency from 3.4 to 21.3 MHz. The discrepancy between the calculated and the experimental values was not explained. An *ab initio* calculation of the magnetic-field dependence of the related molecular property magnetic susceptibility, formulated by Riley and Raynes,<sup>22</sup> was carried out for  $\text{H}_2$ , HF, and BH by Zaucer and Azman.<sup>30</sup> Results indicate a ratio of the order of  $10^{-6}$  for  $B_0 = 6.26$  T for the diamagnetic molecules.

Ideally an experiment demonstrating the magnetic-field dependence of  $\sigma$  should be precise and show an unequivocal quadratic dependence on the field. The frequency separation between two narrow single peaks in a solution containing both species should be measured in several spectrometers covering a range of  $B_0$  values. The chemical shift plotted against  $B_0^2$  should give a straight line with non-zero slope. A heavy nucleus with a large range of chemical shifts would be the best choice. A related electronic property which has a similar magnetic-field dependence is the atomic hyperfine constant. In an elegant experiment reported during this review period, a shift in this constant due to the distortion of the atom in an external magnetic field has been observed for the first time.<sup>31</sup> The hyperfine frequency of  $^{85}\text{Rb}$  atoms plotted as a function of the square of the magnetic field is found to be nicely fitted by a straight line with a slope corresponding to a shift of 93

<sup>26</sup> J. A. B. Lohman and C. MacLean, *Chem. Phys.*, 1978, **35**, 269.

<sup>27</sup> J. A. B. Lohman and C. MacLean, *Chem. Phys. Letters*, 1978, **58**, 483.

<sup>28</sup> N. F. Ramsey, *Phys. Rev.*, 1970, **A1**, 1320.

<sup>29</sup> D. M. Doddrell, D. T. Pegg, and M. R. Bendall, *Austral. J. Chem.*, 1979, **32**, 1.

<sup>30</sup> M. Zaucer and A. Azman, *Phys. Rev.*, 1977, **A16**, 475.

<sup>31</sup> N. P. Economou, S. J. Lipson, and D. J. Larson, *Phys. Rev. Letters*, 1977, **38**, 1394.

Hz at 7.5 T out of a total hyperfine frequency of 3.035 GHz. Fields of 0.2 to 7.5 T were used.

**F. Effects of Vibration and Rotation.**—The theory of the effects of vibration and rotation on the chemical shielding has been reviewed in Volume 8 of this Series. Within the Born–Oppenheimer approximation, chemical shielding can be expressed as in equation (4). The linear terms are due to anharmonic vibration and

$$\sigma = \sigma_e + \sum_s \left( \frac{\partial \sigma}{\partial q_s} \right)_e \langle q_s \rangle + \frac{1}{2} \sum_{s,s'} \left( \frac{\partial^2 \sigma}{\partial q_s \partial q_{s'}} \right)_e \langle q_s q_{s'} \rangle + \dots \quad (4)$$

centrifugal distortion, harmonic vibrational contributions appear in the quadratic and higher order terms. Such effects are manifested experimentally by a temperature-dependent chemical shift in the isolated molecule, as well as shifts induced by isotopic substitution. The latter are discussed in the next Section. One of the authors and her co-workers are continuing experiments on the temperature dependence of the chemical shielding in the isolated molecule, and the theoretical interpretation of the results in terms of anharmonic force fields of the molecules studied.<sup>32, 33</sup> Recent results have been published on CH<sub>3</sub>F, CF<sub>3</sub>H, CF<sub>3</sub>Cl, CF<sub>3</sub>Br, and CF<sub>3</sub>CF<sub>3</sub>.

Molecular-beam studies yielding spin-rotation constants have traditionally been used to obtain the paramagnetic contribution to chemical shielding,  $\sigma^p$ , by exploiting the relationship between the  $\sigma^p$ , with the gauge origin at the nucleus in question, and the spin-rotation constant.<sup>34</sup> This relationship has been a very useful one in providing empirical absolute shielding scales. However, since the dependence of magnetic shielding on molecular configuration has been found to be substantial, the  $R$  dependence of the spin-rotation constant should be examined more carefully. This was done for the spin-rotation constants of the  $J=3$  and  $J=5$  rotational states of H<sub>2</sub>.<sup>35</sup> From the Reid–Chu treatment of the theory, the spin-rotation constant  $C_J$  is made up of three contributions:<sup>36</sup>

$$C_J = C_J^{\text{nuc}} + C_J^{\text{T}} + C_J^{\text{el}} \quad (5)$$

The first and second terms are the nuclear contribution and the Thomas precession contribution (included by Reid and Chu), which have known  $R$  dependences, given the intramolecular potential. The electronic term  $C_J^{\text{el}}$  is the one which is directly related to  $\sigma^p$ . By calculating  $C_J^{\text{nuc}}$  and  $C_J^{\text{T}}$  and subtracting the results from their experimental value of  $C_J$  for the  $J=1, 3$ , and  $5$ , the  $C_J^{\text{el}}$  for these levels were obtained. This electronic term is expanded as a series in  $\xi = (R - R_e)/R_e$ :

$$C_J^{\text{el}} = k \sum_n s_n \left\langle \frac{\xi^n}{R^2} \right\rangle \quad (6)$$

where ( $k$  involves fundamental constants and the proton mass)  $s_n$  are empirical constants to be obtained by fitting the experimental  $C_J^{\text{el}}$ . They find that the leading

<sup>32</sup> C. J. Jameson and A. K. Jameson, *J. Chem. Phys.*, 1978, **69**, 1655.

<sup>33</sup> C. J. Jameson, A. K. Jameson, and H. Parker, *J. Chem. Phys.*, 1978, **69**, 1318.

<sup>34</sup> W. H. Flygare, *Chem. Rev.*, 1974, **74**, 653.

<sup>35</sup> J. Verberne, I. Ozier, L. Zandee, and J. Reuss, *Mol. Phys.*, 1978, **35**, 1649.

<sup>36</sup> R. V. Reid and A. H. Chu, *Phys. Rev.*, 1974, **A9**, 609.

correction term goes as  $\xi/R^2$  rather than  $\xi^2/R^2$ , with no significant improvement by including both  $\xi/R^2$  and  $\xi^2/R^2$ . In a diatomic molecule the empirical constants  $s_n$  are proportional to the derivatives  $\partial^n \sigma^P / \partial \xi^n$ , except for  $s_0$  which is proportional to  $\sigma^P$  at the equilibrium configuration. There is an increasing interest in derivatives such as these for various other molecular electronic properties, e.g., dipole moment and the field gradient.<sup>37</sup>

**G. Isotope Effects.**—As mentioned above, the linear and higher order terms in equation (4) are responsible for the isotope shift in chemical shielding. Many instances of isotopic effects observed in  $^{31}\text{P}$  chemical shifts were reported in this review period. In one of the simplest molecules containing phosphorus,  $\text{PH}_3$ , successive deuteration is accompanied by a rather large low-frequency shift (about 0.85 p.p.m. per D) which is nearly additive.<sup>38</sup> A small but observable deviation from additivity was found. Smaller shifts are expected and observed for smaller fractional change in mass upon  $^{18}\text{O}$  substitution: in the neighbourhood of 0.02 p.p.m.<sup>39–43</sup> These are much smaller than those for deuteration of  $\text{PH}_3$ , not only because of the fractional change in mass being a factor 10 smaller, but also a much smaller  $\partial\sigma/\partial R$  for a nucleus in a nearly tetrahedral site or other highly symmetrical site. The latter situation is suspected to be the main reason for the very small temperature dependence of centrally located nuclei such as  $^{13}\text{C}$  in  $\text{DH}_4$  and  $^{11}\text{B}$  in  $\text{BF}_3$ . The  $^{31}\text{P}$  chemical shifts upon  $^{18}\text{O}$  substitution have been found to be a very useful tool in the study of biochemical reactions.<sup>44</sup>

Equally useful in the study of carbon chemistry in inorganic (carbonyls) and organic systems are the  $^{18}\text{O}$  and deuterium induced isotope shifts in  $^{13}\text{C}$  shielding<sup>45,46</sup> (see also Chapter 2, Section 1A). Large isotope shifts have been observed in the  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  shielding in the tetramethyl stannanes. The  $^{119}\text{Sn}$  resonance shows an isotope shift of 2.86 p.p.m. to low frequency upon full deuteration.<sup>47</sup> Very large isotope shifts are also found in the  $^{59}\text{Co}$  shielding in  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ : 5.2 p.p.m. per deuterium atom.<sup>48</sup>

The relative magnitudes of these shifts can be explained qualitatively in terms of the theory reviewed in Volume 8, which will not be repeated here.<sup>49</sup> A rough way of expressing isotope shifts in shielding is in terms of:

$$\Delta\sigma \simeq (\partial\sigma/\partial R)[\langle R - R_e \rangle_{\text{heavy}} - \langle R - R_e \rangle_{\text{light}}] + (\partial\sigma/\partial\alpha)[\langle \alpha - \alpha_e \rangle_{\text{heavy}} - \langle \alpha - \alpha_e \rangle_{\text{light}}] \quad (7)$$

Of course, quadratic and higher order terms may not be negligible and more than one type of bond extension and angle deformation may need to be considered in a

<sup>37</sup> S. Engstrom and H. Wennerstrom, *Mol. Phys.*, 1978, **36**, 773.

<sup>38</sup> A. K. Jameson and C. J. Jameson, *J. Magn. Resonance*, 1978, **32**, 455.

<sup>39</sup> O. Lutz, A. Nolle, and D. Staschewski, *Z. Naturforsch.*, 1978, **33a**, 380.

<sup>40</sup> G. Lowe and B. S. Sproat, *J.C.S. Chem. Comm.*, 1978, 565.

<sup>41</sup> G. Lowe and B. S. Sproat, *J.C.S. Perkin I*, 1978, 1622.

<sup>42</sup> R. L. Van Etten and J. M. Risley, *Proc. Nat. Acad. Sci. U.S.A.*, 1978, **75**, 4784.

<sup>43</sup> M. Cohn and A. Hu, *Proc. Nat. Acad. Sci. U.S.A.*, 1978, **75**, 200.

<sup>44</sup> M. Cohn and B. D. N. Rao, *Bull. Magn. Resonance*, 1979, **1**, 38.

<sup>45</sup> J. M. Risley and R. L. Van Etten, *J. Amer. Chem. Soc.*, 1979, **101**, 252.

<sup>46</sup> P. E. Pfeiffer, K. M. Valentine, and F. W. Parrish, *J. Amer. Chem. Soc.*, 1979, **101**, 1265.

<sup>47</sup> C. R. Lassigne and E. J. Wells, *J. Magn. Resonance*, 1978, **31**, 195.

<sup>48</sup> M. R. Bendall and D. M. Doddrell, *Austral. J. Chem.*, 1978, **31**, 1141.

<sup>49</sup> C. J. Jameson, *J. Chem. Phys.*, 1977, **66**, 4983.

complex molecule, but most of the shift can be accounted for by the terms in equation (7) for the  $\alpha$  and  $R$  involving the magnetic nucleus being observed and the atom being substituted. This is due to  $\partial\sigma/\partial R$  and  $\partial\sigma/\partial\alpha$  becoming much smaller as the  $\alpha$  and  $R$  being considered are further removed from the magnetic nucleus. The difference in  $\langle R - R_c \rangle$  for the heavy and light isotopomers is greater for a larger fractional mass change and very probably is of the same sign for most molecules, while the derivatives  $(\partial\sigma/\partial R)_c$  are mass-independent and can be of either sign. It has been found in temperature-dependent studies of isolated molecules that the observed temperature dependence is nearly always of the same sign, although at least one exception has been found.<sup>50</sup> Thus, the derivatives  $\partial\sigma/\partial R$  and  $\partial\sigma/\partial\alpha$  are commonly negative but, in at least one instance, may be positive.<sup>51</sup> Indeed, while isotope shifts have been uniformly to low frequency upon heavy-atom substitution, two instances of high-frequency shifts have been reported during this review period: a 0.14 p.p.m. shift in the <sup>119</sup>Cd shielding and a 0.4 p.p.m. shift in the <sup>199</sup>Hg shielding by <sup>13</sup>C substitution in the dimethyl cadmium and mercury compounds, respectively.<sup>52, 53</sup>

Isotope shifts in n.m.r. of paramagnetic molecules have been reported for the first time by Koehler and Proessdorf.<sup>54</sup> The <sup>13</sup>C shielding in metallocenes [the radicals (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>M; M = Co, Fe<sup>+</sup>, Cr, V] exhibited both low- and high-frequency shifts upon deuteration (from 2.0 p.p.m. to low frequency to 7.4 p.p.m. to high frequency). They explained these in terms of differing Fermi contact interactions between <sup>13</sup>C nuclei and the unpaired electron. Since all shifts were referenced to the corresponding diamagnetic ferrocene, the usual isotope shift in diamagnetic molecules has been effectively eliminated. These isotope shifts depend on  $\partial a/\partial R$  where  $a$  is the <sup>13</sup>C hyperfine coupling constant and one should observe isotope shifts in the hyperfine splittings in e.s.r. as well. Thus, these shifts are a measure of  $\partial\rho(\text{spin})/\partial R$ , the change in the spin density at the <sup>13</sup>C nucleus with nuclear configuration. In fact such isotope shifts, though not yet reported in e.s.r. spectra, are to be expected, detection being hampered mainly by line-width problems. The temperature dependence of the hyperfine coupling constants in e.s.r. spectra, also dependent on  $\partial a/\partial R$ , have already been observed and theoretical models proposed for their interpretation.<sup>55, 56</sup>

The isotope shifts discussed here and elsewhere are generally secondary isotope shifts, resulting from substitution of an isotope other than the magnetic nucleus. Some primary isotope shifts have been observed and will become more available for hydrogen with the increasing use of tritium n.m.r. An explanation in terms of the correlation between hydrogen-bonding potentials and the sign of the primary isotope effects has been advanced.<sup>57</sup> The sign of the primary isotope effect measured by observing all three isotopes of hydrogen is assumed to indicate the presence or absence of a double minimum potential.

