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Solid state NMR studies of d-block and p-block metal nuclei: applications to organometallic and coordination chemistry

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CONTENTS

A. INTRODUCTION

In 1978, the book *NMR and the Periodic Table* was published [1]. This text brought together the many diverse reports of high-resolution nuclear magnetic resonance spectra of solutions of compounds as a function of the nucleus examined and acted as a catalyst for the introduction of multinuclear magnetic resonance methods into the arsenal of analytical techniques employed by inorganic chemists

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[2]. The years that followed have seen multinuclear magnetic resonance techniques move from the purview of the spectroscopist into the domain of chemists engaged in studies of synthesis, structure, and mechanism.

This same type of transition* is currently in progress with solid state NMR techniques. It was the physicists that were first interested in solid state NMR spectroscopy and it was only in the late 1950s that developments began that ultimately led chemists to become involved in the field. Andrew et al. and Lowe reported that substantial narrowing of the lines in the NMR spectra of solids could be achieved by rapidly spinning the sample about an axis making an angle of 54°44′ with the applied magnetic field [4–6]. This particular angle is known nowadays as the "magic angle" and the technique as "magic angle spinning" (MAS) (for recent reviews, see ref. 7). During the same period, heteronuclear dipolar decoupling was being investigated theoretically by Bloch [8] and experimentally by Sarles and Cotts [9]. Soon after that, Hartmann and Hahn published their classic paper [10] in which they described how to achieve polarization transfer from protons to dilute spins such as ^{13}C via dipolar interactions and thus enhance the magnetization of the dilute spins. The "Hartmann–Hahn" condition, as it is called, states that the magnetization of the protons in the rotating frame and that of the dilute spins (e.g. ^{13}C) have to obey the relationship:

$$\gamma_H H_{1H} = \gamma_C H_{1C} \tag{1}$$

In other words, the two magnetizations have to precess around their own spin-locking fields at identical angular velocities. It took approximately ten years before a report of a practical application of this work was published. In 1972 and 1973, Pines et al. reported the sequence of radio frequency (rf) excitations for cross-polarization (CP) and spin decoupling experiments [11,12]. Using a combination of these two techniques, they were able to obtain the ^{13}C NMR spectra of organic solids such as adamantane, frozen acetic anhydride, frozen acetone, etc. Further improvement was achieved in 1976: by combining the three techniques of cross-polarization (CP), spin decoupling, and "magic angle spinning" (MAS), the first "high resolution" solid state NMR spectra were obtained. These were reported by Garroway et al. [13], Lippmaa et al. [14], and Schaefer and Stejskal [15].

Although the basics of solid state NMR spectroscopy were worked out in the mid-1970s, instruments capable of analyzing solid samples did not become commercially available until the 1980s [16]. This is because technological problems associated with solid state NMR experiments required a long time before being fully mastered. Such technical difficulties included the development of new kinds of rf circuitries capable of handling extremely powerful rf pulses, the design of turbine spinners

* A recent article [3] that briefly summarizes the application of solid state NMR methods to organometallic and coordination chemistry shows that the number of papers published per year in this area has steadily increased from 1979 to 1989 and that the total exceeded two hundred in 1989.

allowing easy sample loading and variable temperature measurements, the design of sample containers mechanically stable for both machining purposes and for the considerable centrifugal forces in the MAS experiment, etc. Furthermore, it is noteworthy that the utilization of "bullet-shaped" rotors as we know them today was reported by Bartuska and Maciel no earlier than in 1981 [17]. In the early 1980s, however, the field began to expand and chemists started becoming more involved in solid state NMR spectroscopy. Chemists became involved in solid state NMR spectroscopy [18] for mainly two reasons: the first is that they needed a technique that would provide a bridge between solution NMR data and solid state structural results, particularly those obtained by single crystal X-ray diffraction techniques. The second reason lies in the fact that a large number of chemical systems lack crystallinity and order and, therefore, cannot be analyzed by X-ray diffraction techniques. Such chemical systems include polymers, some silicates, resins, celluloses, coals and surface-immobilized reagents. Furthermore, a great number of these systems are insoluble in common laboratory solvents, which makes the number of suitable analytical methods quite scarce. For these materials, solid state NMR spectroscopy appeared to be a potentially powerful technique [18]. The importance of having a technique that bridges solution NMR data with solid state results can be illustrated by considering the ^{31}P NMR spectrum of PCl_5, an example we have cited previously [19]. In carbon disulfide solution, the ^{31}P NMR spectrum of PCl_5 displays one signal at +80 ppm with respect to 85% phosphoric acid [20(a)] whereas, in the solid state, the ^{31}P NMR spectrum of the compound consists of two signals of equal intensity at −96 and +281 ppm with respect to the same reference [20(b)]. By comparison with solution chemical shifts for compounds of known structure, the two signals in the ^{31}P solid state NMR spectrum of PCl_5 were assigned to the species PCl_4^+ (−96 ppm) and PCl_6^- (+281 ppm)*. This experiment is probably the first to indicate clearly to chemists that chemical information similar to that from solution NMR studies could be directly obtained from solid state magic angle spinning NMR experiments.

As the field of solid state NMR spectroscopy has grown [18], studies of ^{13}C (organic molecules, polymers, coals, etc. [21]) and ^{29}Si (zeolites, glasses, silicon-containing polymers, small organic molecules, etc. [22]) have proliferated, just as studies of ^{1}H and ^{19}F proliferated in the early days of solution NMR measurements. Studies of some of the more exotic nuclei in the solid state are now just beginning to be reported [18] and several nuclei that are promising candidates for study still remain largely unexplored. In this article, we discuss studies of inorganic systems of interest to the organometallic or coordination chemist [3] involving direct observation of the d-block and p-block metal nuclei. These metal nuclei are commonly the centers of interest to the organometallic or coordination chemist primarily concerned

* Note that the sign convention for ^{31}P chemical shifts employed in the 1960s was the reverse of the one employed today, i.e. negative shifts represented deshielding.

with synthesis, structure, and reactivity. The non-metals of the p-block are primarily of interest as ligating groups and it transpires that considerable literature on solid state NMR studies [3,18] of these nuclei (e.g. ^{11}B [23], ^{13}C [21], ^{29}Si [22], $^{14,15}N$ [24], and ^{31}P [19]) already exists and so we have excluded these from this article. We have not attempted to reference every report that mentions a solid state NMR measurement of a d-block or p-block nucleus exhaustively but rather to select examples for inclusion that illustrate both the depth and breadth of solid state NMR techniques. Similarly, we have not attempted to describe comprehensively the theory underlying the various solid state NMR experiments since complete discussion is available at a variety of levels of sophistication elsewhere [18,25]. Here, we simply provide an overview of the phenomenon and emphasize the chemical information that can be obtained from solid state NMR experiments before moving on to consider the individual metal nuclei.

B. PROPERTIES OF METAL NUCLEI

Low natural abundances, low magnetogyric ratios, and high quadrupole moments are all encountered with the isotopes of interest among the d-block and p-block metals [1]. Although formidable obstacles to solution NMR measurements, these potential problems can be turned to advantages in solid state NMR spectroscopy [18]. Low natural abundances (i.e. "dilute spins") are advantageous in solid state measurements since, as discussed further in the following section, these lead to a natural circumvention of the problems of dipolar interactions between like spins. Low magnetogyric ratios need not lead to the same types of sensitivity problems as those routinely encountered with solution measurements since the cross-polarization technique, described briefly in the following section, allows an increase in the magnetization of an observed nucleus (S) up to a theoretical maximum of γ_H/γ_S. A nuclear quadrupole adds an additional term to the Hamiltonian describing the interaction of a nucleus with an applied field and can result in considerable sensitivity to local site symmetry, thus resulting in useful structural information.

Some of the important properties of the p-block and d-block metal nuclei are summarized in Tables 1 and 2.

C. SOLID STATE NMR

The interactions of interest in an NMR experiment for a system containing nuclei of non-zero spin are given by eqn. (2) where the individual terms refer to the Zeeman interaction, dipolar interactions, chemical shift interactions, scalar (or indirect) coupling, and quadrupolar interactions, respectively [27].

$$\mathscr{H} = \mathscr{H}_Z + \mathscr{H}_D + \mathscr{H}_{CS} + \mathscr{H}_{SC} + \mathscr{H}_Q \qquad (2)$$

For a spin = 1/2 nucleus, the last term is, of course, not relevant. The first term

TABLE 1

Nuclear properties of the d-block metals[a]

Isotope	I	Abundance (%)	Magnetogyric ratio (10^7 rad T^{-1} s^{-1})	Quadrupole moment (10^{-28} m^2)
^{45}Sc	7/2	100	6.4989	−0.22
^{89}Y	1/2	100	−1.3108	0
^{139}La	7/2	99.91	3.7787	0.21
^{47}Ti	5/2	7.28	1.5084	0.29
^{49}Ti	7/2	5.51	1.5080	0.24
^{91}Zr	5/2	11.23	−2.4868	−0.21
^{177}Hf	7/2	18.50	0.945	4.5
^{179}Hf	9/2	13.75	−0.609	5.1
^{51}V	7/2	99.76	7.0362	−0.052
^{93}Nb	9/2	100	6.5476	−0.2
^{181}Ta	7/2	99.988	3.2073	3
^{53}Cr	3/2	9.55	−1.5120	±0.03
^{95}Mo	5/2	15.72	1.7433	0.12
^{97}Mo	5/2	9.46	−1.7799	1.1
^{183}W	1/2	14.28	1.1145	0
^{55}Mn	5/2	100	6.6195	0.55
^{99}Tc	9/2	100	6.0211	0.3
^{185}Re	5/2	37.07	6.0255	2.8
^{187}Re	5/2	62.93	6.0862	2.6
^{57}Fe	1/2	2.19	0.8661	0
^{99}Ru	5/2	12.72	−1.2343	0.076
^{101}Ru	5/2	17.07	−1.3834	0.44
^{187}Os	1/2	1.64	0.6105	0
^{189}Os	3/2	16.1	2.0773	0.8
^{59}Co	7/2	100	6.3472	0.40
^{103}Rh	1/2	100	−0.8520	0
^{191}Ir	3/2	37.3	0.539	1.5
^{193}Ir	3/2	62.7	0.391	1.4
^{61}Ni	3/2	1.19	−2.3904	–
^{105}Pd	5/2	22.23	−0.756	0.8
^{195}Pt	1/2	33.8	5.7412	0
^{63}Cu	3/2	69.09	7.0965	−0.211
^{65}Cu	3/2	30.91	7.6018	−0.195
^{107}Ag	1/2	51.82	−1.0828	0
^{109}Ag	1/2	48.18	−1.2448	0
^{197}Au	3/2	100	0.357	0.58
^{67}Zn	5/2	4.11	1.6726	0.15
^{111}Cd	1/2	12.75	−5.6714	0
^{113}Cd	1/2	12.26	−5.9328	0
^{199}Hg	1/2	16.84	4.7912	0
^{201}Hg	3/2	13.22	−1.7686	0.50

[a] Data from ref. 26 and references cited therein. Reported values of quadrupole moments may involve significant errors (see ref. 1).

TABLE 2

Nuclear properties of the p-block metals[a]

Isotope	I	Abundance (%)	Magnetogyric ratio (10^7 rad T^{-1} s^{-1})	Quadrupole moment (10^{-28} m^2)
^{27}Al	5/2	100	6.9704	0.149
^{69}Ga	3/2	60.4	6.420	0.178
^{71}Ga	3/2	39.6	8.158	0.112
^{113}In	9/2	4.28	5.8493	1.14
^{115}In	9/2	95.72	5.8618	0.83
^{203}Tl	1/2	29.50	15.3078	0
^{205}Tl	1/2	70.50	15.4584	0
^{73}Ge	9/2	7.76	−0.9331	−0.2
^{115}Sn[b]	1/2	0.35	−8.7475	0
^{117}Sn	1/2	7.61	−9.5319	0
^{119}Sn	1/2	8.58	−9.9756	0
^{207}Pb	1/2	22.6	5.5797	0
^{121}Sb	5/2	57.25	6.4016	−0.53
^{123}Sb	7/2	42.75	3.4668	−0.68
^{209}Bi	9/2	100	4.2986	−0.4

[a] Data from ref. 26 and references cited therein. Reported values of quadrupole moments may involve significant errors (see ref. 1).

[b] Data from ref. 1.

describes the interaction of the spins with the applied magnetic field and so is not intrinsic to the system of nuclei under study. In the case of abundant spins (e.g. ^1H), the second term dominates and the interactions of interest in terms of chemical shifts and coupling constants are largely insignificant. Special techniques, described in detail elsewhere [28], must be employed to overcome this problem. For a dilute spin (e.g. ^{13}C), the dipolar interaction with neighboring protons can be largely removed by high-power proton decoupling and dipolar interactions between dilute spins are unlikely to be significant. The dipolar term can be expressed as shown in the equation [18]

$$\mathscr{H}_D = -g_N^2\beta_N^2 \sum_{i<j} (1/r_{ij}^5)[(r_i \cdot r_j - 3\vec{r}_{iz}\vec{r}_{jz}) \times (I_i \cdot I_j - 3\vec{I}_{iz}\vec{I}_{jz})] \tag{3}$$

where the dipolar interaction between nuclei i and j is represented.

The spatial relationship between i and j and the field is given by the first term in the square brackets while the orientation of the spins is described by the second term. The dipolar interaction can be reduced to zero by causing the spatial term in eqn. (3) to become zero by MAS [7]. This is one of the major line-narrowing techniques employed today since not only the dipolar term but also the chemical shift and scalar coupling terms have $(3\cos^2\theta - 1)$ dependencies [27]. Reducing the latter two terms to their non-zero averages by MAS results in isotropic chemical

shifts and coupling constants with concomitant loss of the three-dimensional nature of these interactions. In the case of the chemical shift, the three-dimensional nature is apparent from the spectrum of a static powdered sample which will typically take the form of a broad envelope from which the principal elements of the chemical shift tensor, the isotropic shift, the chemical shift anisotropy, and the asymmetry factor can all be obtained [27]. The anisotropy of indirect spin–spin coupling tensors is generally less easy to determine directly since separation from direct dipolar coupling is often problematic [29].

