High-resolution Solid-state Tin-119 Nuclear Magnetic Resonance Spectroscopy of Ternary Tin Oxides

Nigel J. Clayden,* Christopher M. Dobson, and Adrian Fern
Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR

A series of ternary tin oxides has been studied by high-resolution solid state ^{119}Sn magic angle spinning n.m.r. spectroscopy. Linear correlations were observed between the ^{119}Sn chemical shift and the cation radius in compounds of the type $MSnO_3$ and M_2SnO_4. Significant chemical shift anisotropies have been identified with bond-angle and bond-length distortions of the SnO_6 octahedra present in these phases, although no straightforward relationship was seen between the chemical shift tensor asymmetry and the crystallographic site symmetry. Spin–spin coupling was observed in several compounds between chemically equivalent but magnetically inequivalent ^{119}Sn and ^{117}Sn nuclei separated by Sn–O–Sn bonds.

Solid-state n.m.r. spectroscopy is a technique with considerable potential in inorganic chemistry particularly in combination with magic angle spinning, m.a.s.,[1–3] which frequently enables distinct resonances from chemically inequivalent nuclei to be resolved. To date most work has concentrated on the spin $\frac{1}{2}$ nuclei of the lighter elements especially ^{13}C, ^{29}Si, and ^{31}P. As n.m.r. spectroscopy is sensitive to short-range order, a detailed description of a solid requires the study of as many nuclei as possible in a sample. Progress towards making this possible in a wide range of materials has recently been made in a number of ways. One of the most important of these has been the observation of well resolved m.a.s. spectra from quadrupolar nuclei, which form the bulk of the n.m.r.-active nuclei.[4–6] In terms of solid-state inorganic chemistry, the ability to obtain high-resolution ^{17}O n.m.r. spectra in complex oxygen-containing compounds, albeit using ^{17}O-enriched samples in the main, is of particular significance.[7–9] Less attention has been paid to the heavier spin $\frac{1}{2}$ nuclei such as ^{195}Pt,[10,11] ^{207}Pb,[12] and ^{119}Sn.[13–15] For certain nuclei such as ^{195}Pt this is a consequence of large chemical shift anisotropies which lead to low sensitivity because the intensity of the n.m.r. signal is dispersed into a large number of spinning sidebands. Not all heavy nuclei need, however, show large anisotropies. The ^{207}Pb n.m.r. spectrum of $Pb(NO_3)_2$, for example has been reported to have no significant spinning sidebands at 42 MHz and a spinning speed of 4 kHz.[1] This result, and a simple consideration of solid-state chemistry, suggests that the approach necessary to explore applications of these spin $\frac{1}{2}$ nuclei is to study high-symmetry local environments where the n.m.r. signal may be readily detected, and then to examine the effect of lowering of the local symmetry. In this paper we explore this approach in the study of a range of ternary tin oxides $MSnO_3$ and M_2SnO_4 (M = bivalent ion) and M_2SnO_3 (M = Group 1A) by ^{119}Sn m.a.s. n.m.r. spectroscopy.

A number of ^{119}Sn solid-state n.m.r. spectra using m.a.s. have been reported although these have generally utilised cross-polarisation to enhance the sensitivity of the ^{119}Sn nucleus.[13,14] Bloch decay ^{119}Sn n.m.r. spectra of a tin compound can be obtained.[15] The structural chemistry of tin(IV) is well known and ternary tin oxides provide an excellent control of the distortion to the local tin environment.[16] The set of compounds studied in the present work was chosen primarily because the tin co-ordination site in the majority of the compounds is octahedral. Distortions were apparent from crystallographic data,[16] but it was hoped that these would not produce chemical shift anisotropies so large that it would be difficult to observe signals. Further, the ternary tin oxides studied, $MSnO_3$ and M_2SnO_4 where M is a Group 2 cation, provide an opportunity to observe any correlations between the ^{119}Sn chemical shift changes and cation size. The ternary oxides are relatively simple to synthesize, generally *via* standard high-temperature solid-state reaction techniques, making them well suited to a study of this type. In addition, they have received much attention in the materials science literature; they are used in the ceramics industry to produce opacity and as components of ceramic dielectric bodies.