<sup>50</sup> C. J. Jameson, A. K. Jameson, and H. Parker, *J. Chem. Phys.*, 1978, **68**, 2868.

<sup>51</sup> C. J. Jameson and A. K. Jameson, *J. Chem. Phys.*, 1978, **69**, 615.

<sup>52</sup> J. Jokisaari, K. Raisanen, L. Lajunen, A. Passoja, and P. Pyykko, *J. Magn. Resonance*, 1978, **31**, 121.

<sup>53</sup> J. Jokisaari and K. Raisanen, *Mol. Phys.*, 1978, **36**, 113.

<sup>54</sup> F. H. Koehler and W. Proessdorf, *J. Amer. Chem. Soc.*, 1978, **100**, 5970.

<sup>55</sup> P. D. Sullivan and E. M. Menger, *Adv. Magn. Resonance*, 1977, **9**, 1.

<sup>56</sup> B. T. Sutcliffe and C. Gaze, *Mol. Phys.*, 1978, **35**, 525.

<sup>57</sup> J. L. Altman, P. Laungani, G. Gunnarsson, H. Wennerstrom, and S. Forsen, *J. Amer. Chem. Soc.*, 1978, **100**, 8264.

**H. Intermolecular Effects.**—Solvent shifts are not considered here. Some gas-phase experiments in  $^{13}\text{C}$  n.m.r. of small molecules have been reported and the density and temperature dependence of the  $^{13}\text{C}$  shielding are interpreted in terms of the binary collision model, with only fair success.<sup>58,59</sup> Here, the measured quantity is  $\sigma_1 = (\partial\sigma/\partial\rho)_{\rho=0}$ , the second virial coefficient of nuclear magnetic shielding. The quantitative theory of intermolecular effects on  $\sigma$  is still in the infant stage. The models used to interpret  $\sigma_1$  fail miserably when applied to the temperature dependence of  $\sigma_1$ . In an effort to fill this need, calculations in the simplest systems have been carried out with the hope that the results will lead to some insight on the improvement of models for more complicated systems. Results for the  $\text{H}_2$ –He interacting pair and the interacting triplet state pair of hydrogen atoms have been reported.<sup>60,61</sup> From the results of the calculation by Riley, Hillier, and Raynes, it is possible to estimate the contribution to  $\sigma_1(\text{H}_2, \text{He})$  arising from the repulsive interaction;  $+3$  p.p.m.  $\text{cm}^3 \text{mole}^{-1}$ , to be compared with an experimental estimate of  $-4.6 \pm 2$  in the same units.<sup>60</sup> They conclude that while attractive contributions are predominant in affecting the shielding changes due to intermolecular interaction, the repulsive contributions are by no means negligible as has sometimes been assumed. The interacting triplet-state pair of H atoms is used as a model to explore the  $R^{-8}$  and  $R^{-10}$  dispersion terms.<sup>61</sup> It is found that almost complete cancellation takes place for the sum of  $R^{-8}$  and  $R^{-10}$  terms on one hand and the repulsive contribution on the other. It is surmised that such cancellation of terms accounts for the qualitative success of earlier  $^1\text{H}$   $\sigma_1$  studies where only an  $R^{-6}$  term was considered.

It is interesting to point out that the interpretation of intermolecular effects in nuclear magnetic shielding suffers from just the same types of difficulties as the interpretation of other similar observables. The second virial coefficient of magnetic shielding is an ensemble average of the pair-shielding function, which is the function the two above calculations have been exploring. The analogous electrical property is the pair-polarizability function, which has recently been the subject of many calculations and models. The counterpart of  $\sigma_1$  in this electrical property is the second Kerr virial coefficient,  $B_K$ . A pair of interesting papers describing the temperature and pressure measurements of the Kerr constant for rare gases and spherical top molecules and the theoretical interpretation appeared during the review period. As was found in the interpretation of  $\sigma_1$  of xenon, it is found here that the experimental  $B_K$  of argon has a temperature dependence which has much more curvature than can be explained by any parametrized  $R^{-6}$  term for the pair-polarizability function.<sup>62,63</sup>

### 3 Inorganic Chemical Shifts

**A. Introduction.**—The increasing volume of inorganic n.m.r. studies necessitates increasing selectivity in this Report, which is helped by the abstracting of the work

<sup>58</sup> B. Tiffon and J. E. Dubois, *Org. Magn. Resonance*, 1978, **11**, 295.

<sup>59</sup> F. M. Mourits, Ph.D. Thesis, 1978, Univ. of Regina, Canada.

<sup>60</sup> J. P. Riley, I. H. Hillier, and W. T. Raynes, *Mol. Phys.*, 1979, **38**, 353.

<sup>61</sup> F. H. A. Rummens and S. Rajan, *J. Magn. Resonance*, 1978, **31**, 497.

<sup>62</sup> D. A. Dunmur and N. E. Jessup, *Mol. Phys.*, 1979, **37**, 697.

<sup>63</sup> D. A. Dunmur, D. C. Hunt, and N. E. Jessup, *Mol. Phys.*, 1979, **37**, 713.

under other headings.<sup>64, 65</sup> Criteria for selection are of intrinsic or extrinsic interest as n.m.r. measurements, in such categories as: exploration of uncharted regions of the Periodic Table or lesser known chemistry of better known nuclei, studies designed to yield up secrets of nuclear magnetic shielding or achieving a synthesis of fragmented information, work in which the shifts illuminate important aspects of structure and reactivity, and so on.

Mann<sup>64</sup> has reported on the use of n.m.r. spectroscopy by (literally) thousands of inorganic and organometallic chemists (1693 references) in 1976—7, with an appendix listing references by nuclei observed (*cf.* also <sup>65</sup>).

**B. Solid-state Studies.**—A pleasing development for inorganic chemists is the growing extension of n.m.r. studies to solids. Vaughan<sup>3</sup> has reviewed high-resolution solid-state n.m.r. (with 119 references), and collective volumes have appeared on techniques and applications.<sup>66, 67</sup> Solid-state studies of particular nuclei are detailed in the periodic sequence which follows.

**C. Proton N.M.R.**—A collective work on transition-metal hydrides is awaited with interest.<sup>68</sup> Abstracted chapters refer to hydrido-bridged Pt complexes with catalytic properties (Green, Stone, *et al.*, 29 references), other Pt hydrides (Roundhill, 24 references), and solid-state shielding tensors for hydrides or carbonyl hydrides of Th, Ru, and Os (Nicol and Vaughan) (*cf.* also <sup>17</sup>).

Other transition metal hydrido complexes studied include  $WH_4L_4$  compounds [ $L = P(OR)_3, PR_2Ar, PRAr_2$ ].<sup>69</sup> 2-naphthyl phosphino complexes of Fe, Ru, and Os,<sup>70</sup> bridging hydride complexes of  $Ru_3$  with mercapto- and mercaptothiazole ligands,<sup>71</sup> and a hydride-bridged binuclear dihydridoplatinum(II) complex.<sup>72</sup> *Trans*-effects of halide or  $SnCl_3^-$  ligands in  $Pt^{II}$  complexes have been estimated from the proton shifts;<sup>73</sup> some hydride complexes of Pt are included in Section 3F.

The relative co-ordinating ability of  $NH_4^+$  and  $M^+$  ( $M = Li, Na, K, Cs$ ) is demonstrated by <sup>1</sup>H measurements of solid and molten  $NH_4NO_3$  with admixtures of  $MNO_3$ .  $NO_3^-$  is bidentate with  $Li^+$  and  $Na^+$  but monodentate with larger  $M^+$ .<sup>74</sup> Cationic carbonyl complexes of Mn and Re react with liquid ammonia to give carbamoyl ( $-CONH_2$ ) complexes.<sup>75</sup>

**D. Group I Nuclei.**—It is interesting how far we are from understanding the nuclear magnetic shielding of some of the simplest chemical systems. Although the interpre-

<sup>64</sup> B. E. Mann in 'Spectroscopic Properties of Inorganic and Organometallic Compounds', ed. N. N. Greenwood, (Specialist Periodical Reports), The Chemical Society, London, 1978. Vol. 11, p. 1.

<sup>65</sup> J. R. Wasson and P. J. Corvan, *Analyt. Chem.*, 1978, **50**, 121R.

<sup>66</sup> 'Recent Developments in the Magnetic Resonance of Condensed Matter,' Proceedings of the 4th Ampère International Summer School, ed. R. Blinc and G. Lahajnar, 1976.

<sup>67</sup> 'N.M.R. of Solids,' *NATO Adv. Study Inst. Ser.*, B22, 1974, with an introduction by C. P. Slichter.

<sup>68</sup> 'Transition Metal Hydrides,' Advances in Chemistry Series No. 167, American Chemical Society, 1978.

<sup>69</sup> K. N. Semenenko, V. D. Makhaev, A. P. Borisov, and G. N. Boiko, *Koord. Khim.*, 1978, **4**, 1550.

<sup>70</sup> C. A. Tolman, S. D. Ittel, A. D. English, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1978, **100**, 4080.

<sup>71</sup> S. Jeannin, Y. Jeannin, and G. Lavigne, *Inorg. Chem.*, 1978, **17**, 2103.

<sup>72</sup> G. Bracher, D. M. Grove, L. M. Venanzi, F. Bachechi, P. Mura, and L. Zambonelli, *Angew. Chem.*, 1978, **90**, 826.

<sup>73</sup> P. G. Antonov, Yu. N. Kukushkin, L. N. Mitronina, L. N. Vasil'ev and V. P. Sass. *Zhur. neorg. Khim.*, 1979, **24**, 1008.

<sup>74</sup> S. V. Volkov and N. I. Buryak, *Ukrain. khim. Zhur.*, 1978, **44**, 678.

<sup>75</sup> H. Behrens, R. J. Lampe, P. Merbach, and M. Moll, *J. Organometallic Chem.*, 1978, **159**, 201.

tation of chemical shifts is often limited by ignorance of the 'absolute' magnitude of the shielding, this is fairly easy to estimate for alkali-metal or halide ions, since the shielding of the spherical ion is simply the Lamb term,<sup>76</sup> which is readily calculated or looked up.<sup>77</sup> So as to obtain chemical shifts on such an 'atomic' shielding scale, Lutz and Nolle and 10 colleagues have made a systematic examination<sup>78</sup> of the chemical shifts of the alkali-metal cations (Table 1) and the halide ions (Table 2) in

**Table 1** *N.m.r. measurements<sup>78</sup> for the alkali nuclei in crystalline salts. The given shielding constants have been referred to the free ions by using the chemical shift of the respective salt relative to infinitely dilute aqueous solutions, for which the shielding constants are:  $\sigma^*$  (<sup>7</sup>Li) =  $-(11.0 \pm 0.7) \times 10^{-6}$ ;  $\sigma^*$  (<sup>23</sup>Na) =  $-(60.5 \pm 1.0) \times 10^{-6}$ ;  $\sigma^*$  (<sup>39</sup>K) =  $-(105.2 \pm 0.8) \times 10^{-6}$ ;  $\sigma^*$  (<sup>87</sup>Rb) =  $-(211.6 \pm 1.2) \times 10^{-6}$*

Nucleus	Salt	$\sigma^*_{\text{cryst}}$ in p.p.m.	Typical line-width/ kHz	Type of spectrum <sup>b</sup>
<sup>7</sup> Li	LiBr	$-33 \pm 9$	5.7	s
<sup>7</sup> Li	Li <sub>2</sub> O <sup>a</sup>	$1 \pm 13$	9.0	s
<sup>7</sup> Li	Li <sub>2</sub> S <sup>a</sup>	$-11 \pm 13$	10.0	s
<sup>7</sup> Li	Li <sub>2</sub> MoO <sub>4</sub>	$-7 \pm 8$	5.8	s
<sup>23</sup> Na	NaF	$-70 \pm 15$	7.0	s
<sup>23</sup> Na	NaCl	$-69 \pm 6$	2.7	s
<sup>23</sup> Na	NaBr	$-69 \pm 7$	3.1	s
<sup>23</sup> Na	NaI	$-55 \pm 6$	2.6	s
<sup>23</sup> Na	NaNO <sub>3</sub>	$-45 \pm 4$	2.0	f.o.
<sup>23</sup> Na	NaReO <sub>4</sub>	$-41 \pm 7$	2.0	f.o./s.o.
<sup>23</sup> Na	NaBiO <sub>3</sub>	$-24 \pm 15$	7.0	s
<sup>23</sup> Na	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	$-48 \pm 13$	6.0	s
<sup>23</sup> Na	Na <sub>2</sub> MoO <sub>4</sub>	$-57 \pm 9$		s.o.
<sup>23</sup> Na	Na <sub>2</sub> WO <sub>4</sub>	$-64 \pm 13$		s.o.
<sup>23</sup> Na	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	$-40 \pm 17$		s.o.
<sup>23</sup> Na	Na <sub>2</sub> SO <sub>4</sub>	$-55 \pm 10$		s.o.
<sup>39</sup> K	K <sub>2</sub> SnCl <sub>6</sub>	$-90 \pm 2$	0.05	s
<sup>87</sup> Rb	RbCl	$-338 \pm 3$	1.3	s
<sup>87</sup> Rb	RbBr	$-362 \pm 3$	1.6	s
<sup>87</sup> Rb	RbI	$-390 \pm 5$	1.6	s

<sup>a</sup> Samples have been enriched in <sup>7</sup>Li to 99.99%. This enrichment yields a line-broadening of about 2 kHz compared with naturally abundant samples

<sup>b</sup> s = single line; f.o. = first-order quadrupole split signal; s.o. = second-order quadrupole split central line

crystalline salts, each shielding constant being referred to that of the free aqueous ion at infinite dilution. This procedure gives a consistent measure of the shielding due to the presence of the counter-ion in the solid or aqueous solution.