In the case of quadrupolar nuclei [30], the last term in eqn. (3) is of importance. The Zeeman levels are directly affected by the quadrupolar interaction and the result is illustrated for the example of a $I = 5/2$ nucleus in Fig. 1 [31]. To a first order approximation, the $+1/2 \leftrightarrow -1/2$ transition is not affected, except for a shift in energy, by the quadrupole. The other allowed transitions are affected in such a way that they are broadened and are usually too far from resonance for observation. In order to minimize the shift in the $+1/2 \leftrightarrow -1/2$ transition, and to minimize distortions in lineshape due to the second-order effects, it is best to utilize the highest magnetic field possible [32]. However, a new problem arises from the fact that operating at high magnetic field strengths increases the chemical shift anisotropy contribution to the spinning sidebands. Consequently, high spinning speeds, typically in the range of 11–17 kHz, are necessary when recording NMR spectra of quadrupolar nuclei at high magnetic fields [33]. Another approach is the so-called "double-rotation" (DOR)

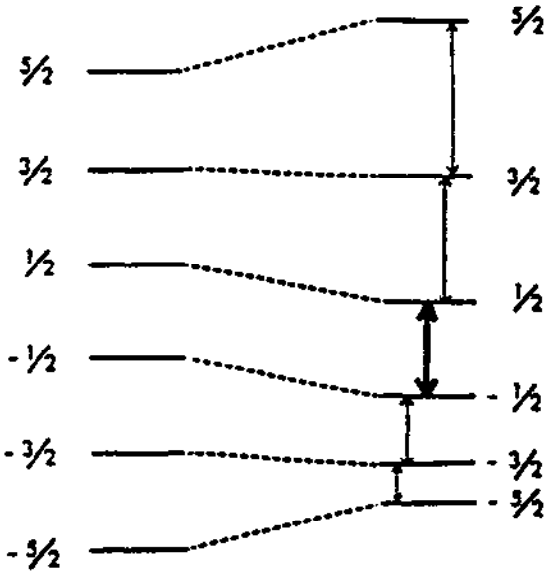

Fig. 1. Energy level diagram for a nucleus of spin = 5/2 showing the effect of the first-order quadrupolar interaction on the Zeeman levels. Reproduced from ref. 31 with permission.

method proposed by Samoson et al. [34]. These workers showed that experiments with a double-rotor on the central $(+1/2 \leftrightarrow -1/2)$ transition of sodium-23 in polycrystalline sodium oxalate led to elimination of the broadening due to second-order quadrupolar effects and resulted in a thirty-fold increase in resolution compared with magic-angle spinning NMR experiments. This technique, of which a theoretical account has been given by Llor and Virlet [35], consists of spinning a small rotor containing the sample inside a bigger rotor spinning at a slower speed (typically 2000 Hz for the inner rotor and 400 Hz for the outer one). The outer rotor is inclined at an angle θ_1 with respect to the external magnetic field B_0 whereas the inner rotor is inclined at an angle θ_2 with respect to the rotation axis of the outer rotor. The "magic angles" θ_1 (54.7°) and θ_2 (30.6°) are the angles for which the second and fourth Legendre polynomials are equal to zero. In a DOR experiment, the rotation axis of the inner spinner precesses about the rotation axis of the outer spinner, thus making the angle between the rotation axis of the inner spinner and the external magnetic field B_0 time-dependent. One drawback about double-rotation experiments, however, is that the resulting NMR spectra contain numerous spinning sidebands owing to the low-frequency rotation of the external rotor. Samoson and Lippmaa have investigated this problem [36(a)]. They have found that the utilization of rotation-synchronized excitation led to cancellation of odd-numbered spinning sidebands, thus facilitating the interpretation of DOR NMR spectra of quadrupolar nuclei. Pines and co-workers [36(b)] recently combined this technique with a new double-rotor design that achieves an outer-rotor speed up to 1 kHz under double-rotation conditions and an associated inner-rotor speed of about 5 kHz. They showed that synchronized DOR spectra of ^{23}Na in polycrystalline sodium oxalate could be obtained with an extremely high resolution despite the static linewidth of the ^{23}Na central transition in this compound of about 10 kHz. An alternative technique to double-rotation is the so-called "dynamic-angle spinning" (DAS) experiment. This experiment is somewhat similar to double-rotation in that it also requires two angles, but, in this case, the spinning axis of the sample is flipped from one angle θ_1 to another angle θ_2 after a given length of time. The complementary DAS angles θ_1 and θ_2 are chosen in such a way that the time-weighted second- and fourth-order Legendre polynomials are zero, thereby removing second-order quadrupolar broadening. This technique has been applied to ^{17}O and ^{23}Na nuclei [37,38].

The DOR and DAS experiments described above involve physical manipulation of the sample. On the other hand, other methods aimed at unraveling the solid state NMR spectra of quadrupolar nuclei have been reported in recent years and involve manipulation of the nuclear spins through various pulse sequences. These include a two-pulse free induction decay (TPF) method [39,40] and nutation spectroscopy. The latter experiment is a two-dimensional experiment that was introduced in 1982 by Samoson and Lippmaa [41–43] and is based on the fact that NMR intensities of half-integer spin quadrupolar nuclei depend upon the rf pulse length and the strength of the quadrupolar interactions [44]. In a 2D NMR nutation spectrum,

information about the quadrupolar interactions is represented by shifts along an additional spectral axis (F1-axis), while shifts along the conventional spectral frequency axis (F2-axis) are determined mainly by the chemical-shift interaction, if the polarizing magnetic field is strong enough and/or magic angle spinning is applied. Thus, this technique has made possible the detection of spin species that had identical chemical shifts but had different quadrupolar interactions owing to differences in local symmetry. Two-dimensional NMR nutation spectroscopy of powders has thus far been applied to ^{7}Li [45], ^{11}B [46], ^{23}Na [41,45,47,48], ^{27}Al [42,45,49–51], ^{45}Sc [45], ^{51}V [52], ^{55}Mn [53], ^{87}Rb [54], and ^{93}Nb [55].

Another potential problem in obtaining solid state NMR spectra is that the longitudinal relaxation times may be very long [31]. To overcome this, cross-polarization [11,12] may be employed to transfer polarization from an abundant spin (e.g. ^{1}H) to a dilute spin (S), thus allowing for recycle delay times determined by T_1 of ^{1}H and not T_1 of S. Additionally, the magnetization of the dilute S spin is increased by the cross-polarization up to a theoretical maximum of γ_H/γ_S.

The high-power proton decoupling, cross-polarization, and magic angle spinning techniques mentioned briefly in this section are often applied simultaneously to obtain high resolution, solid state NMR spectra [18].

D. STUDIES OF METAL NUCLEI

(i) The d-block metals

(a) Group 3 (Sc, Y, La)

Scandium. Although the first solid-state ^{45}Sc NMR spectra were reported in 1987 [56], no studies of organometallic or coordination compounds have appeared of which we are aware [3]. The spectra that were described in the initial report [56] were of powdered samples of $Sc(OAc)_3$, $ScCl_3 \cdot 3H_2O$, $Sc(NO_3)_3 \cdot 2.5H_2O$, and Sc_2O_3. A spin-echo technique needed to be employed for some of the samples in order to reduce probe ringing and observe the very broad resonances. In the case of scandium acetate, for example, the central $+1/2 \leftrightarrow -1/2$ transition and a complex array of sidebands were observed at 8.45 tesla with magic angle spinning (Fig. 2(a)). A 3.52 tesla powder pattern (Fig. 2(b)) allowed the quadrupole coupling constant (5 ± 0.2 MHz) and the asymmetry parameter of the electric field gradient tensor (0 ± 0.05) to be measured. Other samples with higher quadrupole coupling constants (ca. 15 MHz) required that high field static spectra be measured in order to obtain useful linewidths.

A study of $Sc_2(SO_4)_3$ has also been reported [45]. The resonance of the central transition measured at 121.5 MHz was structureless and 2.6 kHz wide. This linewidth could be reduced to 600 Hz by MAS. At 43.8 MHz, the MAS spectrum showed some structure, indicating the presence of sites with the same chemical shift but with different quadrupole parameters. The 2D nutation spectrum (Fig. 3) was well-

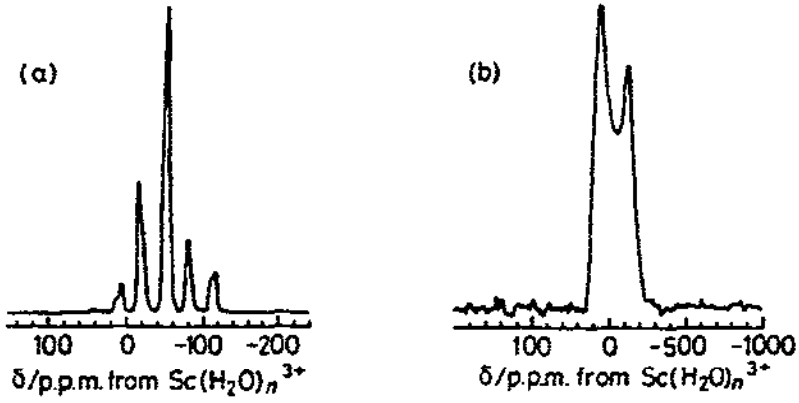

Fig. 2. (a) ^{45}Sc MAS NMR spectrum of $Sc(OAc)_3$ measured at 8.45 tesla. (b) ^{45}Sc NMR spectrum of a static sample of $Sc(OAc)_3$ measured at 3.52 tesla. The spectrum shown in (a) required 5 min for accumulation whereas the spectrum shown in (b) required 8 h. Reproduced from ref. 56 with permission.

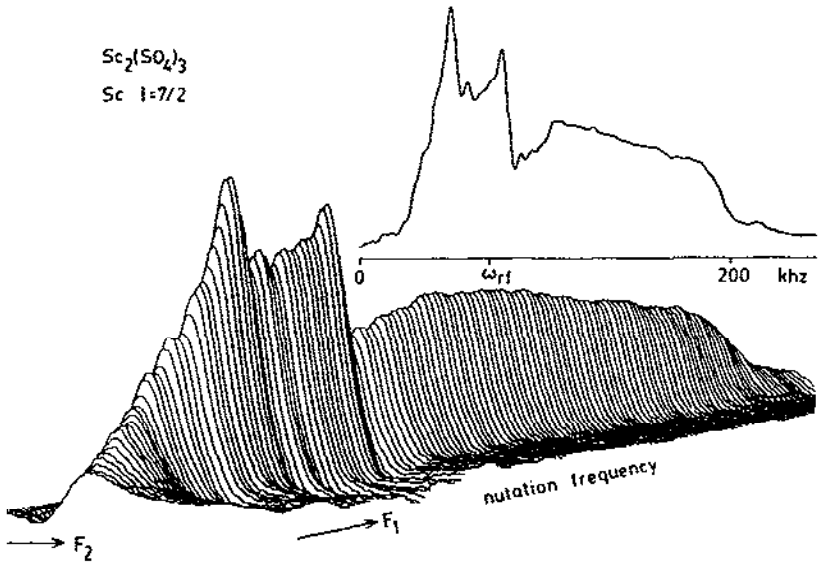

Fig. 3. 2D nutation spectrum of ^{45}Sc in a sample of scandium sulfate together with its F_1 projection. Reproduced from ref. 45 with permission.

structured and indicated that the major contributor to the spectrum had a quadrupole coupling constant of about 2 ± 0.5 MHz with a low asymmetry parameter.

Yttrium. Early ^{89}Y MAS NMR studies involved single-pulse experiments: Thompson and Oldfield [56] recorded ^{89}Y MAS NMR spectra for yttrium oxide, Y_2O_3, and a series of yttrium salts including $Y(OAc)_3$, $YCl_3 \cdot 6H_2O$,

$Y(NO_3)_3 \cdot 6H_2O$, and $Y_2(SO_4)_3 \cdot 8H_2O$ and Dupree and Smith [57] obtained ^{89}Y solid state NMR data for several yttrium aluminates and silicates. The first ^{89}Y CP/MAS NMR results were reported in 1990 by Merwin and Sebald: the compounds that were investigated were hydrates, namely $Y(NO_3)_3 \cdot 6H_2O$, $Y_2(SO_4)_3 \cdot 8H_2O$, $YCl_3 \cdot 6H_2O$, $Y(OAc)_3 \cdot 4H_2O$ and $Y(acac)_3 \cdot 3H_2O$, and the time necessary for accumulating ^{89}Y CP/MAS NMR spectra was said to be several orders of magnitude less than that for single-pulse experiments [58]. Cheetham and co-workers [59] circumvented the aforementioned problems associated with ^{89}Y NMR spectroscopy by incorporating paramagnetic ions into diamagnetic yttrium-containing solids. These studies represent a continuation of the work described elsewhere in this article concerning ^{119}Sn MAS NMR spectroscopy of rare-earth stannates [60]. In this case, however, they also investigated pyrochlore rare-earth-doped yttrium titanates $Y_{2-y}Ln_yTi_2O_7$ (Ln = Ce, Pr, Nd, Sm, Eu, and Yb) in addition to the lanthanide-substituted pyrochlore stannates $Y_{2-y}Ln_ySn_2O_7$. These workers found that changes in the local environment as yttrium ions are replaced by paramagnetic ions could easily be detected, each substitution of a paramagnetic ion into the first coordination sphere of the ^{89}Y ion producing a large additive shift. Additionally, since the relaxation times of yttrium nuclei close to paramagnetic ions are greatly reduced, the detection of these nuclei, which were often present in concentrations of less than 0.5% in the solid, became possible. These workers also proposed that the shifts in the ^{89}Y NMR spectra caused by the paramagnetic ions arose, at least at room temperature, from large contributions from a dipolar mechanism. However, they were unable to obtain confirmation of their interpretation from ^{89}Y NMR spectra of Ho^{3+}-substituted samples which, if the latter were correct, would have shown shifts in the opposite direction to those observed for Eu^{3+}- and Yb^{3+}-containing samples*. Lastly, these results were reported to be in contrast to the shifts observed in the ^{119}Sn NMR spectra of the lanthanide stannates $Ln_2Sn_2O_7$, but were said to be chemically reasonable in view of the nature of the Y–O and Sn–O bonds.

Lanthanum. In 1980, the chemical shift and linewidth of the solid state ^{139}La NMR signal of the high symmetry species LaB_6 were reported [62] and in 1987 the spectra of $La(OAc)_3$ and $La(NO_3)_3 \cdot 6H_2O$ were described [56]. The latter two compounds gave rise to large quadrupole coupling constants and high asymmetry parameters. No applications of solid state ^{139}La NMR spectroscopy to organometallic or coordination chemistry have yet been reported of which we are aware [3].