Experimental

All samples were prepared by standard high-temperature solid-state reaction methods unless otherwise noted. The ratios required by stoicheiometry or reported in the literature, of metal carbonate or oxide and tin(IV) oxide (all BDH, AnalaR), were accurately weighed and ground together in an agate mortar. The mixtures were then fired in air using alumina crucibles. Details of the conditions used in the firings are to be found in the literature, see Table 1.

After an initial firing the products were examined by powder *X*-ray diffraction using a Phillips PW 1710 powder diffractometer. If the reaction was incomplete the firing was repeated. Unless close agreement was found between the observed powder pattern and the JCPDS[17] powder file data for that compound the sample was not studied by n.m.r. spectroscopy.

It is not possible to prepare $MgSnO_3$ or $CdSnO_3$ by a high-temperature route because of the volatility of the bivalent metal oxides MgO and CdO. They were thus prepared by the high-temperature dehydration of the corresponding hydroxostannates $MgSnO_3$ [$MgSn(OH)_6$; 800 °C, 2 weeks[18]] and $CdSnO_3$ [$CdSn(OH)_6$; 700 °C, 24 h[19]], which in turn were prepared by mixing equimolar solutions of recrystallised $Na_2Sn(OH)_6$ and MCl_2 (BDH, AnalaR). The white precipitates formed were filtered off, washed thoroughly with cold water, and dried in air at 90 °C.

The solid-state ^{119}Sn n.m.r. spectra were collected on a Bruker CXP200 spectrometer operating at 74.54 MHz. Magic angle spinning was carried out, using Andrew-type rotors constructed out of Delrin, at speeds of 1.5 to 4 kHz. In order to ensure the magic angle was accurately set the ^{79}Br resonance of added KBr was observed and the angle adjusted appropriately.[20] Long recycle delays (30 s) were used to

---

* *Present address:* Wilton Materials Research Centre, I.C.I. plc, P.O. Box No. 90, Wilton Centre, Middlesbrough, Cleveland TS6 8JE.

Table 1. Method of synthesis and structural data for the ternary tin oxides studied in this work

Compound	Synthesis	Ref.	Structure	Ref.
$MgSnO_3$	From $MgSn(OH)_6$ 800 °C/2 weeks	18	Ilmenite	28
$CaSnO_3$	(1:1) 1 150 °C, 40 h	*a*	Perovskite	31
$SrSnO_3$	(1:1) 1 300 °C, 20 h	*a*	Perovskite	31
$BaSnO_3$	(1:1) 1 150 °C, 40 h	*a*	Perovskite	*b*, *c*
$CdSnO_3$	From $CdSn(OH)_6$ 700 °C, 24 h	19	'Inverse spinel'	*d*
Mg_2SnO_4	(2:1) 1 450 °C, 40 h	*e*	Inverse spinel	*f*
Ca_2SnO_4	(5:2) 1 300 °C, 40 h	*e*	Sr_2PbO_4	*g*
Ba_2SnO_4	(2:1) 1 250 °C, 24 h	*h*	K_2NiF_4 type	*h*
Sr_2SnO_4	(5:1) 1 250 °C, 5 h	*h*	K_2NiF_4 type	*i*
Cd_2SnO_4	(2:1) 1 050 °C, 6 h	*j*	Sr_2PbO_4 type	*k*
Zn_2SnO_4	(2:1) 900 °C, 24 h	*l*	Inverse spinel	*l*
Li_2SnO_3	(1.05:1) 800 °C, 20 h	*m*	'NaCl' type	*m*
Na_2SnO_3	(1.1:1) 850 °C, 24 h	*n*	'NaCl' type	*n*
K_2SnO_3	(1.8:1) 1 050 °C, 16 h	*o*	Complex	*p*