The Tables show that the variation of the shielding constants with the counter-ion is not necessarily monotonic, nor in the same sense in the different series (results

<sup>76</sup> W. E. Lamb, *Phys. Rev.*, 1941, **60**, 817.

<sup>77</sup> G. Malli and C. Froese, *Internat. J. Quantum Chem.*, 1976, **1s**, 95.

<sup>78</sup> W. Gauss, S. Guenther, A. R. Haase, K. Kerber, D. Kessler, J. Kronenbitter, H. Krueger, O. Lutz, and A. Nolle, *Z. Naturforsch.*, 1978, **33a**, 734, and refs. therein.

**Table 2** *N.m.r. measurements<sup>78</sup> of the halogen nuclei in crystalline alkali halides. The chemical shift data are given as  $(\nu - \nu_{\text{Ref}})/\nu_{\text{Ref}}$ , where  $\nu_{\text{Ref}}$  means the Larmor-frequency of sodium-halide solutions with vanishing concentration in H<sub>2</sub>O. For the evaluation of the shielding constant of <sup>35</sup>Cl in the alkali halides the shielding constant of <sup>35</sup>Cl in diluted aqueous solutions,  $\sigma^*$  (<sup>35</sup>Cl) =  $-(170 \pm 12) \times 10^{-6}$ , has been used*

Nucleus	Salt	Chemical shift in p.p.m.	$\sigma^*$ <sub>cryst</sub> in p.p.m.	Typical line-width/ kHz
<sup>35</sup> Cl	LiCl	+4 ± 8	-174 ± 14	1.3
<sup>35</sup> Cl	NaCl	-44 ± 5	-126 ± 13	0.9
<sup>35</sup> Cl	KCl	+4 ± 1	-174 ± 12	0.2
<sup>35</sup> Cl	RbCl	+45 ± 3	-215 ± 12	0.4
<sup>35</sup> Cl	CsCl	+110 ± 3	-280 ± 12	0.5
<sup>79</sup> Br	LiBr	+109 ± 9		4.2
<sup>79</sup> Br	NaBr	-6 ± 5		2.3
<sup>79</sup> Br	KBr	+47 ± 2		1.0
<sup>79</sup> Br	RbBr	+118 ± 3		1.2
<sup>79</sup> Br	CsBr	+275 ± 3		1.4
<sup>127</sup> I	NaI	+213 ± 4		1.5
<sup>127</sup> I	KI	+179 ± 3		0.8
<sup>127</sup> I	RbI	+257 ± 2		0.9
<sup>127</sup> I	CsI	+548 ± 4		1.1

for <sup>19</sup>F are similar<sup>79</sup>). Nor is the variation well described by the theory of Ikenberry and Das<sup>80</sup> or Hafemeister and Flygare,<sup>81</sup> based on the 'overlapping ion' model of Kondo and Yamashita<sup>82</sup> (using a mean excitation energy, but allowing for next-nearest neighbour interactions).

Popov has reviewed work using alkali metal, <sup>25</sup>Mg, and <sup>109</sup>Ag n.m.r. to investigate complex compounds in non-aqueous solvents (27 references).<sup>83</sup> <sup>7</sup>Li and <sup>15</sup>N studies of LiNCS in aprotic solvents demonstrate solvent-dependent equilibria involving ion-pairing (in DMF) or dimerization (in ether or Me<sub>2</sub>CO<sub>3</sub>). The nitrogen line moves to lower frequencies with increasing concentration and shows the formation of N-bonded species in each case, but some S-bonding is present in THF.<sup>84</sup>

Carbanions of diethyl benzyl and cyanomethyl phosphonates have been studied in <sup>1</sup>H, <sup>13</sup>C, <sup>7</sup>Li, and <sup>31</sup>P resonance. These show some charge delocalization into the ring for the benzylic derivatives, but less for the cyano group. For this the cation and solvent effect shows loose ion pairs to be formed in Me<sub>2</sub>SO, and more aggregated tight ion pairs in THF and pyridine.<sup>85</sup>

Laszlo has published a comprehensive survey of the literature of <sup>23</sup>Na n.m.r.,

<sup>79</sup> R. E. J. Sears, *J. Chem. Phys.*, 1974, **61**, 4368.

<sup>80</sup> D. Ikenberry and T. P. Das, *Phys. Rev.*, 1965, **A138**, 822; *J. Chem. Phys.*, 1965, **43**, 2199; 1966, **45**, 1361.

<sup>81</sup> D. W. Hafemeister and W. H. Flygare, *J. Chem. Phys.*, 1966, **44**, 3584; 1965, **43**, 795.

<sup>82</sup> J. Kondo and J. Yamashita, *J. Phys. Chem. Solids*, 1959, **10**, 245.

<sup>83</sup> I. Alexander Popov, 'Characterisation of Solutes in Nonaqueous Solvents,' Proceedings of Symposium on Electrochem. Charact. Solute Species Nonaqueous Solvents, 1976, 47.

<sup>84</sup> J. Vaes, M. Chabanel, and M. L. Martin, *J. Phys. Chem.*, 1978, **82**, 2420.

<sup>85</sup> T. Bottin-Strzalko, J. Seyden-Penne, Marie-Josie Pouet, and M. P. Simonnin, *J. Org. Chem.*, 1978, **43**, 4346.

including physical and bio-inorganic applications, with 225 references.<sup>86</sup> He has also reported studies of competitive solvation of  $^{23}\text{Na}$  in diethylenetriamine–THF mixtures,<sup>87</sup> and of ‘crowned ion pairs’ of sodium ethyl acetoacetate in THF solutions of crown ethers.<sup>88</sup> The role of crown and cryptand complexation of cations in the formation of metal– $\text{NH}_3$ , metal–amine, and metal–ether solutions has been reviewed (with 192 references).<sup>89</sup>  $^{23}\text{Na}$  is one of the nuclei used to demonstrate the structure of chloroaluminate melts.<sup>90</sup>

Chemical shift anisotropies of  $-3.6$  to  $+5.5$  p.p.m. are reported for  $^{133}\text{Cs}$  counter-ions in lyotropic liquid crystals.<sup>91</sup> Solvent shifts of  $^{133}\text{Cs}^+$  in  $\text{H}_2\text{O}$ –DMF and  $\text{D}_2\text{O}$ –DMF were used to establish solvation preferences.<sup>92</sup>

The  $^{87}\text{Rb}$  and  $^{35}\text{Cl}$  shift tensors, quadrupole data, and magnetic moments in  $\text{RbNiCl}_3$  and  $\text{CsNiCl}_3$  at very low temperatures have yielded independent but consistent estimates of the covalency, together with values for the  $p\sigma$  orbital spin density and the Sternheimer shielding ( $S=31$  for Cl, 26 for Rb, 64 for Cs).<sup>93</sup>

**E. Group II Nuclei.**— $^{135}\text{Ba}$  and  $^{137}\text{Ba}$  are quadrupolar and rather unreceptive nuclei. An account by Lutz and Oehler of  $^{135,137}\text{Ba}$  studies on solid and liquid samples, reporting ratios of  $g_1$  factors, hyperfine structure anomalies, magnetic moments, and atomic shielding constants, have appeared.<sup>94</sup> Work with  $^{25}\text{Mg}$  is referred to in Popov’s review.<sup>83</sup>

**F. Transition Metals.**—Levy and co-workers have used  $^{139}\text{La}$  shifts as a probe of contact or solvent-separated complexation of  $\text{La}^{3+}$  in systems containing acetates, chloroacetates,  $\text{Cl}^-$ , and  $\text{SCN}^-$ .<sup>95</sup>

The results reported by Howarth *et al.* on the pH dependence of  $^{51}\text{V}$  shifts in  $[\text{V}_{10}\text{O}_{28}]^{6-}$  suggest that the first protonation site is probably an out-of-plane apex, rather than the bridging oxygen recently proposed on the basis of  $^{17}\text{O}$  studies.<sup>96</sup>

The electric quadrupole of  $^{51}\text{V}$  allows comparison of the chemical-shift tensor with measurements of the electric field gradient at the nucleus. The values for metavanadates of K, Rb, Mg, and Ca, in conjunction with calculations of the field gradient by the Mulliken–Wolfsberg–Helmholtz semi-empirical method, lead to the conclusion that the electric quadrupole interaction does not follow an ionic model in these compounds.<sup>97</sup>  $^{51}\text{V}$  n.m.r. has been used to identify vanadium complexes with oxo, halo, and MeCN ligands.<sup>98</sup>

Rehder and co-workers have reported the temperature and solvent dependence

<sup>86</sup> P. Laszlo, *Angew. Chem. Internat. Edn.*, 1978, **17**, 254.

<sup>87</sup> C. Detellier, A. Gerstmanns, and P. Laszlo, *Inorg. Nuclear Chem. Letters*, 1979, **15**, 93.

<sup>88</sup> A. Cornelis, P. Laszlo, and C. Cambillau, *J. Chem. Res. (S)*, 1978, 462.

<sup>89</sup> J. L. Dye, *Prog. Macrocyclic Chem.*, 1979, **1**, 63.

<sup>90</sup> U. Anders and J. A. Plambeck, *J. Inorg. Nuclear Chem.*, 1978, **40**, 387.

<sup>91</sup> H. Wennerstrom, N. O. Persson, G. Lindblom, B. Lindman, and G. J. T. Tiddy, *J. Magn. Resonance*, 1978, **30**, 133.

<sup>92</sup> H. Gustavsson, T. Ericsson, and B. Lindman, *Inorg. Nuclear Chem. Letters*, 1978, **14**, 37.

<sup>93</sup> W. B. Euler, C. Long, W. G. Moulton, and B. B. Barrett, *J. Magn. Resonance*, 1978, **32**, 33.

<sup>94</sup> O. Lutz and H. Oehler, *Z. Physik A*, 1978, 288.

<sup>95</sup> P. L. Rinaldi, S. A. Khan, G. R. Choppin, and G. C. Levy, *J. Amer. Chem. Soc.*, 1979, **101**, 1350.

<sup>96</sup> O. W. Howarth and M. Jarrold, *J.C.S. Dalton*, 1978, 503.

<sup>97</sup> V. A. Gubanov, N. I. Lazukova, and R. N. Pletnev, *Zhur. neorg. Khim.*, 1978, **23**, 655.