(b) Group 4 (Ti, Zr, Hf)

Titanium. ^{47}Ti ($I = 5/2$) and ^{49}Ti ($I = 7/2$) have nearly identical magnetogyric ratios

* This dichotomy in the paramagnetic shifts between Ho^{3+}-complexes and Eu^{3+}- and Yb^{3+}-complexes has previously been observed in the proton NMR spectra of diethyldithiophosphinato-complexes of these elements. See, for example, ref. 61.

and, accordingly, signals from both isotopes in a titanium-containing sample are typically detected in a single NMR experiment. Early solid state ^{47,49}Ti NMR studies involved both powdered samples (e.g. metallic titanium hydride[63]) and single crystals (e.g. $SrTiO_3$ [64]). Applications to organometallic and coordination chemistry are likely to be limited due to the sensitivity to local site symmetry. The problem is exemplified by a recent study of $BaTiO_3$ [65]. Above the Curie temperature of 135°C, $BaTiO_3$ is cubic and lowering the temperature through the Curie temperature causes a first-order transition to a tetragonal form. At about 140°C, the spectrum of a static powdered sample gave rise to sharp ^{47}Ti and ^{49}Ti resonances for the $+1/2 \leftrightarrow -1/2$ transitions (both with linewidths of ca. 88 Hz). As the sample temperature was lowered through the Curie temperature (Fig. 4), the intensities of the resonances dropped until, below 135°C, there was no observable intensity at all. Thus, even the relatively small change in crystallographic symmetry encountered here gives rise to additional electric field gradients which cause second-order quadrupolar interactions sufficient to broaden the central transition into the baseline. ^{137}Ba NMR measurements [65] support the ^{47,49}Ti NMR results. A 1991 report [66] describes briefly the use of a fast digitizer to detect a ^{47,49}Ti signal for $BaTiO_3$ at room temperature, i.e. for the tetragonal phase. The peak width at half-height was reported to be about 15 kHz (cf. 88 Hz for the cubic phase, described above).

Zirconium. The first report of a ^{91}Zr solid state NMR study appeared in 1991 [66]. MAS spectra of a number of binary oxide powders were described. Only cubic $BaZrO_3$ gave a sharp signal and all oxides of lower symmetry gave rise to broad

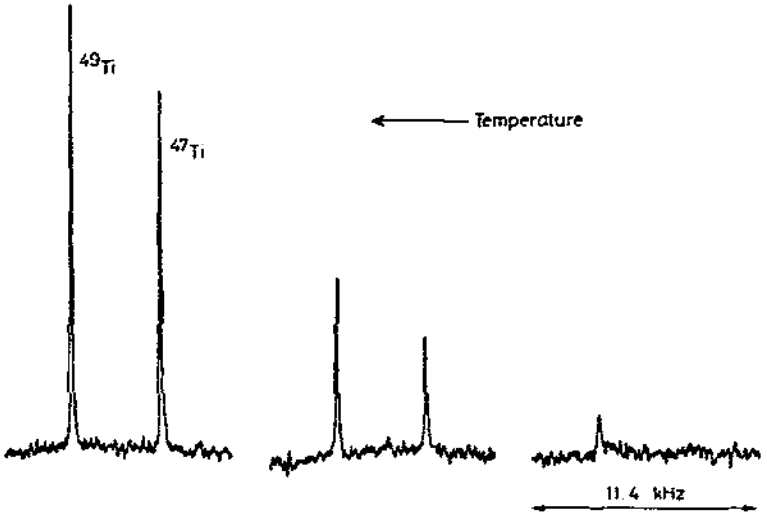

Fig. 4. Temperature dependence of the ^{47,49}Ti NMR spectrum of barium titanate near the Curie point. Spectra were taken at 2–3°C intervals with an uncalibrated variable temperature probe. Reproduced from ref. 65 with permission.

^{91}Zr resonances. Applications to organometallic and coordination chemistry are unlikely to be widespread given the symmetry requirements.

Hafnium. No solid state Hf NMR studies of relevance to this article have been reported of which we are aware [3].

(c) Group 5 (V, Nb, Ta)

Vanadium. ^{51}V NMR studies of a number of extended array materials have been reported. Alkali metal and ammonium metavanadates (MVO_3) have been investigated by several groups [67] at different field strengths. In MAS spectra measured at 9.4 tesla, spinning sidebands spread across a range of over 8000 ppm (840 kHz) with isotropic signals having peak widths at half-height of about 1.2 kHz [67(f)]. Principal values of the shift tensors, the anisotropies, and asymmetries have been reported [67(f)]. All asymmetry parameters lie in the range 0.62–0.71 except that of β-$NaVO_3$ which is reported to be zero. Consistent with this observation was the X-ray powder diffraction pattern which confirmed that the sample was a known polymorph of axial symmetry. There is some evidence that the O–V–O angles correlate with the chemical shift anisotropies in the isostructural (i.e. non-axial) systems [67(f)]. Vanadium oxides deposited on alumina [68–70], important as oxidation catalysts, have been investigated and ^{51}V NMR data of some model compounds (including K_3VO_4, Na_3VO_4, $Ca_3(VO_4)_2$, and $Ca_2V_2O_7$) described [68]. Related studies of vanadium oxide deposited on silica [71], titania [70], and on tin(IV) oxide [72] have been reported and a detailed account of vanadium poisoning of Ni/Mo hydrodesulfurization (HDS) catalysts has appeared [73]. The latter report describes poisoning of HDS catalysts by vanadium porphyrins, an issue of some significance in the petroleum industry where low levels of "petroporphyrins" can cause failure of expensive HDS catalysts. As part of this study, an attempt was made to obtain ^{51}V NMR spectra of solid vanadyl porphyrin complexes but no signals were detected. This represents the only attempted application of solid state ^{51}V NMR methods to coordination chemistry of which we are aware.

Niobium. Applications of solid state ^{93}Nb NMR techniques to organometallic and coordination chemistry have yet to be described [3]. Work on extended array materials has appeared and studies of metal niobates by both NMR and quadrupole resonance methods [74,75] have been reported. Lithium niobate [76] is a particularly important example given its application in integrated optical devices. Studies [75] of the solid solution Li_2O–Nb_2O_5 show that the NMR spectra broaden as the samples deviate from stoichiometry and this effect is attributed to lattice defects. As might be anticipated, Li_3NbO_4, which has a high symmetry (cubic space group $I23$ [77]) gives rise to a simple spectrum with a small quadrupole coupling constant whereas $LiNb_3O_8$ (monoclinic space group $P2_1/a$ [78]) exhibits a complex spectrum with a high quadrupole coupling constant. A study [65] of $BaTiO_3$ doped with

niobium shows that resonances for ^{93}Nb can be obtained for static samples even at the 0.2% doping level. Replacement of Ti(IV) by Nb(V) does not result in the creation of vacancies since line broadening is not evident (vide supra). In such circumstances, electron compensation is believed to be the major mechanism for achieving charge balance.

Tantalum. No reports of the application of solid state ^{181}Ta NMR spectroscopy to organometallic or coordination chemistry have appeared [3]. Indeed, the large quadrupole moment of ^{181}Ta suggests that vanadium and niobium may be better candidates for initial studies of molecular compounds of the Group 5 elements. Some work by other NMR techniques on extended array materials that contain tantalum (e.g. lithium NMR of $LiTaO_3$ single crystals [79,80]) has appeared.

(d) Group 6 (Cr, Mo, W)

Chromium. No solid state ^{53}Cr NMR studies of relevance to this review have been reported of which we are aware [3]. Indeed, very few solution studies of organometallic and coordination compounds by ^{53}Cr NMR methods have yet been described [81].

Molybdenum. Both ^{95}Mo and ^{97}Mo are $I = 5/2$ nuclei. Since ^{95}Mo has the smaller quadrupole moment and the higher sensitivity it is the more suitable nucleus for study. The first solid state ^{95}Mo NMR studies were performed about 20 years ago with a report on Na_2MoO_4 appearing in 1972 [82]. A subsequent report on Ag_2MoO_4 in 1976 [83] was followed by wider ranging studies of molybdates and related compounds in 1988 [84]. Measurement of ^{95}Mo NMR spectra at 19.55 MHz with excitation of the $+1/2 \leftrightarrow -1/2$ transition allowed sharp resonances (linewidths ca. 500 Hz) to be measured for most alkali metal molybdates, an indication of the high symmetry of the MoO_4^{2-} units. Interestingly, samples of potassium molybdate produced three different types of spectrum, depending upon the thermal pretreatment of the particular sample. This observation is entirely in accord with the fact that this material exists in three different structural modifications and the data could be interpreted in terms of interconversion of the α, β, and γ forms. For molybdates of Ca, Ba, and Pb, the spectra indicated second-order quadrupolar effects, a result of the more distorted MoO_4^{2-} tetrahedra. Both MoO_3 and the polyoxo complex $H_3PMo_{12}O_{40} \cdot xH_2O$ produced broad asymmetric spectra. Since the Mo centers are in highly distorted octahedral environments in these materials, both chemical shift anisotropy and second-order quadrupolar effects were said to be responsible. Molybdenum hexacarbonyl (orthorhombic space group *Pnma*, $Z = 4$ [85]) was reported to produce a single sharp peak (linewidth ca. 250 Hz), indicative of the high symmetry about the molybdenum center. An earlier study [86] of $Mo(CO)_6$ at 5.8546 MHz (2.11 tesla) resulted in a spectrum consisting of a split resonance for a static sample with a separation between maxima of ca. 75 Hz. In order to demonstrate that this

splitting resulted from second-order quadrupolar effects, the measurement was repeated at a new field, 2.24 tesla. At this higher field, the two lines coalesced to produce an asymmetrically shaped signal. Thus, at the field used in the 1988 study [84], discussed above, a single sharp signal might be anticipated, exactly as observed. A further report [87] of the static powder spectrum of $Mo(CO)_6$, this time measured at 26.06 MHz, similarly describes a single, sharp resonance (Fig. 5). A study of molybdenum hexacarbonyl adsorbed on alumina has also appeared [88].

Since 1990, Ellis and co-workers [87,89,90] have been engaged in studies of a variety of molybdenum-containing materials of interest in catalysis and bioinorganic chemistry. It has been demonstrated [89] that solid state ^{95}Mo NMR spectra of isotopically enriched $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and natural-abundance $(Bu_4N)_2$-Mo_2O_7 could be obtained using solid echo techniques with both dipolar decoupling and cross-polarization. Excellent cross-polarization enhancements were obtained, indicating that this technique can be usefully applied to the non-integral-spin, quadrupolar ^{95}Mo nucleus. Studies of the cross-polarization dynamics indicate that inequivalent molybdenum sites within a sample behave differently and this information could be of value in the study of polymorphism, phase transitions, etc.

In a study related to HDS catalysis [87], Ellis and co-workers have investigated oxomolybdates and polyoxomolybdates adsorbed onto γ-alumina. Such materials are representative of HDS catalysts prior to sulfiding and the work sheds light on the surface species present. Spectra of static samples of catalysts reveal inhomogeneously broadened signals taken to be indicative of a range of surface species within the samples. MAS spectra suggest that four different species are present on the alumina

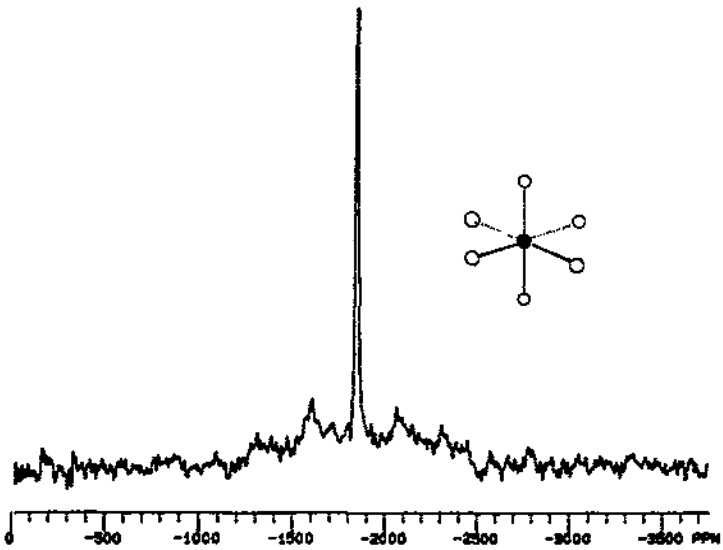

Fig. 5. ^{95}Mo selective excitation static powder spectrum of molybdenum hexacarbonyl. Reproduced from ref. 87 with permission.

surface prior to calcination and that two species remain after heat treatment. Measurement of spikelet echo spectra produced results indicative of the presence of both static and dynamic species on the support surface of the uncalcined catalysts. A spikelet echo spectrum [91] is obtained by digitization of a train of spin echoes whose Fourier transformation generates spikelets. The presence of spikelets of varying linewidth and separation is indicative of the presence of species of different spin–spin relaxation times, T_2, thus suggesting the presence of species of different mobilities. Calcination causes changes in the spikelet echo spectra that suggest loss of the mobile species, and the increases in linewidth seen in both static and MAS spectra after heat treatment indicate a polymerization of the surface species to form a MoO_3-like phase. $Al_2(MoO_4)_3$ appears to be present both before and after heat treatment. Clearly what is needed now is a study of the sulfiding process to examine the changes that occur as the actual HDS catalyst is generated.

Ellis and co-workers have also reported [90] a detailed study of aryldiazenido-, organohydrazido-, and related polyoxomolybdates. These compounds have previously been the subject of a complete solution ^{95}Mo NMR study [92] and the structures of the compounds are well-understood. The presence of both tetrahedral and octahedral molybdenum sites in these materials suggests that they might be useful models for the types of site present in HDS catalysts. Additionally, the presence of nitrogen donor groups in some of the examples studied is of interest in terms of modeling hydrodenitrogenation (HDN) catalysis. The results of the study show that, even in structurally complex cases, octahedral and tetrahedral sites can be differentiated and different octahedral sites within a single molecule can be distinguished by use of computer simulation and X-ray crystallographic data. For the compounds studied, it seems that the degree of distortion in nominally octahedral sites governs the magnitude of the quadrupole coupling constant. A series of ab initio calculations on the species $[MoO_6]^{6-}$ has been performed to investigate further this relationship. It seems that distortions from octahedral (or tetrahedral) symmetry result in changes in the charge anisotropy at sites within the polyhedron and the effect of these changes on the electric field gradient tensor is reflected in the magnitude of the nuclear quadrupole coupling constant.