[a] A. J. Smith and A. J. E. Welch, *Acta Crystallogr.*, 1960, **13**, 653. [b] G. Wagner and H. Binder, *Z. Anorg. Allg. Chem.*, 1959, **298**, 12. [c] H. D. Megaw, *Proc. Phys. Soc.*, 1946, **58**, 133. [d] C. Levy-Clement, I. Morganstern-Badarau, Y. Billet, and A. Michel, *C.R. Acad. Sci., Ser. C*, 1970, 270, 1860. [e] L. W. Coughanour, R. S. Roth, S. Marzullo, and F. E. Sennett, *J. Res. Nat. Bur. Stand.*, 1955, **54**, 149. [f] P. Poix, *Ann. Chim.* (*Paris*), 1965, **10**, 49. [g] M. Tromel, *Z. Anorg. Allg. Chem.*, 1969, **371**, 237. [h] P. Appendino and G. Ramonda, *Ann. Chim.* (*Rome*), 1970, **60**, 407. [i] R. Weiss and R. Faivre, *C.R. Acad. Sci.*, 1959, **248**, 106. [j] A. J. Smith, *Acta Crystallogr.*, 1960, **13**, 749. [k] M. Tromel, *Naturwissenschaften*, 1967, **54**, 17. [l] P. Poix and A. Michel, *Bull. Soc. Chim. Fr.*, 1959, 1653. [m] G. Kreuzeburg, F. Stewner, and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1970, **379**, 242. [n] G. Lang, *Z. Anorg. Allg. Chem.*, 1954, **276**, 77. [o] M. Tournoux and A. Hardy, *C.R. Acad. Sci.*, 1963, **257**, 907. [p] B. M. Gatehouse and D. J. Lloyd, *J. Solid State Chem.*, 1970, **2**, 410.

ensure a significant return of nuclear magnetisation towards a Boltzmann distribution and no problems were observed to arise from excessively long spin–lattice relaxation times. A good signal-to-noise ratio could be obtained in general after 500 transients, that is an accumulation time of 3 h. Further improvements can be expected by doping with paramagnetic ions to decrease the spin–lattice relaxation time, providing the structure is stable to doping.[15,21]

The chemical shift anisotropies were determined by graphical[22] and moment analysis[23] of the spinning sideband intensities. Confirmation of the uniqueness of the tensor components was obtained by simulating the m.a.s. spectrum which also allowed refinement of the tensor components.[24,25] Chemical shifts were referenced with respect to the primary standard tetramethyltin taking its chemical shift as 0.0 p.p.m.

Table 2. Chemical shift data and site symmetries for ternary tin oxides

Compound	σ_{11}	σ_{22}	σ_{33}	σ_{iso}	Site symmetry
	p.p.m.				
SnO_2	−560	−560	−685	−604.3	*mmm*
Mg_2SnO_4	−422	−467	−564	−483.5	3*m*
Ca_2SnO_4	−459	−512	−664	−546.3	2/*m*
Sr_2SnO_4	−510	−548	−681	−579.6	
Ba_2SnO_4	−510	−552	−720	−594.3	
Zn_2SnO_4	−398	−466	−549	−471.4	3*m*
Cd_2SnO_4	n	n	n	−606.7	2/*m*
Li_2SnO_3	−381	−453	−498	−444.3	
Na_2SnO_3	−419	−491	−531	−480.3	
K_2SnO_3	−159	−254	−526	−312.8	
$MgSnO_3$	n	n	n	−586.3	
$CaSnO_3$	n	n	n	−611.7	
$SrSnO_3$	n	n	n	−640.8	
$BaSnO_3$	n	n	n	−679.2	
$CdSnO_3$	−432	−537	−567	−512.6	3*m*
$K_2Sn_3O_7$	nm	nm	nm	−491.8 −520.5 −548.1	

n = Negligible; nm = not measured.