<sup>98</sup> Yu. A. Buslaev, V. D. Kopanev, A. A. Konovalova, S. B. Bainova, and V. P. Tarasov, *Doklady Akad. Nauk S.S.S.R.*, 1978, **243**, 1175.

of  $^{51}\text{V}$  shifts in  $[\text{VO}(\text{OPr})_3]$ ,<sup>99</sup> and have used  $^{51}\text{V}$  shifts in carbonyl complexes as a measure of the ligand field strength of other ligands – bifunctional arsines,<sup>100a</sup> and phosphines, arsines, stibines, and bismuthines.<sup>100b</sup> The monofunctional ligands increase in  $\pi$ -acceptor strength in the order  $\text{EEt}_3 < \text{EMe}_2\text{Ph} \leq \text{EPPh}_3 < \text{E}(\text{OEt})_3$ , and in overall ligand strength in the order  $\text{EPPh}_3 < \text{EMe}_2\text{Ph} = \text{EEt}_3 < \text{E}(\text{OEt})_3$  ( $\text{E} = \text{P}, \text{As}$ ) and  $\text{BiEt}_3 < \text{AsZ}_3 < \text{PZ}_3 < \text{SbZ}_3$ , depending on covalency of the metal–ligand bond, nephelauxetic effects of the donor atom, and inductive effects of the Z substituent.<sup>100</sup>

$^{93}\text{Nb}$  n.m.r. of  $\text{NbX}_5$  ( $\text{X} = \text{Cl}, \text{Br}$ ) in MeCN solutions in the presence of HF indicates the formation of mixed ligand  $[\text{NbX}_6]^-$  complexes, whereas KNCS gives 6-co-ordinate and 7-co-ordinate mixed-ligand species, and similarly for KNCO.<sup>101</sup> The asymmetry parameters of the electric field gradient at the  $^{93}\text{Nb}$  nucleus in Ti–Nb alloy hydrides have been measured at liquid-nitrogen temperatures and show a high degree of ordering of the metal lattice.<sup>102</sup>

$^{95}\text{Mo}$  but not  $^{97}\text{Mo}$  satellites are observable in  $^{31}\text{P}$  spectra of phosphine complexes of molybdenum since  $^{97}\text{Mo}$  quadrupolar relaxation is too fast.<sup>103</sup> (The disparity in electric quadrupole moment of the two nuclei, which have the same spin and similar magnetic moments, has been explained in terms of the outer half-filled  $d_{5/2}$  neutron shell of  $^{95}\text{Mo}$ , which has no permanent electric quadrupole moment, so that the addition of two neutrons gives a large increment in  $Q$ .)<sup>104</sup>

Very good results are reported for the direct observation of  $^{183}\text{W}$  n.m.r. in polytungstates in  $\text{D}_2\text{O}$ . Sharp singlets are obtained for the Keggin structure complexes  $[\text{X}^n + \text{W}_{12}\text{O}_{40}]^{(8-n)-}$  in which twelve equivalent tungstens enclose a heteroatom ( $\text{X} = \text{H}_2^{2+}, \text{B}^{3+}, \text{Si}^{4+}, \text{P}^{5+}$ ), the shift being very sensitive to the nature of the heteroatom. At higher pD one tungsten is lost to form 11-heteropoly species with five pairs of equivalent tungstens. This structure is faithfully reflected in the spectrum, showing the sensitivity of  $^{183}\text{W}$  n.m.r. for elucidating subtle differences in structure.<sup>105</sup>

The first measurements of  $^{57}\text{Fe}$  n.m.r. in organo-iron complexes are described by Koridze and co-workers,<sup>106a</sup> who used  $^{13}\text{C}$ – $\{^1\text{H}, ^{57}\text{Fe}\}$  triple resonance and enriched  $^{57}\text{Fe}$  up to 90% (from the natural abundance of 2.25%) to investigate the structure of  $\alpha$ -ferrocenyl-carbonium ions. From the comparison with the n.m.r. results for 16 ferrocenes and related complexes, the carbonium ion was found to contain a fulvalene bonded to Fe through all six carbons.<sup>106a</sup>

A linear correlation is demonstrated between  $^{59}\text{Co}$  shifts in hexakis (phosphite)–cobalt(III) complexes and the energy of the longest-wavelength  $d$ – $d$  transition, paralleling also the variation in basicity of the ligand. These results, and the differences from complexes with first-row element ligands, suggest the importance of Co-radius changes in the chemical shifts.<sup>106b</sup>  $^{59}\text{Co}$  shifts in complexes of the type

<sup>99</sup> K. Paulsen, D. Rehder, and D. Thoennes, *Z. Naturforsch.*, 1978, **33a**, 834.

<sup>100</sup> (a) W. R. W. Roose, D. Rehder, H. Leuders, and K. H. Theopold, *J. Organometallic Chem.*, 1978, **157**, 311; (b) R. Talay and D. Rehder, *Chem. Ber.*, 1978, **111**, 1978.

<sup>101</sup> E. G. Il'in, V. P. Tarasov, M. M. Ershova, V. A. Ermakov, M. A. Glushkova, and Yu. A. Buslaev, *Koord. Khim.*, 1978, **4**, 1370.

<sup>102</sup> R. Kh. Kashaev, A. N. Gilmanov, K. S. Saikin, and B. Novak, *Zhur. fiz. Khim.*, 1979, **53**, 45.

<sup>103</sup> G. T. Andrews, and W. McFarlane, *Inorg. Nuclear Chem. Letters*, 1978, **14**, 215.

<sup>104</sup> R. R. Vold and R. L. Vold, *J. Magn. Resonance*, 1975, **19**, 365.

<sup>105</sup> R. Acerete, C. F. Hammer, and L. C. W. Baker, *J. Amer. Chem. Soc.*, 1979, **101**, 267.

<sup>106</sup> (a) A. A. Koridze, N. M. Astakhova, P. V. Petrovskii, and A. I. Lutsenko, *Doklady Akad. Nauk*

[Co(CO)<sub>2</sub>(NO)P(MMe<sub>3</sub>)<sub>n</sub>(<sup>t</sup>Bu)<sub>3-n</sub>], where M = Si, Ge, Sn and n = 1, 2, 3, have been related to i.r. and u.v. spectral data.<sup>106c</sup>

Goggin, Goodfellow, *et al.* report that the <sup>103</sup>Rh line moves to lower frequency with increase in the number of SME<sub>2</sub> or TeMe<sub>2</sub> ligands in halide complexes of Rh(III), and that halide substitution affects the spectra more when *trans* to halide.<sup>107</sup> Chini, Heaton, *et al.* find that <sup>103</sup>Rh shifts in the metal cluster [Rh<sub>7</sub>(CO)<sub>16</sub>]<sup>3-</sup> show a large alternation from high to low frequency, along the C<sub>3</sub> cluster axis.<sup>108</sup> They have also determined the structure in solution of the octahedral rhodium–platinum cluster [Rh<sub>5</sub>Pt(CO)<sub>15</sub>]<sup>-</sup> by <sup>195</sup>Pt n.m.r.<sup>109</sup>

Additivity parameters have been given for substitution of Cl by Br in Pt<sup>II</sup> and Pt<sup>IV</sup> complexes; [PtCl<sub>6</sub>]<sup>2-</sup> is recommended as <sup>195</sup>Pt reference standard.<sup>110</sup>

<sup>195</sup>Pt n.m.r. has been used to study a variety of complex compounds: Pt<sup>II</sup> and Pt<sup>IV</sup> in octylaniline extracts,<sup>111</sup> Pt<sup>II</sup> complexes with SnCl<sub>5</sub><sup>-</sup> ligands,<sup>112</sup> and [PtF<sub>6</sub>]<sup>2-</sup> in an investigation of the isothermic solubility in the systems M<sub>2</sub>PtF<sub>6</sub>–HF–H<sub>2</sub>O (with M an alkali metal).<sup>113</sup> Ebsworth and co-workers have used <sup>195</sup>Pt and other nuclei to characterize Pt<sup>II</sup> and Pt<sup>IV</sup> complexes with cyano, halo, hydride, and phosphine ligands,<sup>114</sup> and also complexes with SH and SeH ligands, deducing redistribution mechanisms.<sup>115</sup> Greenwood, Kennedy, *et al.* have examined dihapto complexes of pentaborane(9) with Pd<sup>II</sup> and Pt<sup>II</sup> by <sup>1</sup>H, <sup>11</sup>B, <sup>31</sup>P, and <sup>195</sup>Pt n.m.r.,<sup>116</sup> and Goggin, Goodfellow, *et al.* carbonyl dichloro organoplatinatate(II) salts, in which the <sup>195</sup>Pt alkylation shifts do not follow the <sup>199</sup>Hg pattern.<sup>117</sup>

There are several obstacles to copper n.m.r. spectroscopy: <sup>63</sup>Cu and <sup>65</sup>Cu are difficult nuclei with large quadrupole moments, and the oxidation state Cu<sup>I</sup> giving diamagnetic compounds is unstable in water. Cu<sup>I</sup> can, however, be stabilized in the solid state as in the cuprous halides, or in solvents which are π-acceptor ligands, *e.g.*, MeCN or phosphite. Reports of FT studies of <sup>63</sup>Cu and <sup>65</sup>Cu compounds have appeared, giving ratios of g<sub>1</sub> factors, nuclear magnetic moments, and chemical shifts for solid Cu<sup>I</sup> halides and [CuL<sub>4</sub>]<sup>+</sup> solutions with L = P(OR)<sub>3</sub>, py, or NCMe, with the tetracyano complex as reference.<sup>118, 119</sup>

Becker has studied the temperature dependence of the <sup>65</sup>Cu and halide (<sup>35</sup>Cl, <sup>81</sup>Br, <sup>127</sup>I) shifts in Cu<sup>I</sup> halides from –150 °C to the molten state, as a probe of covalent character. On simple shielding theory assuming tight binding, covalency should

S.S.S.R., 1978, **242**, 117; (b) R. Weiss and J. G. Verkade, *Inorg. Chem.*, 1979, **18**, 529; (c) H. Schumann, M. Meissner, and H. J. Kroth, *Z. Naturforsch.*, 1978, **33b**, 1489.

<sup>107</sup> S. J. Anderson, J. R. Barnes, P. L. Goggin, and R. J. Goodfellow, *J. Chem. Res. (S)*, 1978, 286.

<sup>108</sup> C. Brown, B. T. Heaton, L. Longhetti, D. O. Smith, P. Chini, and S. Martinengo, *J. Organometallic Chem.*, 1979, **169**, 309.

<sup>109</sup> A. Fumagalli, S. Martinengo, P. Chini, A. Albinati, S. Bruckner, and B. T. Heaton, *J.C.S. Chem. Comm.*, 1978, 195.

<sup>110</sup> S. J. S. Kerrison and P. J. Sadler, *J. Magn. Resonance*, 1978, **31**, 321.

<sup>111</sup> S. S. Kurasova, S. N. Ivanova, L. Ya Al't, L. M. Gindin, A. A. Bezzubenko, and V. A. Ershova, *Izvest. sibirsk. Otdel. Akad. Nauk, Ser. khim. Nauk*, 1978, 66.

<sup>112</sup> P. S. Pregosin and S. N. Sze, *Helv. Chim. Acta*, 1978, **61**, 1848.

<sup>113</sup> V. A. Shipachev, S. V. Zemskov, B. I. Peschevitskii, V. I. Belevantsev, K. A. Grigорова, and L. Ya. Al't, *Tezisy Dgklady – Vses. Soveshch. Khim., Anal. Teknol. Blagorodn. Met.*, 10th, 1976, 1, 43.

<sup>114</sup> I. M. Blacklaws, L. C. Brown, E. A. V. Ebsworth, and F. J. S. Reed, *J.C.S. Dalton*, 1978, 877.

<sup>115</sup> I. M. Blacklaws, E. A. V. Ebsworth, D. W. H. Rankin, and H. E. Robertson, *J.C.S. Dalton*, 1978, 753.

<sup>116</sup> N. N. Greenwood, J. D. Kennedy, and J. Staves, *J.C.S. Dalton*, 1978, 1146.

<sup>117</sup> J. Browning, P. L. Goggin, R. J. Goodfellow, N. W. Hurst, L. G. Mallinson and M. Murray, *J.C.S. Dalton*, 1978, 872.

<sup>118</sup> O. Lutz, H. Oehler, and P. Kroneck, *Z. Physik A*, 1978, **288**, 17.

<sup>119</sup> O. Lutz, H. Oehler, and P. Kroneck, *Z. Naturforsch.*, 1978, **33a**, 1021.

correlate with shifts to low frequency, in which case the covalency increases  $\text{CuBr} < \text{CuCl} < \text{CuI}$ , in agreement with estimates by other methods. In the low-temperature cubic phases the cation resonance shifts to lower frequency and the anion resonance to higher frequency as the temperature increases, due to the increase in vibrational overlap.<sup>120</sup>

<sup>109</sup>Ag work is included in Popov's review.<sup>83</sup>

Nolle has reported <sup>113</sup>Cd shielding anisotropies in crystalline  $\text{CdCl}_2$ ,  $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{CdS}$ , and  $\text{CdSe}$ , which are axially symmetric, and isotropic shielding in crystalline  $\text{CdF}_2$ ,  $\text{CdI}_2$ ,  $\text{CdO}$ ,  $\text{CdTe}$ , and  $\text{CdCO}_3$ .<sup>20</sup> New Cd  $\pi$ -arene complexes  $[\text{Cd}\eta^6\text{-L}][\text{AsF}_6]_2$  with  $\text{L} = \text{C}_6\text{Me}_6$ ,  $\text{C}_6\text{Et}_6$ , and  $\text{C}_6\text{Me}_5\text{H}$  have been measured in <sup>113</sup>Cd resonance.<sup>121</sup> Octahedral and tetrahedral co-ordination of  $\text{Cd}^{\text{II}}$  in halide complexes in water and in DMSO has been monitored by <sup>113</sup>Cd n.m.r.<sup>122a</sup> The effect of halide complexation on <sup>113</sup>Cd shifts has been studied in solution and in the solid state (with cross-polarization and magic-angle spinning techniques).<sup>122b</sup>

Goggin, Goodfellow, *et al.* have followed the addition of halide ion or  $\text{SCN}^-$  to (linear)  $\text{RHgX}$  to form  $[\text{RHgX}_2]^-$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CN}$ ) by vibrational spectroscopy and <sup>199</sup>Hg n.m.r.;<sup>123</sup> *cf.* their comparison of  $\delta(^{199}\text{Hg})$  in  $[\text{HgXR}]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{R}$ ) and  $\delta(^{195}\text{Pt})$  in  $[\text{PtCl}_2\text{R}(\text{CO})]$ .<sup>117</sup> Also reported in <sup>199</sup>Hg resonance are organosilyl and organogermeryl mercurials such as  $\text{RHgSiMe}_3$  and  $\text{Hg}(\text{SiMe}_3)_2$ ,<sup>124, 125</sup> plus stannyl derivatives,<sup>125</sup> and benzyl mercuric chlorides, in which *o*-methyl substituents in the benzene ring cause low-frequency shifts of the Hg resonance by departures from planarity.<sup>126</sup>

**G. Group III Nuclei.**—Boron n.m.r. has been applied to the study of tetra-alkyl diboranes,<sup>127</sup> alkylborates (borohydrides),<sup>128–130</sup> bora-alkanes (alkenyl trimethylstannanes),<sup>131</sup> diazadiborines,<sup>132</sup> borane anions,<sup>133</sup> carboranes,<sup>134, 135</sup> tmen-tetraborane,<sup>136</sup>  $\text{B}_2\text{H}_4 \cdot 2\text{PMe}_3$ ,<sup>137</sup> the methanolysis of boron–nitrogen compounds,<sup>138</sup> and scrambling reactions in  $\text{B}(\text{NET}_2)_3 \cdot \text{PCl}_3$  (*etc.*).<sup>139</sup>

<sup>120</sup> K. D. Becker, *J. Chem. Phys.*, 1978, **68**, 3785.