It seems likely that the area of solid state ^{95}Mo NMR spectroscopy will continue to develop and that further applications to organometallic and coordination chemistry will evolve. The recent work of Ellis and co-workers [87,89,90], described briefly in the preceding paragraphs, has laid a suitable foundation for extended applications.

Tungsten. The first solid state ^{183}W NMR spectra were reported in 1986 [93]. MAS spectra, measured at 8.45 tesla (15 MHz), of a series of alkali metal and alkaline earth metal tungstates have been described as well as spectra of $W(CO)_6$, WO_3, and the Keggin cluster compound $H_3[P(W_{12}O_{40})] \cdot nH_2O$. All of the samples exhibited long spin-lattice relaxation times which gave rise to relatively poor signal-to-noise

ratios. All of the simple metal tungstates gave rise to single, sharp resonances, indicating small chemical shift anisotropies and in agreement with reported symmetry information from crystallographic studies. The highly symmetric $W(CO)_6$ gave rise to a single signal with a linewidth of 6 Hz. Tungsten trioxide produced two signals with spinning sidebands, and X-ray crystallographic data confirm the presence of two tungsten sites. The Keggin compound, with its 12 identical tungsten sites, gave rise to a single resonance with an intense set of spinning sidebands. Additional applications of this technique can be expected as, other than the long times required for data accumulation, no problems were encountered in obtaining the spectra.

(e) Group 7 (Mn, Tc, Re)

Manganese. Several investigations of the solid state ^{55}Mn NMR spectrum of potassium permanganate have been reported [41,53,94–96]. Indeed, $KMnO_4$ has been tested for suitability as a standard material for setting the magic angle, but the resonance pattern was found to be too complex to be very useful [96]. A sample of $KMnO_4$, known to be orthorhombic (space group *Pnma*) from X-ray diffraction, has been examined at 24.8 MHz and at 74.4 MHz [53]. At the lower frequency, a second-order quadrupolar effect on the central $+1/2 \leftrightarrow -1/2$ transition is seen but at the higher frequency, such effects are negligible and a symmetrical signal is observed. Static 2D ^{55}Mn NMR spectra at 74.4 MHz, obtained using different solenoids to produce different rf field strengths, reveal more than one signal [53]. A possible interpretation of such an observation is that more than one crystallographic site is present in the sample but this is clearly not correct in this case since both the 24.8 MHz NMR spectrum and the X-ray diffraction data reveal no evidence for multiple sites. An alternative interpretation is that a single site exists and that the signals result from a quadrupolar interaction where the interaction strength is intermediate in comparison with the rf magnetic field strength. This example is quite unusual since the common cases involve quadrupolar interactions that are either small or large in comparison with the rf magnetic field strength. The intermediate case is rarely recognized. 2D MAS experiments support the explanation proposed [53]. No applications of solid state ^{55}Mn NMR methods to organometallic or coordination chemistry seem to have been reported [3].

Technetium. This element has no stable isotopes and so, despite interest in its coordination chemistry [97], applications of NMR spectroscopy are not likely to be forthcoming.

Rhenium. Both ^{185}Re and ^{187}Re have very large quadrupole moments and the resulting quadrupolar interactions in many rhenium compounds are sufficiently large that they prevent investigation even by NQR methods [98(a)]. NMR measurements are correspondingly more challenging. Nonetheless, tetraethylammonium and tetramethylphosphonium metaperrhenates have been successfully investigated [98(a)].

Since ^{185}Re and ^{187}Re have very similar magnetogyric ratios, the $+1/2 \leftrightarrow -1/2$ resonances for both isotopes may be detected in a single NMR experiment. Studies of Et_4NReO_4 and Me_4PReO_4 at 4.698 tesla reveal that no quadrupole couplings are present in the ^{185}Re and ^{187}Re signals of the former compound (Fig. 6), but that typical second-order quadrupole splittings are observed for the latter (Fig. 7) [98(a)]. The linewidths measured for Et_4NReO_4 in the solid state and for $NaReO_4$ in solution were almost the same, indicating that the ReO_4^- ion is undistorted in the crystal lattice of the tetraethylammonium salt. The situation must be quite different for the tetramethylphosphonium salt where a comparison of the solid state spectrum with the solution spectrum of $NaReO_4$ (Fig. 7 [98(a)]) reveals that considerable structural distortion is probable. No X-ray crystallographic data appear to be available for comparison with the NMR results.

A separate study of the salt Me_4AsReO_4 has also been reported [98(b)]. The $^{185,187}Re$ NMR powder pattern is shown in Fig. 8 [98(b)]. The spectrum has been interpreted in terms of the superposition of two sets of $^{185,187}Re$ signals and the unusual lineshapes explained in terms of the presence of two types of ReO_4^- tetrahedra in the crystal lattice. Variable temperature measurements over the range 380–320 K suggest a phase transition and this has been confirmed by DSC measurements. At temperatures below 310 K, no ^{185}Re or ^{187}Re resonances could be observed, presumably because the quadrupole coupling is very large in the low temperature modification. No other solid state $^{185,187}Re$ NMR measurements of relevance to this article have been reported of which we are aware [3].

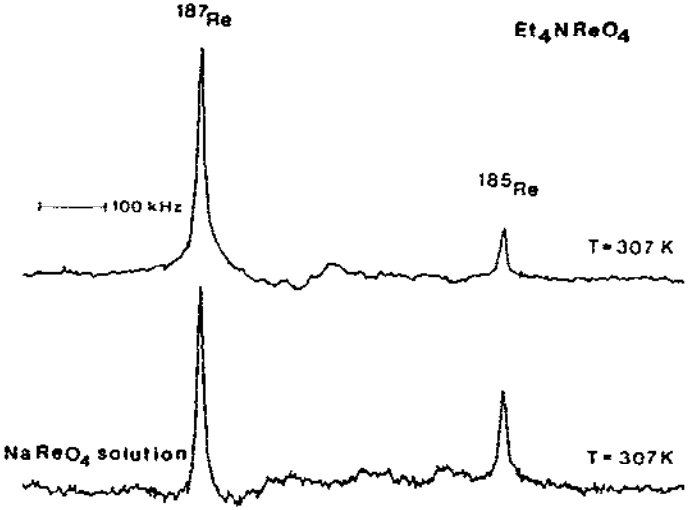

Fig. 6. $^{185,187}Re$ NMR spectra of polycrystalline Et_4NReO_4 (upper trace) and of $NaReO_4$ solution (lower trace). Reproduced from ref. 98(a) with permission.

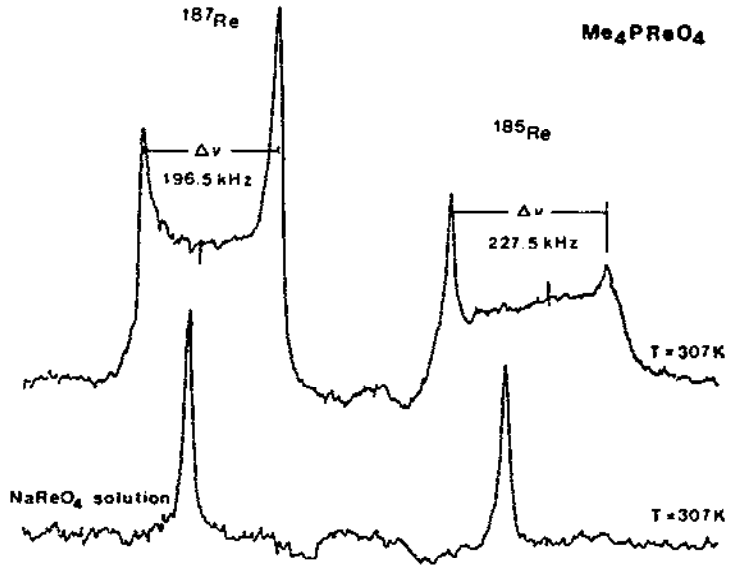

Fig. 7. ^{185,187}Re NMR spectra of polycrystalline Me_4PReO_4 (upper trace) and of $NaReO_4$ solution (lower trace). Reproduced from ref. 98(a) with permission.

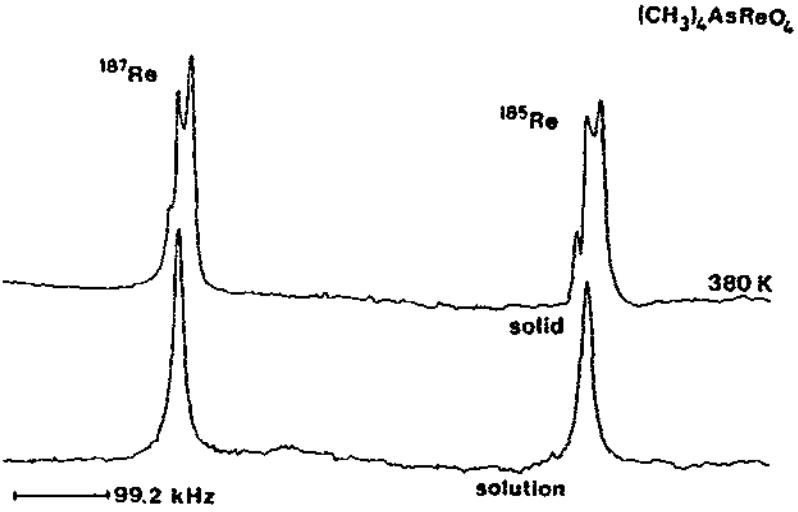

Fig. 8. ^{185,187}Re NMR spectra of polycrystalline Me_4AsReO_4 (upper trace) and of $NaReO_4$ solution (lower trace). Reproduced from ref. 98(b) with permission.

(f) Group 8 (Fe, Ru, Os)

None of the Group 8 nuclei has been the subject of a solid state NMR study of relevance to this review. The nuclear properties of the isotopes of these elements

(Table 1) have almost precluded the use of metal NMR for this triad, either for solutions [1,81] or for solids [3].

(g) Group 9 (Co, Rh, Ir)

Cobalt. Among the Group 9 metals, only cobalt has been the subject of solid state NMR studies [99] of relevance to this review. ^{59}Co has a spin of 7/2 and is 100% abundant with only a moderate quadrupole moment and so this isotope would seem to be a reasonable candidate for future investigations. Reported studies have concerned polycrystalline, high symmetry, octahedral species such as $M_3[Co(NO_2)_6]$ (M = Na, Cs) [99a], $[Co(en)_3]^{3+}$, $[Co(CN)_6]^{3-}$, $[Co(acac)_3]$, $[Co(C_2O_4)_3]^{3-}$, and $[Co(NH_3)_6]^{3+}$ [99(b), (c)], as well as single crystals of the acetylacetonate [99(d)], the cyanide [99(e), (f)], and the hexammine [99(g)] complexes. Available data include chemical shifts, quadrupole coupling constants, values of the chemical shift tensors, and anisotropies. No data on complexes of lower symmetry appear to be available.

Rhodium. ^{103}Rh has a spin of 1/2 and a natural abundance of 100%. Direct observation of rhodium NMR spectra has been hindered by the low magnetogyric ratio of ^{103}Rh and even solution measurements are not particularly common [1,81].

Iridium. Iridium has two isotopes with spins of 3/2 and both of these have large quadrupole moments (Table 1). No solid state or solution measurements of iridium NMR spectra of organometallic and coordination compounds have appeared of which we are aware [1,3,81].

(h) Group 10 (Ni, Pd, Pt)

Neither ^{61}Ni nor ^{105}Pd have been the subject of solid state NMR studies of relevance to this review [3]. ^{195}Pt, with $I = 1/2$ and a natural abundance of 33.8%, has been the focus of some attention. Several reports describing the utilization of ^{195}Pt solid state NMR spectroscopy in the analysis of platinum complexes and supported platinum catalysts have been published: Doddrell et al. [100] measured the anisotropy ($\Delta\sigma$) of the ^{195}Pt chemical shielding for two Pt(IV) complexes, $[Me_3Pt(acac)]_2$ (acac = acetylacetonato) and $[Me_3Pt]_2SO_4 \cdot 4H_2O$, and concluded that, given the magnitude of these, i.e. 1123 and 950 ppm, the chemical shift anisotropy contribution to the ^{195}Pt relaxation was significant at high magnetic field strengths. The chemical shift anisotropy is evident in the powder pattern measured at 64.4 MHz of the acetylacetonato complex, shown in Fig. 9(a). At this frequency, a value of $\Delta\sigma$ of around 1100 ppm is equivalent to about 70 kHz and so an MAS experiment at a reasonable spinning rate yields a spectrum containing a large array of spinning sidebands (Fig. 9(b)) [100]. The isotropic shift is not the most intense signal in this spectrum and so its value must be obtained through measurements at different spinning speeds. Harris et al. reported ^{195}Pt CP/MAS NMR data for the four Pt(IV) complexes [101–103] $K_2[Pt(OH)_6]$, $[Pt(en)_3]Cl_4 \cdot 2H_2O$ (en = ethylenediamine),

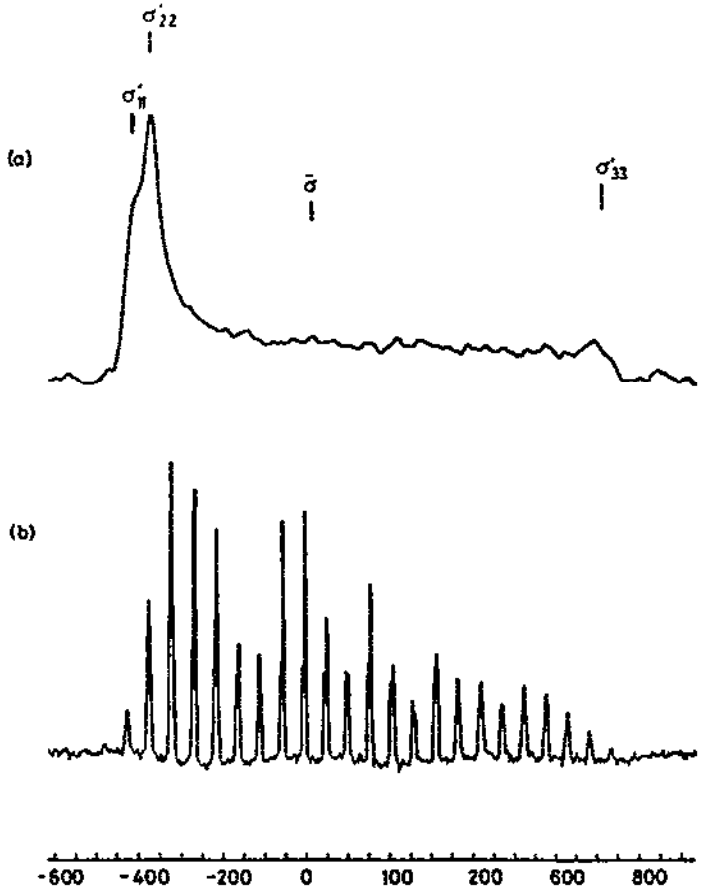

Fig. 9. (a) ^{195}Pt NMR spectrum of a static sample of $[Me_3Pt(acac)]_2$ obtained with cross-polarization. (b) ^{195}Pt NMR spectrum of $[Me_3Pt(acac)]_2$ obtained with cross-polarization and magic angle spinning. Reproduced from ref. 100 with permission.