Results and Discussion

Chemical Shifts.—(*a*) SnO_2. Tin-119 m.a.s. spectra were initially obtained for SnO_2, the parent binary oxide. A typical spectrum is shown in Figure 1(*a*). Despite the intense spinning sidebands which reduce the intensity of the isotropic resonance, an acceptable signal-to-noise ratio could be obtained in only eight transients; this allowed the use of SnO_2 as a secondary shift standard. Analysis of the spinning sideband intensities gave the chemical shift components shown in Table 2; the reported values represent refined components from a simulation.

The oxide SnO_2, cassiterite, crystallises with the rutile structure,[26] a framework lattice derived from edge-linked octahedra forming chains which are vertex linked. Within this structure, the tin atom is found in an approximately octahedral site, with all six Sn–O distances equal within the limits of accuracy. Distortion in the crystal, however, is manifested in the O–Sn–O bond angles which are found to be 78, 102, and 90°. The large anisotropy, apparent in the intense spinning sidebands, can be attributed to this distortion in angles about the tin atom.

(*b*) M_2SnO_4 (M = Mg, Ca, Ba, Sr, Cd, *or*, Zn). The spectra of all these compounds show a single isotropic resonance with a linewidth of between 100 and 500 Hz. All of the structures, see Table 1, reveal unique sites for the tin atoms in accord with this observation. A closer examination of the spectrum of Ca_2SnO_4, Figure 2, reveals a low-intensity resonance at −611 p.p.m. corresponding to impurity $CaSnO_3$ amounting to about 1% of the overall signal intensity; such a low level of impurity was not observed by powder *X*-ray diffraction. Similarly in the spectrum of the barium compound a broad peak at −679 p.p.m. can be attributed to $BaSnO_3$ impurity.

The chemical shift values for the different M_2SnO_4 compounds vary between −471 and −607 p.p.m. and, despite the variations in the crystal structures, there is a strong correlation between the ionic radii of the alkaline-earth-metal cation and the isotropic tin chemical shift, see Figure 3. The spectra of all the M_2SnO_4 compounds showed spinning sidebands of sufficient intensity to enable the principal components of the chemical shift tensor to be determined in all but one case, Table 2. The overall anisotropy was up to 210 p.p.m. but considerable variation was found. Although the co-

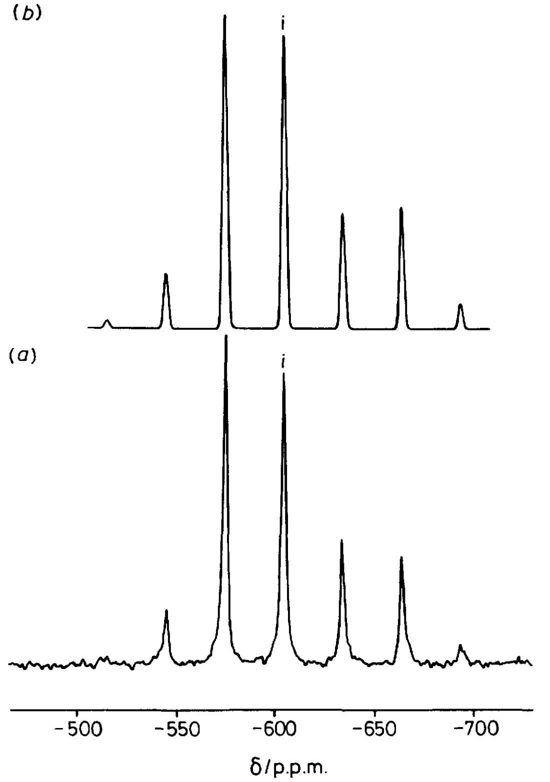

Figure 1. (*a*) Experimentally measured (*a*) and computer simulated (*b*) 74.54-MHz ^{119}Sn m.a.s. n.m.r. spectrum of SnO_2 at a spinning speed of 2 220 Hz. The isotropic resonance is labelled i