<sup>121</sup> L. C. Damude and P. A. W. Dean, *J. Organometallic Chem.*, 1979, **168**, 123.

<sup>122a</sup> T. Drakenberg, N. O. Bjork, and R. Portanova, *J. Phys. Chem.*, 1978, **82**, 2423.

<sup>122b</sup> J. J. H. Ackerman, T. V. Orr, B. J. Bartuska, and G. E. Maciel, *J. Amer. Chem. Soc.*, 1979, **101**, 341.

<sup>123</sup> P. L. Goggin, R. J. Goodfellow, and N. W. Hurst, *J.C.S. Dalton*, 1978, 561.

<sup>124</sup> T. N. Mitchell and H. C. Marsmann, *J. Organometallic Chem.*, 1978, **150**, 171.

<sup>125</sup> M. Flarin, D. V. Gendin, V. A. Pesunovich, O. A. Kruglaya, and N. S. Vyazankin, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1979, 697.

<sup>126</sup> Yu A. Strelenko, Yu G. Bundel, F. H. Kasumov, V. I. Rozenberg, O. A. Reutov, and Yu A. Ustyniuk, *J. Organometallic Chem.*, 1978, **159**, 131.

<sup>127</sup> M. E. Kuimova and V. M. Mikhailov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1979, 314.

<sup>128</sup> C. A. Brown, *J. Organometallic Chem.*, 1978, **156**, C17.

<sup>129</sup> J. L. Hubbard, and G. W. Kramer, *J. Organometallic Chem.*, 1978, **156**, 81.

<sup>130</sup> P. R. Oddy and M. G. H. Wallbridge, *J.C.S. Dalton*, 1978, 572.

<sup>131</sup> A. Schmidt and B. Wrackmeyer, *Z. Naturforsch.*, 1978, **33b**, 855.

<sup>132</sup> H. Schmidt and W. Siebert, *J. Organometallic Chem.*, 1978, **155**, 157.

<sup>133</sup> N. N. Greenwood and J. Staves, *J. Inorg. Nuclear Chem.*, 1978, **40**, 5.

<sup>134</sup> F. R. Scholer, R. Brown, D. Gladkowski, W. F. Wright, and L. J. Todd, *Inorg. Chem.*, 1979, **18**, 921.

<sup>135</sup> H. M. Colquhoun, T. J. Greenhough, M. G. H. Wallbridge, S. Hermanek, and J. Plesek, *J.C.S. Dalton*, 1978, 944.

<sup>136</sup> H. M. Colquhoun, *J. Chem. Res. (S)*, 1978, 451.

<sup>137</sup> R. K. Hertz, M. L. Denniston, and S. G. Shore, *Inorg. Chem.*, 1978, **17**, 2673.

<sup>138</sup> C. R. Balulescu and P. C. Keller, *Inorg. Chem.*, 1978, **17**, 3707.

<sup>139</sup> J. P. Costes, G. Cros, and J. P. Laurent, *J. Inorg. Nuclear Chem.*, 1978, **40**, 829.

Heteroatom boranes studied in boron resonance include diaminoborane,<sup>140</sup> B<sub>10</sub>H<sub>12</sub>E compounds (with E = BH<sup>2-</sup>, CH<sup>-</sup>, CNMe<sub>3</sub>, PR, AsR, As<sup>-</sup>, S, Se, and Te) showing substituent effects on the antipodal boron (B<sub>5</sub>),<sup>141</sup> B<sub>11</sub>H<sub>11</sub>E (E = Se, Te) and 1,2-B<sub>10</sub>H<sub>10</sub>CHAs,<sup>142</sup> a nickeloborane ion [(B<sub>10</sub>H<sub>12</sub>)<sub>2</sub>Ni]<sup>2-</sup>,<sup>143</sup> and Ni<sub>4</sub>B<sub>4</sub> cluster compounds ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>4</sub>Ni<sub>4</sub>B<sub>4</sub>H<sub>4</sub> and ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>4</sub>Ni<sub>4</sub>B<sub>5</sub>H<sub>5</sub>.<sup>144</sup> Pd<sup>II</sup> and Pt<sup>II</sup> derivatives of pentaborane(9) have been studied in <sup>11</sup>B and <sup>195</sup>Pt resonance.<sup>116</sup> Different kinds of boron sites are distinguished in borate glasses by boron n.m.r.<sup>145, 146</sup>

Complex ions of Al investigated in <sup>27</sup>Al resonance include chloroaluminate ions in melts containing Na<sup>+</sup>, K<sup>+</sup>, and NH<sub>4</sub><sup>+</sup>,<sup>90</sup> and polymeric aquated cations produced by hydrolysis of Al salt solutions.<sup>147</sup> <sup>27</sup>Al and <sup>69,71</sup>Ga resonance have been applied to the investigation of contact and solvent-separated ion pairs in Al and Ga halide alcohol solutions,<sup>148, 149</sup> and to thiocyanato and cyanato halide complexes of Al and Ga, in which the chemical shifts agree with values estimated from pairwise additivity.<sup>150</sup>

<sup>205</sup>Tl chemical shifts are large and can serve as a measure of solvent interactions and of covalency in organothallium compounds, and can be used to estimate stability constants of M<sup>+</sup> ions with polyether macrocycles (M = Li, Na, K, Rb, Cs, NH<sub>4</sub>, Ag).<sup>151</sup> <sup>205</sup>Tl shifts have been reported for Tl<sup>III</sup> EDTA complexes,<sup>152</sup> and for Tl<sup>I</sup> complexes with antibiotics (nonactin, monactin, and dinactin).<sup>153</sup> Phosphorus-selenium-thallium glasses have been studied in <sup>205</sup>Tl and <sup>31</sup>P resonance, the chemical shifts indicating covalent interaction with Se.<sup>154</sup>

**H. Group IV Nuclei.**—<sup>13</sup>C measurements are now routine in co-ordination chemistry as in organic and organometallic chemistry, so this account is very selective. A volume in the 'NMR, Principles and Progress' series has been devoted to <sup>31</sup>P and <sup>13</sup>C studies of transition-metal phosphine complexes.<sup>155</sup>

A large anisotropy (> 50 p.p.m.) in chemical shift has been measured for arene ring-carbons in [(C<sub>6</sub>R<sub>6</sub>)Cr(CO)<sub>3</sub>] complexes (R = H, Me, Et) in the solid state by Waugh *et al.*<sup>156</sup> As mentioned above,<sup>15</sup> Grant and co-workers report the first <sup>13</sup>C

<sup>140</sup> T. S. Briggs, W. D. Gwinn, W. L. Jolly, and L. R. Thorne, *J. Amer. Chem. Soc.*, 1978, **100**, 7762.

<sup>141</sup> W. F. Wright, A. R. Garber, and L. J. Todd, *J. Magn. Resonance*, 1978, **30**, 595.

<sup>142</sup> G. D. Friesen and L. J. Todd, *J.C.S. Chem. Comm.*, 1978, 349.

<sup>143</sup> A. R. Siedle, G. M. Bodner, A. R. Garber, R. F. Wright, and L. J. Todd, *J. Magn. Resonance*, 1978, **31**, 203.

<sup>144</sup> J. R. Bowser and R. N. Grimes, *J. Amer. Chem. Soc.*, 1978, **100**, 4623.

<sup>145</sup> G. E. Jellison and P. J. Bray, *J. Non-Cryst. Solids*, 1978, **29**, 187.

<sup>146</sup> Y. H. Yun and P. J. Bray, *J. Non-Cryst. Solids*, 1978, **30**, 45.

<sup>147</sup> J. W. Akitt and A. Farthing, *J. Magn. Resonance*, 1978, **32**, 345.

<sup>148</sup> Yu A. Buslaev, V. P. Tarasov, S. P. Petrosyants, and G. A. Kirakosyan, *Doklady Akad. Nauk S.S.S.R.*, 1978, **241**, 838.

<sup>149</sup> Yu A. Buslaev, V. P. Tarasov, S. P. Petrosyants, and G. A. Kirakosyan, *Koord. Khim.*, 1978, **4**, 1346.

<sup>150</sup> V. P. Tarasov, S. P. Petrosyants, G. A. Kirakosyan, and Yu A. Buslaev, *Doklady Akad. Nauk S.S.S.R.*, 1978, **242**, 156.

<sup>151</sup> J. I. Zink, C. Srivnavit, and J. J. Dechter, *Organometallic Polym. (Symp.)*, 1977, 323.

<sup>152</sup> K. I. Popov, V. V. Vekshin, V. F. Chuvayev, and N. I. Pechurova, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1978, 1195.

<sup>153</sup> R. W. Briggs and J. F. Hinton, *J. Magn. Resonance*, 1979, **33**, 363.

<sup>154</sup> L. A. Baidakov, A. N. Katruzov, and Kh. M. El Labani, *Izvest. Akad. Nauk S.S.S.R., Neorg. Materialy*, 1978, **14**, 1810.

<sup>155</sup> P. S. Pregosin and R. W. Kunz, '<sup>31</sup>P and <sup>13</sup>C NMR of Transition Metal Phosphine Complexes' (NMR, Vol 16), Springer-Verlag, Berlin, 1979.

<sup>156</sup> M. M. Maricq, J. A. Waugh, J. L. Fletcher, and M. J. McGlinchey, *J. Amer. Chem. Soc.*, 1978, **100**, 6902.

measurement on matrix-isolated molecules, the shielding tensor of  $C_2H_4$  in argon or  $CH_4-C_2H_6$ . The Boltzmann factor greatly enhances sensitivity, and the argon matrix does not alter the anisotropy.<sup>156</sup>

$^{13}C$  shifts suggest that the  $\pi$ -acceptor- $\sigma$ -donor capacity of chalcocarbonyl ligands in arene-Cr, and *cp*-Mn and *cp*-Re complexes increases in the order  $CO < CS < CSe$ , the high-frequency shifts from CO to CS to CSe being consistent with the Pople shielding theory.<sup>157</sup>  $Ag^+$  is unsymmetrically co-ordinated to  $C\equiv C$  in  $\pi$ -complexes of  $CF_3SO_3Ag$  with allylacetylenes.<sup>158</sup> Extensive surveys are reported of  $^{13}CN$  co-ordination shifts in the diamagnetic complexes of the transition metals of Groups VIII, IB, and IIB. The range is 92 p.p.m. and all are to low frequency of the free ligand, except for  $[Fe(CN)_6]^{4-}$ . The shifts are discussed in terms of  $\sigma$ - $\pi$  bonding.<sup>159</sup>  $^{13}CN$  shifts are given also for  $[M(CN)_5X]^{n-}$  complexes ( $M=Mo, V, Mn, Fe; X=NO, NH_3, H_2O, NO_2, CN; n=2-4$ ); they correlate well with M-C and C-N stretching frequencies, and with Mössbauer isomer shifts and quadrupole splitting values for the Fe complexes. They do not correlate with the calculated shielding constants.<sup>160</sup>

$^{13}C$  shifts are reported for a range of carboranes with aryl, silyl, germyl, stannyl, (*etc.*) substituents.<sup>161</sup>

Olah and co-workers have used  $^{13}C$  n.m.r. to investigate 5-co-ordinate bridging carbons in dimeric  $Al_2R_6$  compounds ( $R=Me, Et, cyclo-Pr, aryl$ ). The increased shielding (relative to the terminal carbons) is attributed to increased *p* character, and is compared with that of 5- and 6-co-ordinate carbon in several *nido* and *closo* carboranes.<sup>162</sup>

Solid-state  $^{13}C$  studies of practical interest are concerned with diamonds and graphites,<sup>163</sup> coals,<sup>164</sup> and carbides of Ca, Mn, B, Al, and Si.<sup>165</sup>

The value of  $^1H$  and  $^{13}C$  n.m.r. spectroscopy in some paramagnetic molecules is well demonstrated by Koehler and co-workers for bent titanocenes<sup>166</sup> and vanadocene halides.<sup>167</sup> The chemical shifts can be used for rapid determination of structure in solution, and to elucidate electronic effects.  $^{13}C$  shifts to low frequency and  $^1H$  to high frequency (relative to a diamagnetic reference) are ascribed to  $\pi$ -polarization, which dominates the transfer of unpaired electrons on to the five-membered ring, while  $\sigma$ -polarization delocalizes them on to other ligands. The shifts indicate that titanocene halides are antiferromagnetically coupled in solution, the extent depending on the solvent and on substituents in the five-membered ring. Variable temperature n.m.r. shows that the vanadocenes (unlike the titanocenes) do not dimerize in solution.<sup>54, 167</sup>

The first reported n.m.r. observation of  $^{29}Si$  directly bound to transition metals

<sup>157</sup> D. Cozak, I. S. Butler, and I. M. Baibich, *J. Organometallic Chem.*, 1979, **169**, 381.