$Na_2[PtCl_6]\cdot 6H_2O$, and *cis*-$[PtCl_4(NH_3)_2]$, and one platinum(II) phosphine complex [101,103], namely *cis*-$[PtMe_2(PEt_3)_2]$. Scalar couplings were observed in MAS spectra only for ^{195}Pt and ^{31}P in the complex *cis*-$[PtMe_2(PEt_3)_2]$ (Fig. 10) [103]. No scalar couplings involving nitrogen or chlorine were observed. Harris and Sebald [102] have taken advantage of the fact that ^{207}Pb and ^{195}Pt have close resonant frequencies at the field of their spectrometer (4.7 tesla; ^{207}Pb: 41.868 and ^{195}Pt: 42.828 MHz) and have found that setting the Hartmann–Hahn conditions for ^{207}Pb and then using those conditions to measure ^{195}Pt NMR spectra can save considerable time since no really suitable platinum compounds are available for optimization ($K_2Pt(OH)_6$ appears to be the best choice at this time).

Bucher et al. have used solid state ^{195}Pt NMR spectroscopy to investigate the metal-support interaction in Pt/TiO_2 and Pt/SiO_2 heterogeneous catalysts [104]. In

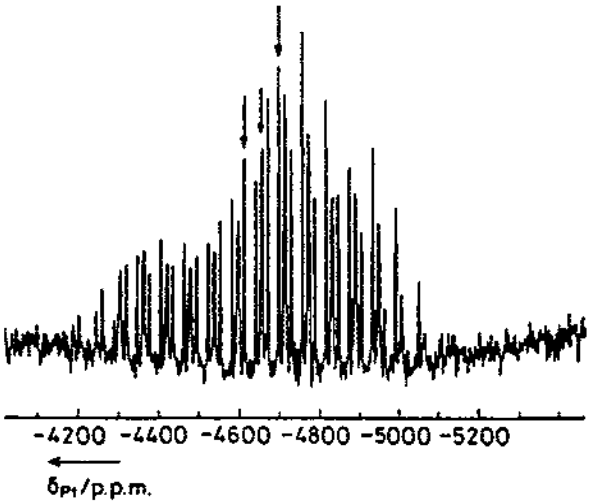

Fig. 10. ^{195}Pt NMR spectrum of *cis*-[$PtMe_2(PEt_3)_2$] obtained with cross-polarization and magic angle spinning at a speed of 2.5 kHz. The centerbands are indicated by arrows. Reproduced from ref. 103 with permission.

the former case, a strong metal support interaction (SMSI) is possible since partially reduced titanium oxide phases exist whereas in the latter case, silicon dioxide is said to be non-reducible and so no SMSI can occur.

(i) Group 11 (Cu, Ag, Au)

Copper. Both ^{63}Cu and ^{65}Cu have $I = 3/2$ and quite large quadrupole moments. Since ^{63}Cu is the more sensitive, it is generally the preferred choice for observation. Paramagnetism can be a problem with compounds of Cu(II) and solution ^{63}Cu NMR studies [1,81] have focussed on compounds of Cu(I). A solid state ^{65}Cu NMR investigation of alkali metal-promoted copper catalysts for the conversion of syngas to methanol has appeared [105] which included studies of some model compounds, e.g. Cu_2O and CuCl. Measurements of ^{65}Cu NMR spectra were made at 62.65 MHz in a 5.2 tesla magnet using a probe constructed with silver wire to avoid a copper background. Observation of ^{65}Cu, rather than ^{63}Cu, was preferred since problems were encountered with samples prepared in glass tubes when ^{63}Cu NMR spectra were measured. Since the magnetogyric ratio of ^{23}Na is very similar to that of ^{63}Cu, the glass caused interference. The ^{65}Cu isotope was found to resonate about 5 MHz upfield of sodium and so caused less interference. The copper linewidth did not decrease under MAS conditions and spectra of static samples of catalysts showed some evidence for both metallic copper and copper(I), formed by interaction of the copper with the alkali metal promoter. The presence of the copper(I) phase was found to correlate with catalytic activity.

In a separate study [106], the ^{63}Cu NMR spectra of Cu_2O cystals were

measured as a function of thermal treatment and it was shown that metallic copper could be detected in crystals annealed in a reducing atmosphere. The presence of metallic copper is believed to cause anomalously large optical absorption in this semiconductor material.

Studies of copper(I) salts [107] have also been reported. It has been shown [107(a)] that ^{63}Cu wideline NMR spectra of CuX (X = Cl, Br, I) and Cu_2HgI_4 could be obtained whereas no resonances could be observed for quaternary chalcogenides, Cu_2MYX_4 (M = Zn, Cd; Y = Ge, Sn). The copper(I) halides all crystallize with the zinc blende structure (space group $F\bar{4}3m$ [108(a)]) and so the copper sites are perfectly tetrahedral, resulting in zero quadrupole splitting of the signals. Cu_2HgI_4 crystallizes in the tetragonal space group $I\bar{4}2m$ with $Z = 2$ [108(b)] and so the copper sites are of lower (S_4) symmetry, resulting in a significant quadrupole coupling. Magic angle spinning studies of copper(I) halides by both ^{63}Cu and ^{65}Cu NMR methods have suggested that the isotropic peak positions change upon changing the spinning rate [107(b)]. The mechanism by which such changes might arise is not known. Other workers, operating at lower fields, have not commented upon any possible dependence of this type [107(c)].

Silver. Despite the fact that the two isotopes of silver both have $I = 1/2$ and reasonable values for their magnetogyric ratios, no solid state ^{107}Ag or ^{109}Ag NMR studies of relevance to this review have been reported [3], perhaps reflecting a lack of interest in the organometallic and coordination chemistry of silver. Some chemical shift data are available [109] for silver halides in the solid state and for some mixed metal halides of interest as superionic conductors.

Gold. The isotope ^{197}Au has $I = 3/2$ and a natural abundance of 100%. No solid state [3] or even solution [1,81,110] measurements of ^{197}Au NMR spectra of relevance to this article have been reported of which we are aware.

(j) Group 12 (Zn, Cd, Hg)

Zinc. As a typical low-magnetogyric ratio, non-integral spin, quadrupolar nucleus, ^{67}Zn presents a number of problems which hinder direct observation. However, spin-echo experiments have been reported [111] that allowed measurement of relatively undistorted second-order powder patterns for the $+1/2 \leftrightarrow -1/2$ transition of ^{67}Zn in a sample of zinc acetate dihydrate at a field of 11.7 tesla. The powder pattern could be simulated using a quadrupole coupling constant of 5.3 MHz. Recording powder patterns that span tens of thousands of Hertz would be extremely difficult in the absence of spin–echo methods of the type employed in this study.

Cadmium. ^{113}Cd is a good probe for the study of metalloproteins and related synthetic systems. It has favorable NMR properties ($I = 1/2$, natural abundance = 12.34%, and sensitivity relative to ^{13}C = 0.685) [112] and physical properties similar

to those of the common metals found in enzymes, e.g. Zn^{2+}, Ca^{2+}, and Mg^{2+}. The original studies on Cd-substituted proteins were performed in the solution state (see, for example, ref. 113). However, the isotropic chemical shift determined in solution is influenced by exchange processes, temperature, concentration, and solvent effects, which may limit the interpretation of the structural changes taking place at the metal during, for example, inhibition. On the other hand, by performing the experiments in the solid state, complete information concerning the shielding tensor can be obtained in principle without the potential difficulties mentioned above. Additionally, from single-crystal NMR experiments, the orientation of the principal elements of the shielding tensor with respect to a coordinate system based upon the molecule may be obtained. The knowledge of the magnitude and the orientation of the ^{113}Cd shielding tensor in turn provides information regarding the coordination of the metal at the active site of metalloproteins. The early ^{113}Cd solid state NMR spectra were obtained on inorganic cadmium compounds of known solid state structures with the aim of providing "benchmark" chemical shift data [114]. Soon after that, high-resolution ^{113}Cd CP/MAS NMR data obtained on cadmium complexes mimicking biological systems started being reported in the literature: Kurtz and co-workers [115] reported the results of their ^{113}Cd solid state NMR studies on the decanuclear cation $Cd_{10}(SCH_2CH_2OH)_{16}^{4-}$ which led them to conclude that the ^{113}Cd resonances observed for metallothionein were due to CdS_4 coordination sites rather than CdS_4O or CdS_3O_3 sites. Ellis et al. gave an account of their studies of Cd-substituted *meso*-tetraphenylporphyrin and its pyridine adduct, these systems being considered as model compounds for cadmium-substituted hemeproteins [116]. Upon coordination of pyridine to cadmium, gross changes for all tensor elements were observed leading to a 33 ppm shift to lower shielding of the isotropic value of the ^{113}Cd shielding tensor. These results were proposed to arise from a combination of both pyridine ligation and the geometric change resulting from the metal atom being pulled out of the plane of the porphyrin ring. In other work, Rodesiler and Amma [117] used ^{113}Cd solid state NMR spectroscopy to study a number of benzoyloxy and other carboxylato complexes of Cd^{2+}, these systems providing the metal environment found in proteins containing an all-oxygen coordination at the active site (e.g. concanavalin A, parvalbumin, skeletal muscle troponin C, calmodulin, and insulin). They concluded that ^{113}Cd resonances for systems with oxygen donor ligands in the -30 to -100 ppm region (more shielded than 0.1 M $Cd(ClO_4)_2$ aqueous solution) represented a higher coordinate species than six, i.e. at least seven or perhaps more. These results also led them to suggest that the ^{113}Cd resonances observed for the EF site of parvalbumin and the S_2 site of concanavalin A may be due to higher oxygen coordination than six. Following this work, Ellis and co-workers published a series of papers concerning ^{113}Cd single-crystal NMR studies of compounds containing cadmium–oxygen linkages such as $Cd(NO_3)_2 \cdot 4H_2O$ [118], $3CdSO_4 \cdot 8H_2O$ [118], $CdCa(CH_3COO)_4 \cdot 6H_2O$ [119], $Cd(C_4H_2O_4) \cdot 2H_2O$ [119], $Cd_2(HCOO)_4 \cdot 4H_2O$ [119], $Cd(NH_4)_2(SO_4)_2 \cdot 6H_2O$ [119], $Cd(CH_3COO)_2 \cdot 2H_2O$ [119,120],

$Cd(NH_2CH_2CO_2)_2 \cdot H_2O$ [121], and $Cd(C_5H_{12}N_2S)_2(NO_3)_2$ [121], and also published the ^{113}Cd CP/MAS NMR spectra of two ^{113}Cd-substituted lyophylized and hydrated metalloproteins [122], namely parvalbumin and concanavalin A. Other work in this area includes Amma's investigations of $Cd(\alpha,\alpha'\text{-bipyridyl})_2X_2$ (X = Cl, Br, NCS, NO_3) complexes [123,124] and related species containing nitrogen, oxygen, or sulfur donor groups [125–131], Munakata et al.'s studies of tris(diamine)cadmium(II) complexes [132], and Schauer and Anderson's work on cadmium complexes of $EGTA^{4-}$ (H_4EGTA = 3,12-bis(carboxymethyl)-6,9-dioxa-3,12-diazatetradecanedioic acid) [133]. Furthermore, the field was reviewed in 1988 by Summers [134]. Very recently, however, additional ^{113}Cd CP/MAS NMR spectroscopic studies of biologically relevant synthetic systems have been published by Ellis and co-workers. These studies were performed on the cadmium complex of an unsaturated nitrogen analog of 18-crown-6 [135], cadmium protoporphyrin IX dimethyl ester [136], cadmium protoporphyrin IX [136], Cd^{2+}-substituted myoglobin [136], poly(bis(acetato)-bis(imidazole)cadmium(II) [137], which is a model compound for Cd^{2+}-substituted carboxypeptidase-A and thermolysin, the dimer of diaquobis(2-hydroxybenzoato)-cadmium(II) [138], tetrakis(4-picolinato) (nitrato-*O*,*O'*) (nitrato-*O*) cadmium(II) [138], the $CdCl_2 \cdot$ 18-crown-6 complex [139], and the cadmium salt of texaphyrin, and its pyridine and benzimidazole adducts [140].

Also, since Summers' 1988 review [134], Koch and co-workers have reported studies [141] of structural and spectroscopic analogues of $[M(S\text{-}Cys)_2(His)_2]$ centers. A series of compounds of formula $[Cd(SR)_2(N\text{-donor})_2]$ was synthesized and investigated by solution and solid state ^{113}Cd NMR methods and by X-ray crystallography. A single crystal NMR study of $[Cd(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_2H_2)_2(bpy)]$ provided values of the ^{113}Cd shielding tensor components σ_{11} = 814 ppm, σ_{22} = 630 ppm, σ_{33} = 32 ppm, and similar large chemical shift anisotropies were observed for the other compounds investigated. Most of the examples studied gave similar values for the isotropic shifts in solution and in the solid state except for $[Cd(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_2H_2)_2(phen)]$ where the solid state value (371.5 ppm) was found to be quite different from the solution value (450 ppm). X-ray crystallography revealed that the compound was dimeric in the solid state, thus explaining the shift difference. A number of compounds of the type $[Cd(SR)_3]^-$ have also been investigated [142] by ^{113}Cd NMR methods and, along with data from solid state ^{199}Hg NMR measurements on $[Hg(SR)_m]^{x-}$ complexes, the results used to aid in understanding the structure of the metal centers in bacterial mercury resistance proteins.