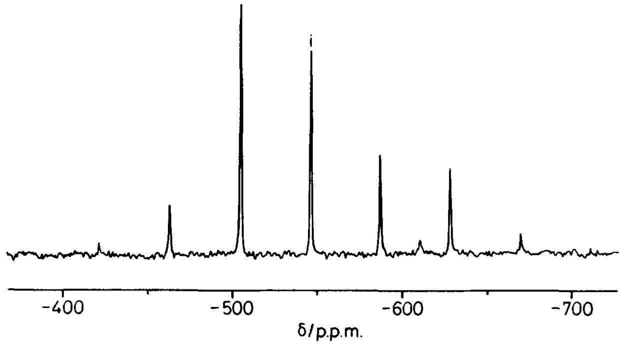

Figure 2. The 74.54-MHz ^{119}Sn m.a.s. n.m.r. spectrum of Ca_2SnO_4 at a spinning speed of 3 070 Hz. The isotropic resonance is labelled i

ordination about the tin atom in all these compounds is essentially octahedral the SnO_6 octahedra are in fact distorted both in bond lengths and angles. The structures of the different compounds were examined in detail to discover if the symmetry or magnitude of the anisotropy could be understood simply in terms of the immediate environment around the tin atom, or the crystallographic site symmetry. Other than the observation that the distorted octahedral environments are generally revealed by significant but not large anisotropies this did not prove possible. For example, the calcium and cadmium compounds are isostructural with closely similar cell parameters and hence similar bond lengths and bond angles. Yet the anisotropies appear very different, that of the cadmium compound being very much smaller than that of the calcium tin oxide, Table 2. On the other hand the magnesium and zinc compounds, which are also isostructural, have similar anisotropies of the chemical shift tensor. However, the tin site symmetry, $\bar{3}m$, implies that the chemical shift anisotropy should be axially symmetric yet a significant non-axial component is seen for both the zinc and magnesium compounds.

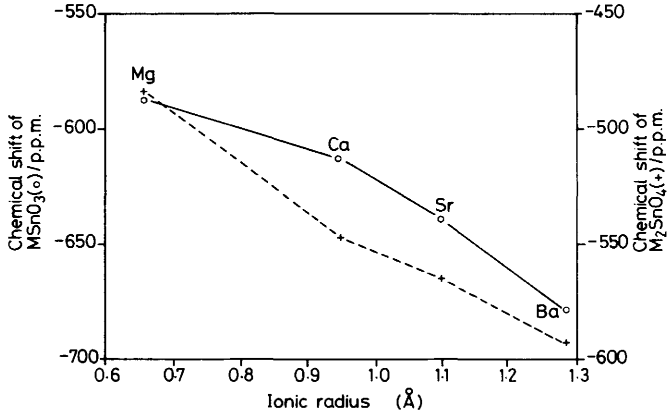

Figure 3. Correlation between the isotropic ^{119}Sn n.m.r. chemical shift and the metal ionic radius

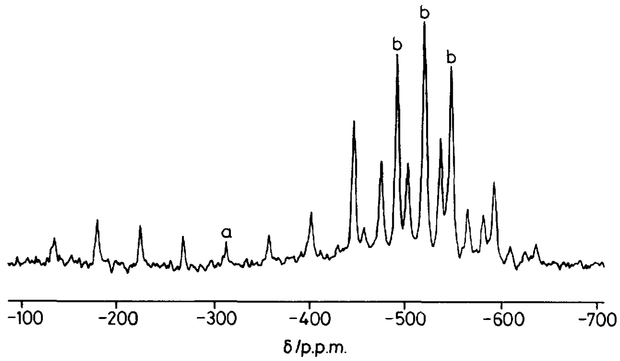

Figure 4. The 74.54-MHz ^{119}Sn m.a.s. n.m.r. spectrum of K_2SnO_3. The peak labelled a is the isotropic resonance of K_2SnO_3 and the peaks b are from $K_2Sn_3O_7$ impurity

(*c*) M'_2SnO_3 (M′ = Li, Na, *or* K). The ^{119}Sn m.a.s. n.m.r. spectra of both the lithium and sodium compounds show single isotropic resonances flanked by series of spinning sidebands. In contrast to the case with the M_2SnO_4 compounds, however, the crystal structures reveal two unique crystallographic environments. For β-Li_2SnO_3 the bond-length variations between the two sites are of the same order of magnitude as found between the variety of structures of the M_2SnO_4 compounds. It is worth noting, however, that if the corresponding sets of bond lengths are compared then the bond-length differences are less than 0.007 Å and bond-angle differences less than 2°. The observed equivalences of chemical shifts may therefore simply reflect that the chemical shift is not sensitive to such small differences. If this is the case it sets a lower limit to the type of structural changes observable by ^{119}Sn n.m.r. spectroscopy.