<sup>158</sup> G. S. Lewandos, *Tetrahedron Letters*, 1978, 2279.

<sup>159</sup> J. J. Pesek and W. R. Mason, *Inorg. Chem.*, 1979, **18**, 924.

<sup>160</sup> B. A. Narayanan and P. T. Manoharan, *J. Inorg. Nuclear Chem.*, 1978, **40**, 1993.

<sup>161</sup> O. A. Subbotin, T. V. Klimova, V. I. Stanko, and Yu. A. Ustynyuk, *Zhur. obshchei Khim.*, 1979, **49**, 415.

<sup>162</sup> G. A. Olah, G. K. S. Prakash, G. Liang, K. L. Hennold, and G. B. Haigh, *Proc. Nat. Acad. Sci. U.S.A.*, 1977, **74**, 5217.

<sup>163</sup> C. A. Wilkie, T. C. Ehler and D. T. Haworth, *J. Inorg. Nuclear Chem.*, 1978, **40**, 1983.

<sup>164</sup> C. A. Wilkie and D. T. Haworth, *J. Inorg. Nuclear Chem.*, 1978, **40**, 1989.

<sup>165</sup> D. T. Haworth and C. A. Wilkie, *J. Inorg. Nuclear Chem.*, 1978, **40**, 1689.

<sup>166</sup> F. H. Koehler and D. Cozak, *Z. Naturforsch.*, 1978, **33b**, 1274; *cf. ref. 54*.

<sup>167</sup> F. H. Koehler and W. Proessdorf, *Chem. Ber.*, 1978, **111**, 3464.

has used the technique of selective population transfer. The  $^{29}\text{Si}$  results for  $\text{Me}_3\text{Si}$  carbonyl complexes of Mn, Re, Co, and Fe were compared with those for more conventional  $\text{Me}_3\text{SiX}$  compounds, and with  $^{119}\text{Sn}$  results for homologous  $\text{Me}_3\text{Sn}$ -metal complexes.<sup>168</sup>

$\text{Ni}(0)$  complexes with EPh ligands (E = Si, Ge, Sn) have been investigated in  $^{29}\text{Si}$  resonance and compared with  $\text{MSiPh}_3$  compounds (M = Li, Na, K).<sup>169</sup>

In work by Fischer and co-workers on carbyne and carbene complexes of Cr, Mo, and W with (*e.g.*)  $\text{R}_3\text{SiCY}$  ligands (Y = OMe, NMe<sub>2</sub>),  $^{29}\text{Si}$  n.m.r. shifts show that the carbene and carbyne fragments behave as vinyl groups, and also demonstrate hyperconjugative effects and the electron-releasing power of the Y group.<sup>170</sup>

Harris and Robins report  $^{29}\text{Si}$  spectral investigation of mixtures of dimethylsiloxane oligomers.<sup>171</sup>  $^{13}\text{C}$  and  $^{29}\text{Si}$  n.m.r. results provide new evidence for the involvement of  $\text{SiF}_2$  rather than  $\text{SiF}_2\text{-SiF}_2$  in reactions with olefins.<sup>172</sup>

Haas *et al.* conclude that there is no (*p-d*) $\pi$  interaction between Si and X in  $\text{H}_{4-n}\text{Si}(\text{XCF}_3)_n$  compounds (X = S, Se;  $n = 1-4$ ), on the basis of  $^{29}\text{Si}$  n.m.r.<sup>173a</sup>  $^{29}\text{Si}$  shifts are reported for silylazo compounds.<sup>173b</sup>

A useful review has appeared of  $^{119}\text{Sn}$  shifts in organotin compounds.<sup>174</sup> Wrackmeyer has studied alkylnylstannanes  $\text{Me}_3\text{SnC}\equiv\text{CX}$  and  $\text{R}_2\text{Sn}(\text{C}\equiv\text{CX})_2$  (X = H, alkyl, Ph, SiMe<sub>3</sub>, GeMe<sub>3</sub>, SnMe<sub>3</sub>, PbMe<sub>3</sub>, OEt; R = Me, Et) in  $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,  $^{119}\text{Sn}$ , and  $^{207}\text{Pb}$  resonance, and discussed the nature of the bonding; Russian work in this field finds linear relations between the n.m.r. shifts and  $\sigma$  constants.<sup>175</sup>  $^{119}\text{Sn}$  spectral data are reported for thienylstannanes,<sup>176</sup> benzyltin compounds,<sup>177</sup>  $\text{Et}_3\text{SnX}$  compounds (X = Cl, Br, I) and their complexes with 1-vinyl and 1-ethyl imidazoles,<sup>178</sup> the cyclic stannanes  $\text{Ph}_2\text{Sn}$ -cyclopentane and 1,6-( $\text{Ph}_2\text{Sn}$ )-cyclododecane,<sup>179</sup> propenyl and isopropenyl compounds,<sup>180</sup> and  $(\text{Me}_3\text{Sn})_2\text{CNN}$ .<sup>181</sup>

The nature of naked-metal cluster polyanions of Sn with Pb or Sb has been studied by  $^{119}\text{Sn}$  and  $^{207}\text{Pb}$  n.m.r. ( $\text{Sn}_{9-x}\text{Pb}_x$ )<sup>4-</sup> ( $x = 0-9$ ) and Sn-Sb clusters are present in ethylenediamine extracts of Na-Sn, Na-Sn-Pb, and Na-Sn-Sb alloys.<sup>182</sup> Forty-five organo-lead compounds have been measured in  $^{13}\text{C}$  and  $^{205}\text{Pb}$  resonance, the shifts showing similar trends to those of organo-tin compounds.<sup>183</sup>  $^{13}\text{C}$  and  $^{207}\text{Pb}$

<sup>168</sup> S. Li, D. L. Johnson, J. A. Gladysz and K. L. Servis, *Organometallic Chem.*, 1979, **166**, 317.

<sup>169</sup> E. Uhlig, B. Hipler and P. Mueller, *Z. anorg. Chem.*, 1978, **442**, 11.

<sup>170</sup> F. H. Kohler, H. Hoilfelder and E. O. Fischer, *J. Organometallic Chem.*, 1979, **168**, 53.

<sup>171</sup> R. K. Harris and M. L. Robins, *Polymer*, 1978, **19**, 1123.

<sup>172</sup> J. C. Thompson, A. P. G. Wright and W. F. Reynolds, *J. Amer. Chem. Soc.*, 1979, **101**, 2236.

<sup>173a</sup> A. Haas and M. Vongehr, *Z. anorg. Chem.*, 1978, **447**, 119.

<sup>173b</sup> J. Kroner, W. Schneid, N. Wiberg, B. Wrackmeyer, and G. Ziegler, *J.C.S. Faraday II*, 1978, **74**, 1909.

<sup>174</sup> P. J. Smith and A. P. Tupciauskas, *Ann. Rep. N.M.R. Spectroscopy*, 1978, **8**, 291.

<sup>175</sup> B. Wrackmeyer, *J. Organometallic Chem.*, 1978, **145**, 183; 1979, **166**, 353; V. A. Pestunovich, E. O. Tsetlina, M. G. Voronkov, E. Liepins, E. T. Bogorodovskii, V. S. Zavgorodnii, V. L. Maksimov, and A. A. Petrov, *Doklady Akad. Nauk S.S.S.R.*, 1978, **243**, 149.

<sup>176</sup> B. Wrackmeyer, *Z. Naturforsch., Chem.*, 1979, **34b**, 235.

<sup>177</sup> B. De Poorter and M. Gielen, *Bull. Soc. chim. belges*, 1978, **87**, 881.

<sup>178</sup> V. K. Voronov, M. G. Voronkov, L. V. Baikalova, B. Z. Shternberg, E. S. Domnina, and R. G. Mirskov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1978, 1655.

<sup>179</sup> A. G. Davies, Man-Wing Tse, J. D. Kennedy, W. McFarlane, G. S. Pyne, M. F. C. Ladd, and D. C. Povey, *J.C.S. Chem. Comm.*, 1978, 791.

<sup>180</sup> T. N. Mitchell and C. Kummertat, *J. Organometallic Chem.*, 1978, **157**, 275.

<sup>181</sup> A. Fadini, E. Glozback, P. Krommes, and J. Lorberth, *J. Organometallic Chem.*, 1978, **149**, 297.

<sup>182</sup> R. W. Rudolph, W. L. Wilson, F. Parker, R. C. Taylor, and D. C. Young, *J. Amer. Chem. Soc.*, 1978, **100**, 4629.

<sup>183</sup> T. N. Mitchell, J. Gmehling, and F. Huber, *J.C.S. Dalton*, 1978, 960.

shifts for  $\text{Me}_2\text{Pb}^{\text{IV}}$  complexes with ONO tridentate Schiff-base ligands vary with the donor strength of the solvent.<sup>184</sup>

**I. Group V Nuclei.**—Isocyanide ligands in metal complexes give sharp  $^{14}\text{N}$  lines because of low-field gradients,  $^{14}\text{N}$  being quadrupolar.  $^{14}\text{N}$  results are reported for MeNC complexes of  $\text{Au}^{\text{I}}$ ,  $\text{Pd}^{\text{II}}$ , and  $\text{Pt}^{\text{II}}$ .<sup>IV</sup> by Goggin, Goodfellow, *et al.*<sup>185</sup> and for t-BuNC complexes of Pd with N–C chelating ligands by Yamamoto *et al.*<sup>186a</sup>  $^{14}\text{N}$  wideline measurements are reported for ammine–nitroso and halonitroso complexes of Co, Ru, and Os.<sup>186b</sup>  $^{14}\text{N}$  shifts in a range of azo compounds correlate with the  $n \rightarrow \pi^*$  transition energies, and with appropriate u.v.–p.e. orbital energies.<sup>173b</sup>

$^{13}\text{C}$  and  $^{14}\text{N}$  shifts in paramagnetic  $\text{Ln}^{3+}$  complexes with aqueous  $\text{SCN}^-$  ( $\text{Ln} = \text{Pr}$ , Nd, Eu, Tb, Dy, Ho, Yb) are dominated by the contact effect.<sup>187</sup>

Moniz and co-workers report sensitivity enhancement in  $^{15}\text{N}$  n.m.r. spectroscopy of liquids using the *J*-cross-polarization technique.<sup>188</sup> Mueller's work on azides continues with  $^{15}\text{N}$  spectroscopy of (enriched)  $\text{HN}_3$  and  $\text{ClN}_3$ ,<sup>189</sup> and  $[\text{Me}_2\text{AlN}_3]_3$ ,  $[\text{Me}_2\text{GaN}_3]_3$ ,  $[\text{Me}_2\text{AsN}_3]$ , and  $[\text{Me}_3\text{SnN}_3]$ , in which there is temperature-dependent exchange of the azido groups.<sup>190</sup> In the diazostannane  $(\text{Me}_3\text{Sn})_2\text{CNN}$ ,  $^{119}\text{Sn}$  and  $^{15}\text{N}$  n.m.r. show a regular distribution of enhanced electron density along the CNN group.<sup>181</sup>

Dinitrogen ligands in Mo and W complexes which are model compounds for nitrogen fixation resonate at medium frequencies (in contrast to the higher frequencies previously observed for titanium and zirconium complexes).<sup>191</sup> Further studies with enriched  $^{15}\text{N}$  include those of octaethyl porphyrins and their complexes with Mg, Zn, Cd, Ni, and  $\text{Fe}^{\text{II}}$ ,<sup>192</sup> 1:1 complexes of Zn *meso*-tetraphenylporphyrin with substituted pyridines,<sup>193</sup> the co-ordination of Cd to imidazole,<sup>194</sup> and mercaptophosphazenes  $^{15}\text{N}_3\text{P}_3\text{Cl}_{6-n}(\text{SR})_n$  ( $\text{R} = \text{Et}, \text{Ph}; n = 0, 2, 4, 6$ ) and  $^{15}\text{N}_4\text{P}_4\text{Cl}_{8-n}(\text{SEt})_n$  ( $n = 0, 4, 8$ ) in which the nitrogen line shifts to lower frequencies with increase in mercapto substitution.<sup>195</sup> A complex in which lead is 6-co-ordinated by an azamacrocyclic and two nitrate ions, (1,4,8,11-tetra-azacyclotetradecane)lead(II) dinitrate, has been measured in natural abundance of  $^{15}\text{N}$ .<sup>196</sup> Reference was made in Section 3D to the use of  $^{15}\text{N}$  in solution studies of LiNCS.<sup>84</sup>

Tebby has reported on  $^{31}\text{P}$  shifts in organophosphorus compounds and some ligands.<sup>197</sup> The use of  $^{31}\text{P}$  n.m.r. for phosphine complexes now seems to be routine.