In a different area, ^{113}Cd NMR spectroscopy has been employed to study host–guest systems [143] where the host consists of a layered framework of metal atoms bridged by cyanide groups and held apart by ligands, such as ammonia, coordinated to the metal centers and perpendicular to the layers. The resulting cavities within this type of structure may be occupied by organic guests such as benzene. In these Hofmann-type clathrates, the metal centers most typically consist of square planar nickel and octahedral cadmium but a number of variations is

possible. Although X-ray crystallography has proved to be very valuable in characterizing these types of compounds, a problem may be encountered in determining the orientation of the cyanide bridges between metal centers and, accordingly, ^{113}Cd NMR methods were applied to see if different coordination environments could be distinguished. By examination of model compounds where the cyanide orientation is known, it was possible to establish the sensitivity of the cadmium chemical shift to small changes in coordination environment and to apply the method to a class of samples where X-ray methods failed to distinguish the carbon and nitrogen of the bridging cyanides, i.e. $[Cd(CN)_2 \cdot guest]$. It was shown that static disorder of the cyanides was responsible for the problems with the X-ray structure since separate resonances for each type of coordination environment could be observed (i.e. CdC_4, CdC_3N, CdC_2N_2, $CdCN_3$, CdN_4).

Mercury. In 1987, Harris and Sebald [102] reported some preliminary results on the study of mercury-containing compounds by ^{199}Hg CP/MAS NMR spectroscopy: ^{199}Hg CP/MAS NMR studies performed on mercury(II) acetate, $Hg(OAc)_2$, revealed that one of the major limitations of this technique would be the huge chemical shift anisotropies due to the linear molecular geometry of most organomercury(II) compounds. Furthermore, it was observed that the ^{199}Hg CP/MAS NMR results obtained for $Hg(OAc)_2$ did not agree with the results from its X-ray crystal structure determination but that the ^{13}C CP/MAS NMR results were in full agreement with the X-ray data. Mercury(II) acetate was reported to crystallize in the monoclinic space group $P2_1/a$ with $Z = 4$ [144], and so the asymmetric unit contains one entire molecule*. As a result, one would anticipate the ^{13}C CP/MAS NMR spectrum of $Hg(OAc)_2$ to consist of four signals and the ^{199}Hg CP/MAS NMR spectrum to contain no more than one single absorption. The ^{13}C CP/MAS NMR spectrum of the compound indeed displays four signals, two for the methyl carbons and two for the carboxyl carbons, whereas the ^{199}Hg CP/MAS NMR spectrum consists of two very close absorptions with approximately the same intensities (Fig. 11(a)). To explain their findings, Harris and Sebald suggested the possibility of having two rather than one molecule per asymmetric unit with intramolecularly equivalent acetate groups. This condition would be fulfilled in the case where the size of the actual unit cell would be twice the size of that reported, i.e. if the length of the c-axis were doubled. The situation described here would be a classical example of a crystallographic "superstructure"**. Another possibility that has not been considered by Harris and

* Note that in ref. 102, the authors incorrectly used the words "unit cell" while they actually mean "asymmetric unit". Additionally, in the same reference, it is incorrectly stated that the environment of Hg in $Hg(OAc)_2$ is almost tetrahedral: the interaction of Hg with a fifth oxygen situated at 2.75 Å away from it actually yields a coordination polyhedron for Hg that has been described as a "tetragonal pyramid" [144].

** ^{77}Se solid state NMR spectroscopy has recently been employed to confirm the existence of a superstructure in the case of the ferroelectric phase of $NH_4(H)SeO_4$ (see ref. 145(a)).

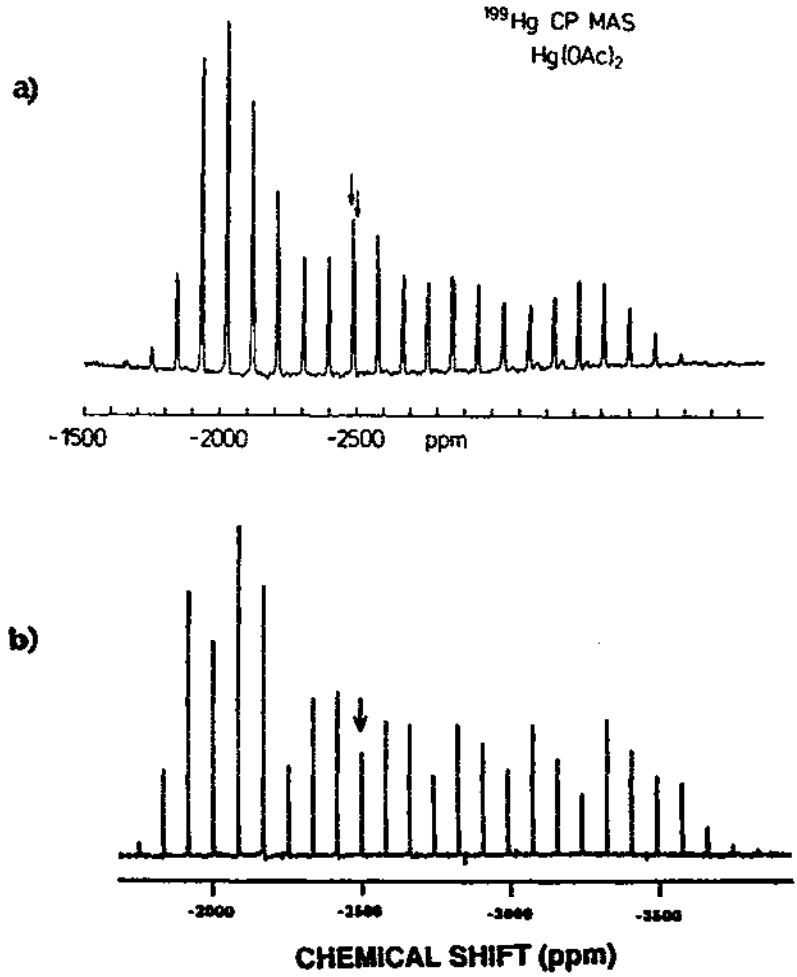

Fig. 11. (a) ^{199}Hg NMR spectrum of $Hg(OAc)_2$ obtained with cross-polarization and magic angle spinning at a speed of 3.3 kHz. The arrows indicate that two centerbands are present in the spectrum. Reproduced from ref. 102 with permission. (b) ^{199}Hg NMR spectrum of $Hg(OAc)_2$ obtained with cross-polarization and magic angle spinning at a speed of 4.4 kHz. The arrow indicates that one centerband is present in the spectrum. Reproduced from ref. 142 with permission.

Sebald, however, is the case where the structure would be disordered. Indeed, one could envision a situation where the $Hg(OAc)_2$ molecule in the asymmetric unit would be disordered between two sites; the two Hg sites would be responsible for the two signals observed in the ^{199}Hg CP/MAS NMR spectrum of the compound whereas the four disordered acetate ligands would give rise to only four signals in the ^{13}C CP/MAS NMR spectrum as a result of high thermal motion of the light atoms. Such a situation is actually not unreasonable since the X-ray data of the compound [144] show the isotropic equivalent displacement parameter of the Hg

atom, B, to be as high as those of some of the lighter atoms ($B(\mathrm{Hg}) = 3.62$ Å^2) and, additionally, one of the anisotropic thermal parameters of the Hg atom, namely B_{22}, to be significantly larger than the others ($B_{11} = 2.14$; $B_{22} = 5.71$; $B_{33} = 3.01$). Careful reinvestigation of the X-ray crystal structure of $Hg(OAc)_2$ would certainly prove most valuable in resolving this discrepancy. Additionally, measurement of the ^{13}C CP/MAS NMR spectrum of $Hg(OAc)_2$ at low temperature may also prove most helpful. Interestingly, a 1991 paper by Koch et al. [142] shows a solid state ^{199}Hg NMR spectrum of mercury acetate (Fig. 11(b)), where only a single isotropic signal is seen. The linewidth of this signal (35 Hz, 0.7 ppm) is much less than the separation of the two signals reported by Harris (6 ppm). The authors attribute the splitting observed by Harris to an error in setting the magic angle.

In 1990, a further report describing results obtained by ^{199}Hg solid state NMR spectroscopy was published: Natan et al. [145(b)] used ^{199}Hg CP/MAS NMR spectroscopy to probe the structure and bonding in two-, three-, and four-coordinate organomercury(II) complexes. These workers found that, in the case of tetrahedral organomercury(II) compounds such as $[Me_4N]_2[Hg(4\text{-chlorothiophenolate})_4]$, the chemical shift anisotropy was small ($\Delta\sigma = -176$ ppm) and the shielding anisotropy factor, η, was close to zero, thus indicating the presence of an axially symmetric chemical shift tensor for the compound (i.e. $\sigma_{11} = \sigma_{22}$). Analysis by ^{199}Hg CP/MAS NMR spectroscopy of a less symmetrical tetracoordinate organomercury(II) compound such as the polymer of empirical formula $Hg(S^tBu)_2$* gave a larger shift anisotropy of -478 ppm and a higher shielding anisotropy factor of 0.32, thus demonstrating the sensitivity of the technique to changes in geometry within a given coordination number. During the same studies, these workers further observed that the isotropic solid state ^{199}Hg NMR shifts for both $[Me_4N]_2[Hg(4\text{-chlorothiophenolate})_4]$ and $Hg(S^tBu)_2$ were significantly different (by approximately 100 ppm) from the values obtained in solution. Studies of the dependence of the solution ^{199}Hg chemical shifts of these two complexes upon the concentration of RS^- led them to the conclusion that the apparent discrepancy between the solid state and solution NMR results was actually due to the presence in solution of rapidly exchanging Hg-thiolate species. The ^{199}Hg solid state NMR spectra of two planar three-coordinate Hg(II) thiolates, namely $[Et_4N][Hg(S^tBu)_3]$ and $[^nBu_4N][Hg(SPh)_3]$, revealed substantially higher shift anisotropies (-821 and -978 ppm, respectively) and shielding anisotropy factors (0.6–0.7) than the tetrahedral thiolates, thus showing that the technique could be successfully employed to distinguish between three- and four-coordinate organomercury(II) complexes. Furthermore, as already observed in the case of four-coordinate compounds, the chemical shift anisotropy in three-coordinate organomercury(II) complexes was found to be sensitive to slight changes in geometry: the greater distortion of $[^nBu_4N][Hg(SPh)_3]$ toward a T-shape geometry relative

* In the solid state structure of $Hg(S^tBu)_2$, the Hg(II) center is surrounded by a very distorted tetrahedron of bridging thiolates [146].

to the more trigonal complex $[Et_4N][Hg(S^tBu)_3]$ was proposed to account for the 159 ppm increase in $\Delta\sigma$. On the other hand, from the close agreement between the solid state and solution isotropic shifts for both three-coordinate compounds, it was concluded that the predominant species in solution was indeed three-coordinate. As a further test, Natan and his colleagues re-examined the ^{199}Hg solid state NMR spectrum of $Hg(OAc)_2$ published by Harris and Sebald [102]: from the large chemical shift anisotropy, namely -1656 ppm, exceeding by far the values previously reported for trigonal compounds, it was concluded that the coordination of mercury in this complex is best described as being two-coordinate linear with three additional secondary bonding interactions with neighboring acetate oxygen atoms instead of four-coordinate as described by Harris and Sebald. Clearly, this interpretation must be viewed with caution as the original data published by Harris have been questioned (vide supra).

In addition to the work of Natan et al. [145(b)], Koch and co-workers [142] have described ^{199}Hg NMR studies of mercury thiolates as a function of coordination number and geometry. These two variables were found to affect the shielding tensor components, the isotropic shift, the chemical shift anisotropy, and the asymmetry parameter in a systematic way. The results of this study were applied to the problem of characterization of the mercury centers in bacterial resistance proteins.

(ii) The p-block metals

(a) Group 13 (Al, Ga, In, Tl)

Aluminum. ^{27}Al is the quadrupolar nucleus to which most attention has been given by solid state NMR spectroscopists. The vast bulk of the reported work is concerned with the structural identification of zeolites and related materials or with studies of reactivity of these substances. The technique is often applied in conjunction with solid state ^{29}Si NMR techniques to provide detailed structural information. A complete account of work in this area can be found in the book by Engelhardt and Michel [22(a)] and so no details of this topic will be repeated here. Applications of solid state ^{27}Al NMR methods outside the general area of zeolite chemistry have been quite scarce*. Certainly, valuable structural information could be obtained for organoaluminum compounds and the field appears to be ready for exploration [3].

Gallium. ^{69}Ga and ^{71}Ga MAS NMR spectra have been reported for a series of gallosilicates, some model compounds, and some extended array semiconductor materials [148]. Despite the fact that ^{69}Ga, ^{71}Ga, and ^{27}Al have reasonably similar magnetogyric ratios and quadrupole moments, measurement of gallium NMR spectra is more difficult than the measurement of aluminum NMR spectra because of the

* Areas that have begun to receive attention include 5-coordination of aluminum [147(a), (b)] as well as the complexation of aluminum halides by Lewis bases such as THF [147(c)].

difference in spin quantum numbers (^{69}Ga, $I = 3/2$; ^{71}Ga, $I = 3/2$; and ^{27}Al, $I = 5/2$). Because of this difference, under the same conditions, second-order quadrupolar effects will result in much broader signals for gallium than for aluminum. Interestingly, Timken and Oldfield have shown [148(a)] that measurement of both ^{69}Ga and ^{71}Ga NMR spectra of a given sample provides a useful approach to obtaining quadrupole coupling constants. Thus, for a sample of gallium sodalite, the observed chemical shifts were 178 and 183 ppm for ^{69}Ga and ^{71}Ga, respectively, with the difference being due to different second-order quadrupole-induced shifts caused by the differences in Larmor frequencies and in quadrupole moments. From the observed values, both quadrupole coupling constants for the two isotopes and the isotropic chemical shift can be calculated. The method is fully described in ref. 148(a) and may be useful for other pairs of quadrupolar isotopes (e.g. Mo, Re, Ir).

No reports of the utilization of solid state gallium NMR methods in organometallic or coordination chemistry have appeared of which we are aware [3].