In contrast to the ^{119}Sn n.m.r. spectra of the lithium and sodium tin oxides, that of the potassium compound reveals four isotropic resonances, Figure 4. Only one of these, however, that at −312.8 p.p.m., in fact arises from K_2SnO_3 itself; the resonances at −491.8, −520.5, and −548.1 p.p.m. are from $K_2Sn_3O_7$ presumably formed by the decomposition of K_2SnO_3 by loss of K_2O.[27] This assignment was made by obtaining the spectrum of a prepared sample of $K_2Sn_3O_7$.[27] A marked

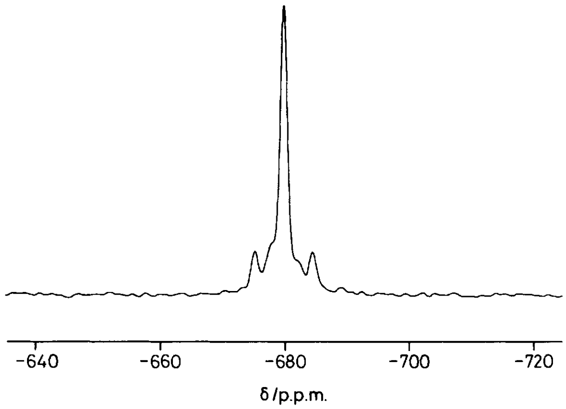

Figure 5. The 74.54-MHz ^{119}Sn m.a.s. n.m.r. spectrum of $BaSnO_3$

difference in isotropic chemical shift (140 p.p.m.) is apparent between the potassium and the earlier alkali-metal tin oxides, and this can be attributed to the change in the tin co-ordination; in K_2SnO_3 the tin site is five-co-ordinated with an approximately square-pyramidal geometry.

In all three oxides the ^{119}Sn resonance is characterised by a significant chemical shift anisotropy, Table 2. The non-axial character of the chemical shift anisotropy for β-Na_2SnO_3 and β-Li_2SnO_3 is in agreement with the two-fold crystallographic site symmetry. The large anisotropy for K_2SnO_3 can be attributed to the lower co-ordination number and lower symmetry of the local environment.

(*d*) $M''SnO_3$ (M'' = Mg, Ca, Sr, Ba, *or* Cd).The spectra of the $M''SnO_3$ oxides, except that of Cd, consist of single isotropic resonances with very low-intensity spinning sidebands. A strong correlation is seen between the isotropic chemical shift and the ionic radius in good agreement with that observed for the M_2SnO_4 oxides, Figure 3. The small chemical shift anisotropies seen are consistent with the regular octahedral geometry about the tin atom found in all these compounds despite differences in their overall three-dimensional geometry resulting from the adoption of a variety of stacking patterns for the octahedra. By contrast, $CdSnO_3$ in the spinel modification,[28] whilst still having only one isotropic resonance, shows a large anisotropy. The tin atoms are found on the B sites of the spinel structure, just as in the case of Mg_2SnO_4, but note that the anisotropies are quite dissimilar in the two cases both in terms of the overall magnitude and of the individual components.