<sup>184</sup> T. Majima and Y. Kawasaki, *Bull. Chem. Soc. Japan.*, 1978, **51**, 2924.

<sup>185</sup> J. Browning, P. L. Goggin, and R. J. Goodfellow, *J. Chem. Res. (S)*, 1978, 328.

<sup>186</sup> Y. Yamamoto and J. Uzawa, *Chem. Letters*, 1978, 1213.

<sup>186a</sup> A. I. V. Suvorov, V. A. Shcherbakov, and A. B. Nikol'skii, *Zhur. obshchei Khim.*, 1978, **48**, 2169.

<sup>187</sup> C. Musikas, C. Cuillerdier, and C. Chachaty, *Inorg. Chem.*, 1978, **17**, 3610.

<sup>188</sup> R. D. Bertrand, W. B. Moniz, A. N. Garroway, and G. C. Chingas, *J. Magn. Resonance*, 1978, **32**, 465.

<sup>189</sup> J. Mueller, *Z. Naturforsch.*, 1978, **33b**, 993.

<sup>190</sup> J. Mueller, *Z. Naturforsch.*, 1979, **34b**, 531, 536.

<sup>191</sup> J. Chatt, M. E. Fakley, R. L. Richards, J. Mason, and I. A. Stenhouse, *J. Chem. Res. (S)*, 1979, 44.

<sup>192</sup> K. Kawano, Y. Ozaki, Y. Kyogoku, H. Ogoshi, H. Sugimoto, and Z. Yoshida, *J.C.S. Perkin II*, 1978, 1319.

<sup>193</sup> D. Gust and D. N. Neal, *J.C.S. Chem. Comm.*, 1978, 681.

<sup>194</sup> M. Alei, W. E. Wageman, and L. O. Morgan, *Inorg. Chem.*, 1978, **17**, 3314.

<sup>195</sup> B. Thomas and G. Grossmann, *Z. anorg. Chem.*, 1979, **448**, 107.

<sup>196</sup> N. W. Alcock, N. Herron, and P. Moore, *Inorg. Chim. Acta*, 1979, **32**, L25.

<sup>197</sup> J. C. Tebby in 'Organophosphorus Chemistry,' ed. D. W. Hutchinson and S. Trippett (Specialist Periodical Reports), The Chemical Society, London, 1979, Vol. 10, p. 262.

Chemical shift tensors have been determined for  $^{31}\text{P}$  in binary phosphides by multiple-pulse experiments on powdered samples. For  $\text{Mg}_3\text{P}_2$  there are two different sites, one isotropic and one slightly anisotropic. For  $\text{Zn}_3\text{P}_2$  the anisotropy is large, and the shift indicates partial ionic character of the binding. For  $\text{P}_4\text{S}_{10}$  one sharp line is observed, indicative of rapid molecular motion even at room temperature.<sup>198</sup>

Anisotropies of  $^{31}\text{P}$  shifts were observed in solid co-ordination compounds of  $\text{POCl}_3$  ( $=\text{L}$ ), namely  $\text{SbLCl}_5$ ,  $\text{NbLCl}_5$ ,  $\text{TaLCl}_5$ ,  $\text{TiL}_2\text{Cl}_4$ ,  $\text{TiLCl}_4$ , and  $\text{SnL}_2\text{Cl}_4$ ; all show axial symmetry.<sup>199</sup>  $^{31}\text{P}$  chemical shift anisotropies were observed also for phosphabenzene partially oriented in the nematic liquid crystal EBBA.<sup>200</sup>

The  $^{31}\text{P}$  spectra of five cyclotetraphosphanes  $(\text{RP})_4$  ( $\text{R} = \text{CF}_3$ ,  $\text{Me}_3\text{C}$ ,  $\text{Me}_2\text{CH}$ ,  $\text{Et}$ , cyclohexyl) oriented in nematic phases clearly demonstrate the tetrameric structure. The ring puckering was measured and agrees with the  $X$ -ray results. The  $^{31}\text{P}$  shift anisotropy is large, ranging from 130 p.p.m. ( $\text{R} = \text{CF}_3$ ) to 172 p.p.m. ( $\text{R} = \text{Me}_2\text{CH}$ ).<sup>201</sup>

In interactions of chlorophosphines with  $\text{AlCl}_3$ ,  $^{31}\text{P}$  n.m.r. can be used to distinguish between the formation of molecular complexes (giving shifts to lower frequency) or phosphonium salts.  $\text{MePCl}_2$ ,  $\text{PhPCl}_2$ , and  $\text{Ph}_2\text{PCl}$  form complexes (in contrast to earlier suppositions).  $\text{PCl}_3$  does not interact, but  $\text{PhPCl}_2 \cdot \text{AlCl}_3$  with  $\text{Me}_2\text{C}=\text{CMe}_2$  gives the ions  $[\text{RPhPCl}_2]^+[\text{AlCl}_4]^-$  and not the adduct previously postulated.<sup>202</sup>

The  $^{31}\text{P}$  spectra have been compared for the  $[\text{P}(\text{OMe})_n(\text{NMe}_2)_{4-n}]^+$  cations ( $n=0-4$ ).<sup>203</sup>  $\text{Ag}$  salts react with  $\text{L}=\text{P}(\text{CMe}_3)_3$  to form a linear cation  $[\text{L}-\text{Ag}-\text{L}]^+$  and non-ionic complexes  $[(\text{Me}_3\text{C})_3\text{PAgX}]$  which were investigated by  $^{31}\text{P}$  n.m.r., vibrational spectroscopy, and conductance measurements. The non-ionic complexes are monomeric for  $\text{X} = \text{Cl}$ ,  $\text{AcO}$ , and  $\text{NO}_3^-$ , and dimeric for  $\text{X} = \text{Br}$ . The  $\text{CN}^-$  and  $\text{SCN}^-$  complexes appear to contain bridging  $\text{CN}$  and  $\text{SCN}$ .<sup>204</sup>

In tertiary phosphine complexes of  $\text{Hg}^{\text{II}}$ , the  $^{31}\text{P}$  co-ordination shift depends on the basicity and bulkiness of the phosphine, the geometry at  $\text{Hg}$ , and the electro-negativity of the anion, and correlates with the  $\text{Hg}-\text{P}$  coupling constant. The largest co-ordination shift and lowest  $J$  is displayed by  $[\text{Hg}(\text{Pcy}_3)_2][\text{ClO}_4]_2$ .<sup>205</sup>

Richman has made a new  $\text{P}^{\text{V}}$  tautomer, cyclen phosphorane (1), which has been characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  n.m.r.<sup>206</sup> The crystal and molecular structure and  $^{31}\text{P}$  and  $^{19}\text{F}$  n.m.r. spectra are reported for  $[\text{P}(\text{acac})\text{F}_4]$ .<sup>207</sup>

$^{31}\text{P}$  spectra have been compared for  $\text{Me}_2\text{N}$  derivatives of the ring systems  $(\text{NPCl}_2)_3$ ,  $(\text{NPCl}_2)_2\text{NSOCl}$ , and  $\text{NPCl}_2(\text{NSOCl})_2$ .<sup>208</sup> The products of aminolysis of the ring systems *cis*- $\text{NPCl}_2(\text{NSOCl})_2$  and  $(\text{NPCl}_2)_2\text{NSOCl}$  by cyclic amines were

198 T. Taki, *Phys. Status Solidi B*, 1978, **86**, K147.

199 A. R. Grimmer, *Z. Chem.*, 1978, **18**, 233.

200 T. C. Wong and A. J. Ashe, *J. Mol. Structure*, 1978, **48**, 219.

201 J. P. Albrand, A. Cogne, and J. B. Robert, *J. Amer. Chem. Soc.*, 1978, **100**, 2600.

202 C. Symmes and L. D. Quin, *J. Org. Chem.*, 1978, **43**, 1250.

203 K. D. Pressl and A. Schmidt, *Z. anorg. Chem.*, 1977, **434**, 175.

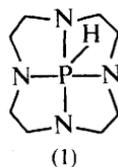
204 R. G. Goel and P. Pilon, *Inorg. Chem.*, 1978, **17**, 2876.

205 E. C. Alyea, S. A. Dias, R. G. Goel, W. O. Oginii, P. Pilon, and D. W. Meek, *Inorg. Chem.*, 1978, **17**, 1697.

206 J. E. Richman and T. J. Atkins, *Tetrahedron Letters*, 1978, 4333.

207 W. S. Sheldrick and M. J. C. Hewson, *Z. Naturforsch.*, 1978, **33b**, 834.

208 B. De Ruiter and J. C. Van de Grampel, *Inorg. Chim. Acta*, 1978, **31**, 195.



characterized by  $^{31}\text{P}$  and other spectral properties,<sup>209</sup> and similarly for diazadiphosphetidines formed by cycloaddition of phosphazenes with  $\text{SiMe}_3$  substituents.<sup>210</sup>  $\text{Ph}_2\text{P}$  bridging two platinum in a 4-membered ring with nitrogen shows a large shift to low frequency in the phosphorus resonance.<sup>211</sup>

**J. Group VI Nuclei.**— $^{17}\text{O}$  is slowly becoming more accessible to n.m.r. spectroscopy. Klemperer's studies of oxoanions continue with a report of over 100  $^{17}\text{O}$  chemical shifts for twenty-seven diamagnetic polyoxoanions of the early transition metals. Efficient procedures for obtaining  $^{17}\text{O}$ -enriched compounds are described, as are factors affecting sensitivity and resolution. The shifts are determined largely by metal–O bond strengths.<sup>212</sup>

The  $^{17}\text{O}$  spectrum of  $[\text{V}_2\text{W}_4\text{O}_{19}]^{4-}$  establishes a *cis*-vanadium relationship in an octahedral array and demonstrates that the proton in  $[\text{HV}_2\text{W}_4\text{O}_{19}]^{3-}$  is bound to the unique oxygen bridging the vanadium<sup>213</sup> (*cf.* 96).

$^{17}\text{O}$  measurements for reduced mixed-valence heteropolymolybdates with a delocalized electron pair provide evidence as to the rate of delocalization with respect to the twelve Mo atoms.<sup>214</sup>  $^{17}\text{O}$  shifts in mononuclear oxomolybdenum(vi) complexes are related to Mo–O bond distances and stretching-force constants, through the dependence on the  $\pi$ -bond order;  $^{17}\text{O}$  and  $^{18}\text{O}$  enrichment confirms assignments of the stretching frequencies.<sup>215</sup>

$^{17}\text{O}$  n.m.r. spectroscopy of aqueous  $\text{Na}_2\text{AsO}_3$  solutions has given the rate and mechanism of oxygen exchange between arsenite ion and water.<sup>216</sup>

$^{17}\text{O}$  shifts, measured in 31 aliphatic ethers ROR', are proportional to corresponding  $^{13}\text{C}$  shifts in ROR' and in RCH<sub>2</sub>R', according to the respective values of the radial term  $\langle r^{-3} \rangle_{2p}$  for the (oxygen or carbon) 2*p* electrons, the correlation involving hyperconjugative and electric field effects in the rotamer conformation.<sup>217</sup>

Electronic effects in CO, CS, and CSe ligands in cyclopentadienyl complexes of Cr, Mn, and W have been studied by  $^{17}\text{O}$  n.m.r.  $\text{C}^{17}\text{O}$  shifts to high frequency are attributed to the greater net electron-attracting ability ( $\sigma$ -donor *vs.*  $\pi$ -acceptor) of CS and CSe compared to CO. The opposing trends for  $^{17}\text{O}$  and  $^{13}\text{C}$  resonances result from the synergistic bonding to the transition metal.<sup>218</sup>

<sup>209</sup> H. H. Baalman and J. C. Van de Grampel, *Z. Naturforsch.*, 1978, **33b**, 964.

<sup>210</sup> M. Halstenberg and R. Appel, *Chem. Ber.*, 1978, **111**, 1815.

<sup>211</sup> R. Meiji, D. J. Stufkens, K. Vrieze, A. M. F. Brouwers, and A. R. Overbeek, *J. Organometallic Chem.*, 1978, **155**, 123.

<sup>212</sup> M. Filowitz, R. K. C. Ho, W. G. Klemperer, and W. Shum, *Inorg. Chem.*, 1979, **18**, 93.

<sup>213</sup> W. G. Klemperer and W. Shum, *J. Amer. Chem. Soc.*, 1978, **100**, 4891.

<sup>214</sup> L. P. Kazanskii, M. A. Fedotov, I. V. Potapova, and V. I. Spitsyn, *Doklady Akad. Nauk S.S.S.R.*, 1979, **244**, 372.