Indium. No solid state indium NMR studies of compounds of interest in this review article have been reported of which we are aware [3]. Some studies of extended array materials (e.g. semiconductors [148(b)]) by ^{113}In and ^{115}In MAS NMR methods have been described.

Thallium. Thallium solid state NMR spectroscopy has received some attention: Hinton et al. used this technique to obtain the components of the chemical shift tensor of several complexes of Tl^+ with antibiotic ionophores such as valinomycin [149(a)], lasalocid [149(b)], and gramicidin-A [149(b)]. These workers also used ^{203}Tl and ^{205}Tl solid state NMR spectroscopies to study the influence of the ionic environment on the thallium shielding anisotropy in compounds such as $TlClO_4$ [150(a)] and $TlNO_3$ [150(b)]. A comprehensive review of thallium NMR spectroscopy, which includes details of studies of solids and melts, was published in 1982 and the reader is referred to this excellent article for details of earlier studies [151(a)]. More recently, Lippmaa and co-workers have described the utilization of ^{205}Tl MAS NMR spectroscopy in the study of thallium-exchanged zeolites A, X and Y [151(b)] and a report on thallous formate and thallous acetate by Hinton and Metz has appeared [151(c)]. No recent applications of solid state thallium NMR methods to organometallic and coordination chemistry have appeared of which we are aware [3].

(b) Group 14 (Ge, Sn, Pb)

Germanium. No solid state ^{73}Ge NMR studies of organometallic or coordination compounds appear to have been reported [3]. Indeed, only a very limited number of applications of solution ^{73}Ge NMR methods to these areas have yet been described [1,81].

Tin. Among the several spin-1/2 heavy-metal nuclei that have been studied, ^{119}Sn is certainly the one to which the most effort has been devoted. The first report describing the analysis of organotin compounds, namely tetracyclohexyltin and di-*n*-butyltin dichloride, by ^{119}Sn CP/MAS NMR spectroscopy was published in 1978 by Lippmaa et al. [152]. A few years later, Harris et al. published the ^{119}Sn CP/MAS NMR data of tri-*n*-butyltin fluoride [153]: they found that the ^{119}Sn CP/MAS NMR spectrum of this compound consists of one triplet at $\delta = -9.3$ ppm with respect to Me_4Sn with $^1J(^{119}Sn,^{19}F) = 1291$ Hz. These workers explained their findings by pointing out that tin is known to be pentacoordinated in the solid state and that chains of –F–Sn–F–Sn–F– atoms have been reported to exist in similar compounds such as Me_3SnF. The observed coupling between tin and two magnetically equivalent fluorines in tri-*n*-butyltin fluoride therefore suggests that, in the solid state, the fluorine atoms must lie midway between tin atoms or that, on the NMR timescale, the fluorines are rapidly exchanging between equivalent unsymmetrical positions; the exact origin of the splitting of the tin resonance, however, remains unidentified. The important conclusions that could be drawn about the solid state structure of tri-*n*-butyltin fluoride from its ^{119}Sn CP/MAS NMR spectrum and the lack of other available ^{119}Sn solid state NMR data prompted Harris and others to undertake a systematic study of organotin compounds using this technique. Harris et al. first studied organotin hydroxides such as Me_3SnOH and Ph_3SnOH [101, 154(a)–(c)]. They found that these compounds displayed considerable shift anisotropy (−264 and +383 ppm for Me_3SnOH and −272 ppm for Ph_3SnOH) and that their solid state ^{119}Sn chemical shifts were significantly different from the values observed in solution, thus suggesting a change in the coordination of tin on passing from the solution to the solid state. This work led to a study of the structure of polymeric dialkyltin oxides, $[R_2SnO]_n$, by solid state ^{119}Sn NMR spectroscopy [154(d)]. From the values of the isotropic chemical shifts of −152 ppm for $[Me_2SnO]_n$ and −177 ppm for $[^nBu_2SnO]_n$, it was concluded that tin in these compounds is pentacoordinated. The large shielding anisotropies and asymmetry parameters of these two polymers could also be satisfactorily rationalized assuming a trigonal bipyramidal *cis*-R_2SnX_3 (X = oxygen) geometry. Lastly, the very efficient cross-polarization observed for both compounds and the single relatively sharp resonances observed in the spectra of both materials were interpreted in terms of long-range order resulting from a fairly rigid lattice. These observations led Harris and Sebald to suggest that the polymeric lattice made of R_2SnO units might be a cross-linked network rather than a linear ladder-type structure. Many other tin(IV) compounds containing tin–oxygen bonds have been analyzed by $^{117}Sn/^{119}Sn$ solid state NMR spectroscopy. Among these are found $K_2Sn(OH)_6$ [102], $^nBu_3SnOAc$ [155], and two diorganotin compounds of potential biochemical significance [156(a)]. Harris and Sebald [157] and Lockhart et al. [156(b)] have determined $^2J(^{119}Sn,^{119}Sn)$ coupling constants for several linear and cyclic organotin oxides and, in the latter study, a linear relationship between the Sn–O–Sn bond angle and the $^2J(^{119}Sn,^{119}Sn)$ coupling constant was established. Molloy

[156(c)] has compared the solution and solid state ^{119}Sn isotropic shifts of several triorganotin carboxylates and determined whether the compounds were monomeric or polymeric in the solid state. Komoroski et al. [155] have obtained the ^{119}Sn CP/MAS NMR spectrum of polymeric di(*n*-octyl)tin maleate and found that the chemical shift anisotropy of this compound was approximately 1100 ppm. Dialkyldioxastannolanes and dialkyloxathiastannolanes have also received some attention: Harris et al. [101] have reported the ^{119}Sn chemical shift data of a tin-containing glucose derivative, a compound that has also been studied in some detail by Grindley et al. [158], and Davies and co-workers [159] have used the combination of solution ^{119}Sn and solid state ^{117}Sn/^{119}Sn NMR spectroscopies and X-ray crystallography to determine the degree of association of dialkyldioxastannolanes and dialkyloxathiastannolanes in solution and in the solid state. In the case of 2,2-di-*t*-butyl-1,3,2-dioxastannolane, it was determined that the structure in solution was the same as that in the crystal, i.e. the compound is a dimer containing five-coordinate tin atoms in severely distorted trigonal bipyramidal environments [159(a)]. In the case of 2,2-di-*n*-butyl-1,3,2-dioxastannolane, however, the observed upfield shift of 41 ppm between the solution and solid state ^{119}Sn NMR data was ascribed to structural reorganization of the compound from five-coordinate dimer to six-coordinate polymer [159(b)]. Four dialkyloxathiastannolanes, namely 2,2-di-*t*-butyl- [159(a)], 2,2-dimethyl- [159(c)], 2,2-diethyl- [159(c)], and 2,2-di-*n*-butyl-1,3,2-oxathiastannolane [159(c)] have been analyzed by solution ^{119}Sn and solid state ^{117}Sn/^{119}Sn NMR spectroscopies. The isotropic shifts measured for 2,2-diethyl- and 2,2-di-*n*-butyl-1,3,2-oxathiastannolane in solution were close to those measured in the solid state, indicating that these compounds had similar structures in both states. Furthermore, in the case of 2,2-di-*n*-butyl-1,3,2-oxathiastannolane, single crystal X-ray diffraction studies indicated that the individual oxathiastannolane units were intermolecularly coordinated through oxygen, giving rise to a linear polymeric chain containing five-coordinate tin atoms in distorted trigonal bipyramidal environments [159(c)]. Regarding 2,2-di-*t*-butyl- and 2,2-dimethyl-1,3,2-oxathiastannolane, it was determined that their structures in solution were different from those in the solid state as indicated by the large differences between the ^{119}Sn isotropic shifts measured in solution and the ^{117}Sn/^{119}Sn isotropic shifts measured in the solid state. Single crystal X-ray diffraction studies of 2,2-di-*t*-butyl-1,3,2-oxathiastannolane indicated that the compound had a similar structure to that of the corresponding dioxastannolane, i.e. it is a dimer in which the oxathiastannolane units are intermolecularly coordinated through oxygen [159(a)]. Some of these results have, moreover, been discussed in a review by Davies and Slater [160]. A final interesting note concerning the work on stannolanes comes from the experimental section of one of the papers [159(a)]. It seems that the decision to observe ^{117}Sn rather than ^{119}Sn was made because the ^{119}Sn resonant frequency on the spectrometer (111.914 MHz) allowed for interference by the frequencies used by the communications system at the nearby London (Heathrow) Airport. The ^{117}Sn frequency (109.904 MHz) avoided interference from this source.

$^{117}Sn/^{119}Sn$ solid state NMR investigations of second-, third-, and fourth-row tin chalcogenides have also been reported. Harris and co-workers have measured the ^{119}Sn isotropic shifts of several linear and cyclic organotin(IV) compounds containing sulfur or selenium and, in each case, determined the $^2J(^{119}Sn,^{119}Sn)$ coupling constant. The compounds that were analyzed include $[(c\text{-}C_6H_{11})_3Sn]_2S$ [102,157], $(^tBu_2SnS)_2$ [157], $(Me_2SnS)_3$ [102,157], $(Me_2SnSe)_3$ [157], and $(Ph_2SnS)_3$ [157]. Davies and co-workers [159(a)] have combined the results from solution ^{119}Sn and solid state ^{117}Sn NMR investigations with those from single crystal X-ray diffraction studies and determined the structure of 2,2-di-*t*-butyl-1,3,2-dithiastannolane in both states. The results from the single crystal X-ray diffraction study indicated that the compound was a four-coordinate monomer with distorted tetrahedral geometry of the four ligands about the tin atom. These findings were confirmed by the small chemical shift anisotropy of the compound in the solid state, i.e. $\Delta\sigma = 39$ ppm. Solution ^{119}Sn NMR analysis of 2,2-di-*t*-butyl-1,3,2-dithiastannolane gave the same chemical shift value as that observed in the solid state, indicating that the structure of the compound was the same in both states. However, a few dialkyldithiastannolanes have also been encountered for which the solution ^{119}Sn and solid state ^{117}Sn NMR data were different, indicating the presence, in the solid state, of interactions between the tin centers and sulfur atoms from neighboring dithiastannolane molecules [161]. Gay et al. [162] have reported the results of their multinuclear solid state NMR investigations of dimethyltin chalcogenides $((CH_3)_2SnE)_3$ (E = S, Se, Te) and the same group has described the use of the INADEQUATE pulse sequence to obtain homonuclear couplings in solid samples of these compounds [163]. The X-ray crystal structure of the tetragonal polymorph of $((CH_3)_2SnS)_3$ was originally reported in the space group $P4_1$ [164(a)] but this result was found to be in error by Krebs and co-workers who, based on results obtained from rotation photographs, concluded that the correct space group was, in fact, $P4_12_12$ (Laue symmetry 4/mmm) [164(b)]. In space group $P4_12_12$, a two-fold axis of symmetry passing through one tin atom and the opposing sulfur is present, thus making only half of the molecule crystallographically unique. As a result, no more than two tin resonances are expected to be observed in the ^{119}Sn CP/MAS NMR spectrum of the compound if the correct space group is $P4_12_12$, whereas no more than three tin resonances are expected to be seen in the case where the correct space group is $P4_1$. The ^{119}Sn CP/MAS NMR data reported by Gay et al. show two sets of signals in a 1 : 2 intensity ratio. These data are thus in accord with the correct space group for the tetragonal form of $((CH_3)_2SnS)_3$ being $P4_12_12$ but, on the other hand, they do not rule out $P4_1$ as being the correct space group since the possibility exists of having isochronous signals. Similar comments may be made about the ^{13}C CP/MAS NMR spectrum of the compound. Indeed, the presence of three methyl resonances may be accounted for in either of the space groups $P4_12_12$ or $P4_1$. Confirmation that $P4_12_12$ is, in fact, the correct space group was obtained from the Sn–Sn coupling pattern observed in the ^{119}Sn CP/MAS NMR spectrum. Indeed, the four Sn–Sn couplings expected in

the ^{119}Sn NMR spectrum of a compound with a single Sn(1) and two Sn(2) atoms, namely ^{119}Sn(1)–^{117}Sn(2), ^{119}Sn(2)–^{117}Sn(1), ^{119}Sn(2)–^{117}Sn(2), and ^{119}Sn(1) ^{119}Sn(2), were all observed and easily assigned*. A second polymorph of $((CH_3)_2SnS)_3$ has been reported to crystallize in the monoclinic space group $P2_1/c$ with $Z = 4$ [165]. Gay et al. also analyzed this monoclinic form of $((CH_3)_2SnS)_3$ by ^{119}Sn CP/MAS NMR spectroscopy and found that the ^{119}Sn solid state NMR spectrum of this polymorph displayed three sets of signals in accord with the results from the X-ray crystal structure determination. These results were further confirmed by recording the ^{13}C CP/MAS NMR spectrum of the compound, which showed five main signals in a 1 : 1 : 2 : 1 : 1 intensity ratio. Furthermore, Gay et al. noticed a most interesting feature about the ^{119}Sn CP/MAS NMR spectrum of the monoclinic form of $((CH_3)_2SnS)_3$: the most downfield resonance was found to be narrower by a factor of two than the other two main resonances present in the spectrum. The selective broadening of the two most upfield tin resonances was proposed to arise from motion of the atoms corresponding to these signals, thus leading to reduced effectiveness of MAS or of decoupling, or to the sampling of more diverse chemical-shift environments. Examination of the reported X-ray crystal structure indeed shows that one of the tin atoms, namely Sn(3), has much smaller thermal parameters than the other two. Consequently, these workers tentatively assigned the narrower resonance in the ^{119}Sn CP/MAS NMR spectrum to Sn(3). $((CH_3)_2SnSe)_3$ was also reported to crystallize in the tetragonal space group $P4_12_12$ with $Z = 4$ [164(b)]. The ^{119}Sn CP/MAS NMR data of this compound were in agreement with the X-ray data, i.e two sets of signals in a 1 : 2 intensity ratio were observed [162]. The presence of a two-fold axis of symmetry passing through one tin atom and the opposing selenium was also confirmed by the fact that the tin resonance with the relative intensity of 1 shows a single coupling to ^{77}Se whereas the tin resonance with the relative intensity of 2 shows two different couplings to ^{77}Se. Furthermore, the ^{13}C CP/MAS NMR spectrum shows only three methyl resonances and the ^{77}Se solid state NMR spectrum consists of two main signals in a 1 : 2 intensity ratio with appropriate couplings to ^{119}Sn and ^{117}Sn isotopes. Lastly, $((CH_3)_2SnTe)_3$ was reported to crystallize in the orthorhombic space group $Pnam$ or $Pna2_1$ with $Z = 12$ [166] and in the tetragonal space group $I4_1/a$ with $Z = 8$ [162]. The tetragonal form was analyzed by solid state NMR spectroscopy and the resulting ^{119}Sn, ^{13}C, and ^{125}Te CP/MAS NMR data were all found to be in accord with the results from the X-ray crystal structure determination [162].