Spin–Spin Coupling.—The ^{119}Sn n.m.r. spectrum of $BaSnO_3$ in Figure 5 shows clearly the single isotropic resonance anticipated from the unique crystallographic tin site in the lattice. The most important and interesting aspect of this spectrum, however, is the presence of satellite peaks at 346.6 Hz from the isotropic resonance. These are attributed to spin–spin coupling between the crystallographically equivalent but magnetically inequivalent ^{119}Sn and ^{117}Sn nuclei. Support for this conclusion is provided by observation of the ^{117}Sn n.m.r. spectrum where satellites are seen with a similar splitting but with increased intensity. The latter is anticipated from the higher natural abundance of ^{119}Sn (8.7%) compared with ^{117}Sn (7.4%). The oxide $BaSnO_3$ adopts an ideal perovskite structure and any spin–spin coupling must therefore be transmitted through Sn–O–Sn bonds. Tin-119 to tin-117 spin–spin coupling has recently been reported in the solid state but in this case involved transmission through a Sn–Sn bond.[29]

The intensity of the satellites is difficult to measure accurately in the spectra, but simulations show it to be not less than 12.5% of the total spectral intensity for both $BaSnO_3$ and $SrSnO_3$. This estimate permits discussion of the number of nearest-neighbour tin atoms giving rise to the coupling effects. Distortion of perovskite lattices are common and well documented, involving tilting of the anion octahedra, cation displacements, and distortions of the octahedra.[30] Such distortions could lead to different sets of coupling constants from the various neighbouring atoms, through variations in Sn–O–Sn bond angles; this would affect the number and intensity of the satellite peaks. For the case of equivalent coupling through six octahedrally arranged oxygen atoms, an intensity of 15.4% of the total intensity is predicted for each component of the doublet, in reasonable agreement with those found experimentally. By contrast, for a situation where distortion resulted in only four equivalent neighbours being responsible for the satellite resonance an intensity of only 10.3% would be predicted. An accurate structure determination of $CaSnO_3$ indicates that although tilting of the anion octahedra is present this only leads to a 2° difference in the two sets of Sn–O–Sn bond angles.[31] Such a small difference is unlikely to give rise to distinguishable coupling constants. There is, however, some evidence from spectra such as that shown in Figure 5 that additional coupling effects are present in the spectrum; the linewidths of the resonances suggest additional intensity between the centre peak and the satellites. This could indicate the presence of longer range spin–spin coupling, ^4J(Sn–Sn), which is not resolvable in these spectra. If such long-range coupling can be measured it would be of considerable interest in defining the structure of three-dimensional solids by n.m.r. spectroscopy.

Conclusions

A study of a variety of structurally well characterised ternary tin oxides has demonstrated the ease with which ^{119}Sn, or indeed ^{117}Sn, m.a.s. n.m.r. spectra can be obtained from ionic tin compounds without the need for cross-polarisation techniques. Although the large chemical shift range observed for the tin oxides suggests a sensitivity to the local environment, indeed allowing the observation of crystallographically inequivalent sites in $K_2Sn_3O_7$, it is of note that similar inequivalence was not observed, where expected, in β-Li_2SnO_3 and Na_2SnO_3. A linear relationship was found between the ^{119}Sn chemical shift and the ionic radius of the cation for ternary tin oxides of the same stoicheiometry regardless of the structure adopted. No clear correlation was found between the ^{119}Sn chemical shift anisotropy and the crystallographic site symmetry, although in general large anisotropies were associated with large distortions from octahedral symmetry.

A particularly interesting aspect of the ^{119}Sn solid-state n.m.r. studies has been the observation of scalar coupling between crystallographically equivalent but magnetically inequivalent ^{119}Sn–^{117}Sn nuclei. Analysis of spin–spin coupling is of major importance in structural studies by n.m.r. spectroscopy for the solution state. The observation of this coupling in a three-dimensional structure suggests that it could form the basis for the novel investigation of short-range order in the crystalline state.

Acknowledgements

We acknowledge support from the S.E.R.C. towards purchase of the n.m.r. spectrometer; N. J. C. thanks Shell, Thornton Research Centre for financial assistance.