<sup>215</sup> K. F. Miller and R. A. D. Wentworth, *Inorg. Chem.*, 1979, **18**, 984.

<sup>216</sup> W. C. Copenhafer and P. H. Rieger, *J. Amer. Chem. Soc.*, 1978, **100**, 3776.

<sup>217</sup> C. Delseth and J. P. Kintzinger, *Helv. Chim. Acta*, 1978, **61**, 1327.

<sup>218</sup> J. P. Hickey, I. M. Baibich, I. S. Butler, and L. J. Todd, *Spectroscopy Letters*, 1978, **11**, 671.

The chemical shift tensor has been determined for selenium in  $\text{H}_2\text{SeO}_3$  in high resolution by cross-polarization of the  $^{77}\text{Se}$  nuclei by protons.<sup>219</sup>

Twenty-seven Se-containing compounds have been studied in  $^{77}\text{Se}$  resonance, including dialkyl diselenocarbamate complexes of Ni, Pd, Pt, Zn, and Cd, other selenocarbamate compounds, and selenium-DL-cystine and -methionine. Low-frequency shifts in the Ni, Pd, and Pt complexes are attributed to magnetic anisotropy.<sup>220</sup> Intramolecular rearrangements of  $[\text{Pt}(\text{Se}_2\text{CN}-i\text{-Bu}_2)_2\text{PR}_3]$  have been followed by  $^{77}\text{Se}$  n.m.r.<sup>221</sup>  $\text{Pt}^{\text{II}}$  and  $\text{Pt}^{\text{IV}}$  hydride complexes with SeH ligands were characterized by  $^{77}\text{Se}$  as well as  $^{31}\text{P}$  and  $^{195}\text{Pt}$  resonance.<sup>115</sup>

$^{13}\text{C}$  and  $^{77}\text{Se}$  shifts are reported for aryl selenides,<sup>222</sup> and  $^{77}\text{Se}$  and  $^{125}\text{Te}$  shifts for some selenol and tellurol esters.<sup>223</sup>

Koch, Lutz, and Nolle report a high-resolution determination of the ratio of Larmor frequencies for  $^{77}\text{Se}$  and  $^1\text{H}$  in aqueous  $\text{Na}_2\text{SeO}_3$ , and chemical shifts of  $\text{H}_2\text{SeO}_3$ ,  $\text{NaHSeO}_3$ , and  $\text{Na}_2\text{SeO}_4$ .<sup>224</sup> From the same authors,  $^{77}\text{Se}$  and  $^{125}\text{Te}$  shifts in the solid binary compounds with Zn, Cd, Hg, and Pb (relative to aqueous solutions of  $\text{Na}_2\text{SeO}_3$  or  $\text{K}_2\text{TeO}_3$ ) have been compared with calculated values. An anisotropic shift was observed for  $^{77}\text{Se}$  in hexagonal CdSe, and linesplittings for  $^{125}\text{Te}$  in CdTe and PbTe.<sup>225</sup>

Cyclic and cluster cations  $\text{Te}_6^{4+}$ ,  $\text{Te}_{4-n}\text{Se}_n^{2+}$ ,  $\text{Te}_2\text{Se}_4^{2+}$ , and  $\text{Te}_3\text{Se}_3^{2+}$  have been identified by  $^{123}\text{Te}$ ,  $^{125}\text{Te}$ , and  $^{77}\text{Se}$  FT n.m.r.<sup>226</sup>  $^{123,125}\text{Te}$  studies showed  $[\text{Te}_n\text{Se}_{4-n}]^{2+}$  ions to be present in the Te-Se-oleum system.<sup>227</sup>

**K. Group VII Nuclei.**—The  $^{19}\text{F}$  shift tensor for *p*-nitrofluorobenzene in a nematic solvent is not axially symmetric about the C—F bond; anisotropies of 81 and 156 p.p.m. are observed.<sup>228</sup> Axially symmetric tensors were measured for  $^{19}\text{F}$  in  $\text{CF}_2$  and  $\text{CF}_3$  groups in liquid-crystal perfluoro-octanoate–water systems.<sup>229</sup>

The use of  $^{19}\text{F}$  n.m.r. to study the stereochemistry of  $d^0$  transition-metal complexes is reviewed with 41 references.<sup>230</sup> Holloway *et al.* have characterized  $[\text{MoO}_2\text{F}_2]$ ,  $[\text{MoO}_2\text{ClF}]$ ,  $[\text{WO}_2\text{F}_2]$ , and  $[\text{XeF}_2 \cdot \text{MoF}_4]$  by  $^{19}\text{F}$  n.m.r. and other techniques.<sup>231</sup>

Dove has investigated ligand-displacement reactions of  $[\text{Co}(\text{NH}_3)_5\text{X}]$  cations with anhydrous HF by  $^{19}\text{F}$  n.m.r. and visible spectroscopy. The solvent substitutes  $\text{F}^-$  for  $\text{H}_2\text{O}$ ,  $\text{ONO}_2^-$ ,  $\text{OCO}_2^{2-}$ ,  $\text{ONO}^-$ , and  $\text{NO}_2^-$ , but  $\text{Cl}^-$  replaces  $\text{F}^-$  if free HCl is present. Solvolysis of co-ordinated  $\text{ONO}_2^-$ ,  $\text{OCO}_2^{2-}$ ,  $\text{ONO}^-$ , and  $\text{NO}_2^-$  by HF proceeds *via*  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ ; the  $\text{N}_3^-$  ligand is protonated.<sup>232</sup>

<sup>219</sup> A. G. Lundin, Yu N. Moskvich, and A. A. Sukhovskii, *Pis'ma Zhur. Eksp. Teor. Fiz.*, 1978, **27**, 623.

<sup>220</sup> W. H. Pan and J. P. Fackler, *J. Amer. Chem. Soc.*, 1978, **100**, 5783.

<sup>221</sup> J. P. Fackler and W. H. Pan, *J. Amer. Chem. Soc.*, 1979, **101**, 1607.

<sup>222</sup> G. A. Kalabin, D. F. Kushnarev, G. A. Chmutova, and L. V. Kashurnikova, *Zhur. org. Khim.*, 1979, **15**, 24; *cf.* also 1978, **14**, 2478.

<sup>223</sup> B. Kohne, W. Lohner, K. Praefcke, H. J. Jakobsen, and B. Villadsen, *J. Organometallic Chem.*, 1979, **166**, 373.

<sup>224</sup> W. Koch, O. Lutz, and A. Nolle, *Z. Naturforsch.*, 1978, **33a**, 1025.

<sup>225</sup> W. Koch, O. Lutz, and A. Nolle, *Z. Physik A*, 1978, **289**, 17.

<sup>226</sup> G. J. Schrobilgen, R. C. Burns, and P. Granger, *J.C.S. Chem. Comm.*, 1978, 957.

<sup>227</sup> C. R. Lassigne and E. J. Wells, *J.C.S. Chem. Comm.*, 1978, 956.

<sup>228</sup> J. Van der Giessen and C. A. De Lange, *Chem. Phys. Letters*, 1978, **56**, 121.

<sup>229</sup> A. Jasinski, P. G. Morris, and P. Mansfield, *Mol. Crystals Liquid Crystals*, 1978, **45**, 183.

<sup>230</sup> E. G. Il'in and Y. A. Buslaev, *Koord. Khim.*, 1978, **4**, 1179.

<sup>231</sup> J. Atherton and J. H. Holloway, *J.C.S. Chem. Comm.*, 1978, 254.

<sup>232</sup> M. F. A. Dove, *J. Fluorine Chem.*, 1978, **11**, 317.

$^{19}\text{F}$  n.m.r. has been used also to study mono- and di-nuclear Ti–Mo and Ti–W anions,<sup>233</sup>  $[\text{WOF}_4\text{L}]^-$  complexes (HL = oxime or phenylhydroxylamine),<sup>234</sup>  $\text{BrF}_3$  complexes with  $\text{BF}_3$ ,  $\text{PF}_5$ , and  $\text{AsF}_5$ ,<sup>235</sup> the intercalation of  $\text{IF}_5$ ,  $\text{ClF}_5$ ,  $\text{ClF}_3$ ,  $\text{BrF}_5$ , and  $\text{BrF}_3$  into graphite,<sup>236</sup> and complex formation by  $\text{AsF}_5$ ,  $\text{SbF}_5$ , or  $(\text{SbF}_5)_2$  with  $\text{IOF}_5$ , which binds through oxygen.<sup>237</sup>

The  $\text{N}_2\text{F}_3^+$  cation has been re-examined, in salts with  $\text{SbF}_6^-$  and  $\text{SnF}_5^-$ , and found to be planar.<sup>238</sup>

$[(\text{Me}_2\text{N})_x\text{SF}_{3-x}]^+$  compounds with  $x = 1-3$  have been studied by  $^{19}\text{F}$  n.m.r., as has the reaction producing  $[(\text{Me}_2\text{N})_3\text{S}]^+$  from  $\text{SF}_4$  and  $(\text{Me}_2\text{N})_3\text{B}$  in  $\text{SO}_2$  at low temperatures.<sup>239</sup> Acylsulphur difluoride di-imides used in the preparation of cyclic sulphur difluoride di-imides have been characterized by  $^{19}\text{F}$  n.m.r.,<sup>240</sup> which has been applied also to  $\text{CF}_3$  derivatives of Zn and Cd,<sup>241</sup> Si, Ge, Sn, and Pb,<sup>242</sup> and of S and Se, P, and As (used as ligands in complexes of Mn and Re).<sup>243</sup>

Work on the halogen nuclei  $^{35}\text{Cl}$ ,  $^{79}\text{Br}$ , and  $^{127}\text{I}$  has been done in conjunction with n.m.r. studies of the counter-ions, and so has been described under the headings of the alkali metals,<sup>78, 93</sup> aluminium,<sup>90</sup> and copper.<sup>120</sup>

A review of the solvent properties of the interhalogens includes n.m.r. studies.<sup>244</sup>  $^{35}\text{Cl}$  shifts in alkyl and alkenyl chlorides correlate in linear fashion with  $^{19}\text{F}$  shifts of the corresponding fluorides.<sup>245</sup>  $^{35}\text{Cl}$  shifts were used to investigate the complexing of  $\text{Yb}^{\text{III}}$  by  $\text{ClO}_4^-$  in water–acetone solutions, and a co-ordination number of 8 was calculated.<sup>246</sup> Absolute values of the elements of the iodine nuclear magnetic shielding tensor in  $\text{CH}_3\text{I}$  have been obtained from measurements of the spin-rotation constants in the high-resolution microwave spectrum (by Doppler-free molecular-beam double resonance, and by the Lamb dip method).<sup>247</sup>

**L. Group 0 Nuclei.**— $^3\text{He}$  has been observed in the gas phase,<sup>59</sup> and the remarkable n.m.r. properties of the liquid and superfluid phases are discussed in a recent review.<sup>248</sup> Very comprehensive  $^{129}\text{Xe}$  FT n.m.r. studies of xenon compounds were published in early 1978.<sup>249</sup>

233 J. Sala-Pala and J. E. Guerschais, *J. Chem. Res. (S)*, 1978, 227.

234 Yu. A. Buslaev, S. G. Sakharov, Yu. V. Kokunov, and I. I. Moiseev, *Doklady Akad. Nauk S.S.S.R.*, 1978, **240**, 338.

235 T. Cyr and S. Brownstein, *J. Inorg. Nuclear Chem.*, 1977, **39**, 2143.

236 H. Selig, W. A. Sunder, M. J. Vasile, F. A. Stevie, P. K. Gallagher, and L. B. Ebert, *J. Fluorine Chem.*, 1978, **12**, 397.

237 M. Brownstein, R. J. Gillespie, and J. P. Krasznai, *Canad. J. Chem.*, 1978, **56**, 2253.

238 K. O. Christe and C. J. Schack, *Inorg. Chem.*, 1978, **17**, 2749.

239 A. H. Cowley, D. J. Pagel, and M. L. Walker, *J. Amer. Chem. Soc.*, 1978, **100**, 7065.

240 I. Stahl, R. Mews, and O. Glemser, *J. Fluorine Chem.*, 1978, **11**, 455.

241 E. K. S. Liu and L. B. Asprey, *J. Organometallic Chem.*, 1979, **169**, 249.

242 R. Eujen and R. J. Lagow, *J.C.S. Dalton*, 1978, 541.

243 J. Grobe and R. Rau, *J. Fluorine Chem.*, 1978, **11**, 291.

244 J. J. Lagowski, *Chem. Non-Aqueous Solvents*, 1978, **5B**, 157.

245 K. Barlos, J. Kroner, H. Noeth, and B. Wrackmeyer, *Chem. Ber.*, 1978, **111**, 1833.

246 Y. Ya. Kavun and B. N. Chernyshov, *Koord. Khim.*, 1979, **5**, 53.

247 D. Boucher, J. Burie, D. Dangoisse, J. Demaison, and A. Dubrulle, *Chem. Phys.*, 1978, **29**, 323.

248 J. Woelfle, *Reports Progr. Phys.*, 1979, **42**, 269.

249 G. J. Schrobilgen, J. H. Holloway, P. Granger, and C. Brevard, *Inorg. Chem.*, 1978, **17**, 980.