Several tetraorganotin(IV) compounds have been analyzed by ^{119}Sn CP/MAS NMR spectroscopy, and the spectra and NMR characteristics of these, e.g. contact times, proton T_1 values, signal linewidths, signal multiplicities, and shielding anisotropies, have been compared and contrasted in order to find suitable standard com-

* The ^{119}Sn NMR data reported here clearly demonstrate that coupling between crystallographically equivalent but magnetically different nuclei does occur in the solid state.

pounds to optimize spectrometer performance [101,102,155,167(a)]. The compounds that were analyzed include Ph_3SnR (R = phenyl, allyl, alkyl), $(c\text{-}C_6H_{11})_4Sn$, $(Me_3Sn)_4C$, and the 1,4-isomer of $Me_3SnC_6H_4SnMe_3$. In the case of $(Me_3Sn)_4C$, moreover, the calculated $^2J(^{119}Sn,^{119}Sn)$ was found to be very similar to the value obtained from solution measurements [167(a)]. Harris et al. also reported the ^{119}Sn CP/MAS NMR spectrum of 1,1,2,2,4,4,5,5-octamethyl-1,2,4,5-tetrastannacyclohexane [101,167(a)]: based on the reported X-ray crystal structure of *cis*-1,1,2,2,3,4,4,5,5,6-decamethyl-1,2,4,5-tetrastannacyclohexane, i.e space group $P2_1/n$ with $Z = 4$ [167(b)], the four signals observed in the solid state ^{119}Sn NMR spectrum of the former compound were assigned to the four crystallographically unique tin atoms present in the asymmetric unit. Furthermore, the tin–tin coupling constants obtained from the solid state NMR spectrum were said to be, within experimental error, identical to the values obtained from solution measurements [167(a)]. Organotin halides of the types R_3SnX and R_2SnX_2 (R = alkyl, aryl; X = Cl, Br) have also been studied by ^{119}Sn solid state NMR spectroscopy [155,168]. In the latter study, it was concluded from the rather small differences observed between the ^{119}Sn chemical shift values obtained in solution and those obtained in the solid state that the organotin halides under consideration did not display gross changes in coordination on passing from the solution to the solid state. Furthermore, the extensive spinning sideband pattern observed in the case of diorganotin halides R_2SnX_2 was attributed to more severely distorted tetrahedral geometry at tin as compared with triorganotin compounds. In the case of benzyl derivatives, however, the differences between the ^{119}Sn chemical shift values obtained in solution and those obtained in the solid state were more pronounced than in the other cases. This phenomenon was attributed to the fact that, in solution, a hyperconjugative interaction between the π orbitals of the phenyl moiety and the Sn–C σ-bond is present, thus resulting in an abnormal shielding of the tin nucleus. In the solid state, on the other hand, the shielding of the tin nucleus owing to hyperconjugative interaction is lost because of crystal packing forces. The study of organotin halides also led Harris et al. to explain the origin of the unsymmetrical splitting pattern observed in the ^{119}Sn CP/MAS NMR spectrum of some of these compounds. They concluded that the unsymmetrical 1 : 1 : 2 splitting patterns observed in the case of Ph_3SnCl, $(PhCH_2)_3SnCl$, and $(cyclohexyl)_3SnCl$ were the result of residual dipolar/indirect coupling interactions between ^{119}Sn and the quadrupolar nuclei ^{35}Cl and ^{37}Cl. Also, it was shown that, for some of the organotin dichlorides under consideration, such residual interactions resulted in 1 : 2 : 4 : 1 : 4 : 4 multiplets (with the first spacing being twice the size of the others and the chemical shift being at the central weak peak) when the two chlorines were considered to be equivalent. The correctness of this analysis was confirmed later by Harris [169(a)] who demonstrated that the unsymmetrical 1 : 1 : 2 splitting pattern could be easily generated via modification of the splitting of the energy levels of a spin-3/2 nucleus using a perturbation approach. Interestingly, no such tin–chlorine coupling was observed in the ^{119}Sn solid state MAS NMR spectrum of the host–

guest complex resulting from coordination of the chloride anion of benzyltriphenylphosphonium chloride to the Lewis acidic host 1,10-dichloro-1,10-distannabicyclo-[8.8.8]hexacosane [169(b)]. However, coupling between ^{119}Sn and ^{14}N has recently been observed in the ^{119}Sn CP/MAS NMR spectra of organotin(IV) coordination polymers containing trigonal bipyramidal –C≡N Sn– N≡C– bridges [169(c)] and in the ^{119}Sn solid state NMR spectra of organotin(IV) oxinates and thiooxinates [169(d)]. Dobson and co-workers have employed ^{119}Sn solid state NMR spectroscopy to study ternary tin oxides such as M_2SnO_3 (M = Li, Na, K), $MSnO_3$ (M = Mg, Ca, Sr, Ba, Cd), and M_2SnO_4 (M = Mg, Ca, Ba, Sr, Cd, Zn) [170]. They have found that a linear relationship exists between the ^{119}Sn chemical shift and the ionic radius of the cation for ternary tin oxides of the same stoichiometry regardless of the structure adopted. These workers have also applied ^{119}Sn MAS NMR spectroscopy to the analysis of rare-earth stannates $Ln_2Sn_2O_7$ (Ln = La, Pr, Nd, Sm, Eu, Tm, Yb, Lu, and Y), all of which adopt the pyrochlore structure, and to the analysis of several tin pyrochlore solid solutions, namely $Y_{2-y}Ln_ySn_2O_7$ where Ln = Sm, Nd, Pr, and Eu and $La_{2-y}Nd_ySn_2O_7$ [60]. Apart from $La_2Sn_2O_7$, $Lu_2Sn_2O_7$, and $Y_2Sn_2O_7$, these compounds are paramagnetic and exhibit a very large variation in ^{119}Sn chemical shifts (from approximately +5400 to −4200 ppm), which can be attributed principally to a Fermi contact shift mechanism. The spectra from the paramagnetic samples have large overall linewidths associated with the substantial anisotropy of the shift, but the individual peaks within the spinning sideband manifolds remain sharp. Regarding the tin pyrochlore solid solutions, when the short relaxation times of nuclei close to paramagnetic centers were exploited, a series of peaks was observed which was associated with the substitution of paramagnetic for diamagnetic lanthanide ions in the local coordination around a tin atom. For $Y_{2-y}Sm_ySn_2O_7$, the composition of the solid solution could be determined from the intensities of these peaks. Additionally, in the solid solutions, the ^{119}Sn nuclei were found to be sensitive not only to neighboring paramagnetic ions but also to paramagnetic centers in the second and third coordination spheres. The shifts induced in these cases arise primarily from a through-space dipolar "pseudocontact" mechanism and can be interpreted with a model for the site symmetry based on the crystal structure.

The ^{119}Sn solid state NMR data described so far were all obtained on Sn(IV) compounds, presumably because +IV is the most stable oxidation state for tin. ^{119}Sn solid state NMR data obtained on Sn(II) compounds are quite scarce and, in fact, only very few reports of such data could be found in the literature. Wrackmeyer and co-workers [171] have obtained the ^{119}Sn solid state NMR spectra of several stannocenes R_2Sn where $R = (PhCH_2)_5C_5$, Ph_5C_5, Ph_4HC_5, and $(^tBuPh)Ph_4C_5$. Harris and co-workers [172] have reported the ^{119}Sn CP/MAS NMR spectrum of a bicyclic tin(II) dimer. Zilm et al. [173] have used ^{119}Sn CP/MAS NMR methods to investigate the nature of the tin–tin double bond in $\{Sn[CH(SiMe_3)_2]_2\}_2$. The ^{119}Sn MAS NMR spectrum of bis(pentamethylcyclopentadienyl)tin(II) has been

reported [174] (Fig. 12). The spectrum reveals two isotropic signals, consistent with the presence of two different molecules in the asymmetric unit of the compound [175]. The ^{207}Pb NMR spectrum of the lead analog (vide infra) shows only a single signal, also consistent with the reported structure.

Lead. Early ^{207}Pb MAS NMR studies were performed on inorganic samples such as $Pb(NO_3)_2$ [176,177] and the first reported ^{207}Pb CP/MAS NMR data were obtained on simple organolead compounds such as $Pb(p\text{-tolyl})_4$, $Pb(o\text{-tolyl})_4$, $PbPh_4$, and $Pb_2(p\text{-tolyl})_6$ [101,102,178]. More recently, other organolead compounds have been investigated by ^{207}Pb CP/MAS NMR spectroscopy: these include the plumbocene $(Ph_5C_5)_2Pb$ [171], three triorganolead halides R_3PbX (R = cyclohexyl, mesityl; X = Cl, Br, I) [179], several hexaorganodiplumbanes Pb_2R_6 (R = phenyl, cyclohexyl, *o*-tolyl, *m*-xylyl, mesityl) [179], two triorganolead methoxides and one alkynyl-stabilized triorganolead cation [180], and the dinuclear lead chalcogenide $(Ph_3Pb)_2S$ [157]. The ^{207}Pb NMR spectrum of bis(pentamethylcyclopentadienyl)lead(II) has been reported [174] and compared with the ^{119}Sn NMR spectrum of the tin analog (vide supra). The spectrum (Fig. 13) shows a single isotropic signal among the extended array of spinning sidebands, consistent with the reported structure [181] which shows a single molecule per asymmetric unit. Additionally, ^{207}Pb solid state NMR spectra have been obtained for two long alkyl chain lead(II) carboxylates (soaps), namely lead(II) decanoate and lead(II) tetradecanoate [182(a)], and several inorganic lead compounds [182(b),(c)].

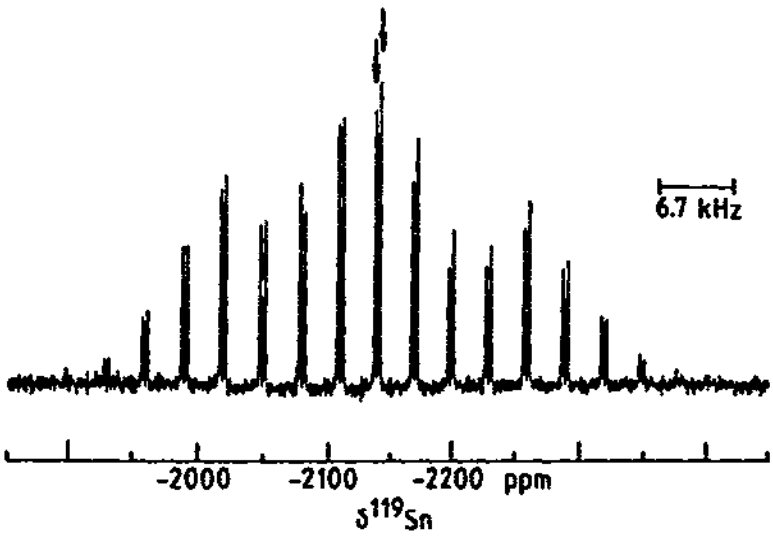

Fig. 12. ^{119}Sn NMR spectrum of $(Me_5C_5)_2Sn$ obtained with cross-polarization and magic angle spinning at a speed of 3.3 kHz. The arrows indicate that two centerbands are present in the spectrum. Reproduced from ref. 174 with permission.

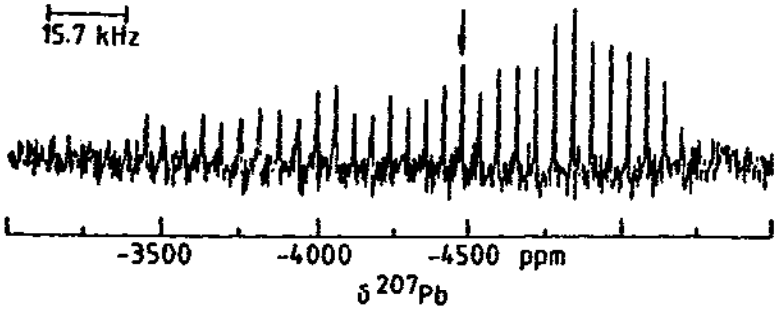

Fig. 13. ^{207}Pb NMR spectrum of $(Me_5C_5)_2Pb$ obtained with cross-polarization and magic angle spinning at a speed of 3.8 kHz. The arrow indicates that one centerband is present in the spectrum. Reproduced from ref. 174 with permission.

(c) Group 15 (Sb, Bi)

No reports of solid state ^{121}Sb, ^{123}Sb, or ^{209}Bi NMR spectroscopy applied to organometallic or coordination chemistry have appeared of which we are aware [3]. Indeed, application of solution ^{121}Sb, ^{123}Sb, or ^{209}Bi NMR methods to inorganic systems in general is quite uncommon [1,81].

E. CONCLUDING REMARKS

From the preceding discussion, it is clear that solid state NMR studies of metal nuclei have begun to impact organometallic and coordination chemistry but that there remains much to be accomplished. In the study of spin one-half nuclei, the work of Harris and others on tin NMR shows how much can be achieved in the area of structural chemistry once the necessary benchmark data have been accumulated. Similar developments might be expected for other nuclei in this category. With quadrupolar nuclei, the sensitivity to site symmetry provides a valuable structural probe. The example of titanium NMR studies of the barium titanate phase transition shows this remarkable sensitivity to what is really quite a modest change in crystal structure. Future developments that exploit the sensitivity of quadrupolar nuclei to subtle changes in local symmetry might be anticipated. Once momentum begins to develop, it is clear that experiments involving variable temperature measurements, measurements at variable pressures [183], examination of paramagnetic compounds*, etc. will all begin to be applied to problems in organometallic and coordination chemistry. Certainly, solid state NMR methods, particularly the cross-polarization and magic angle spinning experiments, are beginning to be adopted as part of the chemists' arsenal of analytical methods.

* A number of reports of the ^{13}C solid state NMR spectra of paramagnetic organometallic and coordination compounds have appeared (see, for example, ref. 184).

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