References

1 C. A. Fyfe, 'Solid State NMR For Chemists,' CFC Press, Guelph, 1983.

2 M. Mehring, 'Principles of High Resolution NMR in Solids,' 2nd edn., Springer, Berlin, 1983.
3 N. J. Clayden, *Chem. Scr.*, 1988, **28**, 211.
4 R. K. Harris, in 'NMR and the Periodic Table,' eds. R. K. Harris and B. E. Mann, Academic Press, London, 1984.
5 D. Muller, W. Gessner, A. Samoson, E. Lippmaa, and G. Scheler, *Polyhedron*, 1986, **5**, 770.
6 R. Tabeta and H. Saito, *Chem. Lett.*, 1984, 293.
7 S. Schramm and E. Oldfield, *J. Am. Chem. Soc.*, 1984, **106**, 2505.
8 G. L. Turner, S. E. Chung, and E. Oldfield, *J. Magn. Reson.*, 1985, **64**, 316.
9 E. Oldfield, M. A. Keniry, S. Shinoda, S. Schramm, T. L. Brown, and H. E. Gutowsky, *J. Chem. Soc., Chem. Commun.*, 1985, 791.
10 D. M. Doderell, P. F. Barron, D. E. Clegg, and C. Bowie, *J. Chem. Soc., Chem. Commun.*, 1982, 575.
11 R. K. Harris, P. Reams, and K. J. Packer, *J. Chem. Soc., Dalton Trans.*, 1986, 1015.
12 J. R. Ascenso, R. K. Harris, and P. Granger, *J. Organomet. Chem.*, 1986, **C23**, 301.
13 E. Lippmaa, M. A. Alla, T. J. Penk, and G. Engelhardt, *J. Am. Chem. Soc.*, 1978, **100**, 1929.
14 R. K. Harris, K. J. Packer, and P. Reams, *Chem. Phys. Lett.*, 1985, **115**, 16.
15 A. K. Cheetham, C. P. Grey, C. M. Dobson, and R. K. B. Jakeman, *Nature (London)*, 1987, **328**, 706.
16 J. A. Zubieta and J. J. Zuckerman, *Prog. Inorg. Chem.*, 1978, **24**, 251.
17 JCPDS, Powder Diffraction File, International Centre for Diffraction Data, Swathmore, Pennsylvania.
18 H. Strunz and B. Contag, *Acta Crystallogr.*, 1960, **13**, 601.
19 W. W. Coffeen, *J. Am. Chem. Soc.*, 1953, **36**, 207.
20 J. S. Frye and G. E. Maciel, *J. Magn. Reson.*, 1980, **48**, 125.
21 D. G. C. Ghoberdan, N. J. Clayden, C. M. Dobson, and S. A. Rodger, unpublished work.
22 J. Herzfeld and A. E. Berger, *J. Chem. Phys.*, 1980, **73**, 6021.
23 M. M. Maricq and J. S. Waugh, *J. Chem. Phys.*, 1980, **70**, 3300.
24 N. J. Clayden, C. M. Dobson, L-Y. Lian, and D. J. Smith, *J. Magn. Reson.*, 1986, **69**, 476.
25 H. J. Jakobsen, P. D. Ellis, R. R. Inners, and C. F. Jensen, *J. Am. Chem. Soc.*, 1982, **104**, 7442.
26 W. H. Baur, *Acta Crystallogr.*, 1956, **9**, 515.
27 M. Tournoux and A. Hardy, *C.R. Acad. Sci.*, 1964, **258**, 1811.
28 C. Levy-Clement, I. Morganstern-Badarau, Y. Billet, and A. Michel, *C.R. Acad. Sci., Ser. C*, 1967, **265**, 585.
29 R. K. Harris, T. N. Michell, and G. J. Nesbitt, *Magn. Reson. Chem.*, 1985, **23**, 1080.
30 H. D. Megaw, 'Crystal Structures a Working Approach,' Saunders, Philadelphia, 1973.
31 A. Vega, M. Vallet-Regi, J. M. Gonzalez-Calbet, and M. A. Alario-Franco, *Acta Crystallogr., Sect. B*, 1986, **42**, 167.

Received 29th March 1988; *Paper* 8/01301B