High-resolution Solid-state Platinum-195 Nuclear Magnetic Resonance

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The potential of solid-state ^{195}Pt n.m.r. spectroscopy for chemical applications has been explored. Spectra have been obtained using the cross-polarisation, high-power decoupling, and magic-angle rotation techniques. The large shielding anisotropy present for most compounds gives rise to many spinning sidebands, which contain a wealth of information regarding shielding tensors. Two different solid-state (^{195}Pt, ^{31}P) scalar coupling constants are reported for *cis*-$[PtMe_2(PEt_3)_2]$, and an *X*-ray diffraction study confirms that the PEt_3 groups are non-equivalent. The interplay of scalar, dipolar, and shielding tensors is discussed.

Low-resolution n.m.r. of the solid state has now been accessible for a considerable number of years, producing information regarding the geometry and electronic structure of many solid systems. The development of magic-angle rotation (m.a.r.), cross-polarisation (c.p.), and high-power decoupling techniques now makes the study of spectra of dilute nuclear spins possible[1] with high resolution.

The three main anisotropic interactions present in solids (for spin $\frac{1}{2}$ nuclei) are (*a*) dipole–dipole coupling, (*b*) magnetic shielding, and (*c*) indirect (scalar) spin–spin coupling. This anisotropic information is usually sacrificed for the improvement in resolution, as has been the case for most of the recent ^{13}C, ^{29}Si, and ^{31}P solid-state n.m.r. studies. By the use of slow-spinning techniques such information can be retrieved with spinning sideband analysis.[2,3] The only requirement is that the spinning speed is less than the bandwidth caused by the relevant inhomogeneous anisotropic interactions. For heavy metallic nuclei, the shielding anisotropy is expected to be the dominant interaction, and may be much greater than the attainable spinning rates.[4] This situation gives rise to a multitude of spinning sidebands. We have recently shown this to be the case with the solid-state ^{119}Sn n.m.r. of trimethyltin hydroxide[5] and also tributyltin fluoride.[6] The latter work reveals the interplay of the above-mentioned tensor properties. The potential of solid-state n.m.r. to study suitable nuclei such as ^{119}Sn, ^{207}Pb, ^{195}Pt, and ^{199}Hg is considerable, and we have embarked on a systematic evaluation of this area.

Platinum-195 is the only isotope of platinum with a non-zero spin ($I = \frac{1}{2}$). It has a relatively high abundance (33.8%), a receptivity which is 19 times greater than that of carbon, and a low magnetogyric ratio ($\gamma = 5.77 \times 10^7$ rad T^{-1} s^{-1}), which makes it suitable for cross-polarisation studies in the solid state. However, despite these favourable characteristics there has only been one report of solid-state ^{195}Pt n.m.r.[7] This revealed a large shielding anisotropy for $[\{PtMe_3(acac)\}_2]$ (acac = acetylacetonate) and for $[PtMe_3]_2SO_4{\cdot}4H_2O$. Solution-state n.m.r. studies[8,9] have used spectra at different magnetic fields to investigate the shielding anisotropy contribution to relaxation for several compounds. One such study has shown that for Pt^{II} complexes the shielding anisotropy may be as large as 10 000 p.p.m.,[8] which can create severe problems in direct n.m.r. observations of the solid state. However, the spinning sidebands, sometimes thought to confuse the spectrum, can reveal information regarding the shielding and spin-coupling tensors, as noted above.

We have obtained solid-state ^{195}Pt n.m.r. spectra for four Pt^{IV} compounds, *viz.* $K_2[Pt(OH)_6]$, $[Pt(en)_3]Cl_4{\cdot}2H_2O$ (en = ethylenediamine), $Na_2[PtCl_6]{\cdot}6H_2O$, and *cis*-$[PtCl_4(NH_3)_2]$, and one Pt^{II} compound, *cis*-$[PtMe_2(PEt_3)_2]$. The results are given in the Table. This work has included the calculation of effective tensor components using the spinning sideband patterns. Solution-state ^{195}Pt data are available in the literature (see Table) for three of the compounds and, in addition, we have obtained a spectrum for *cis*-$[PtMe_2(PEt_3)_2]$ in solution in CD_3CN, but $[Pt(en)_3]Cl_4{\cdot}2H_2O$ appears to be insufficiently soluble.

Experimental

All the samples were obtained from Johnson Matthey Research Centre and used without further purification. The experiments were carried out using a Bruker CXP200 spectrometer operating at 43.0 MHz for ^{195}Pt with ambient probe temperature. The Hartmann–Hahn matching condition for cross-polarisation was set using $K_2[Pt(OH)_6]$, which proved to be the most sensitive sample. The proton relaxation parameters of this compound were found to be $T_1 \simeq 1$ s and $T_{1\rho} \simeq 1.5$ ms. Using a series of exploratory experiments the most favourable conditions for cross-polarisation to ^{195}Pt were found to be a recycle time of 2 s and a contact time of 1 ms; a reasonable signal could be seen after 10 transients. For all the ^{195}Pt spectra described here a spectral width of 62.5 kHz was used (digitisation rate of 15 Hz per point), with a ^{1}H 90° pulse length (measured for a sample of silicone gum) of 5 μs (50 kHz proton decoupling field). The powdered samples were contained in delrin rotors (0.42 cm^3 volume) and rotated at the magic angle at *ca.* 3 kHz. Platinum-195 chemical shifts were referenced to the $[PtCl_6]^{2-}$ ion in an aqueous (D_2O) solution of the sodium salt using the replacement method. The absolute frequency for the reference was found to be 43.022 MHz, and this value was used to convert frequency differences into p.p.m. The solution-state ^{195}Pt spectrum of *cis*-$[PtMe_2(PEt_3)_2]$ was also recorded using the CXP200 spectrometer.

The chemical shift range for platinum complexes is *ca.* 13 000 p.p.m.,[4] and this can pose a problem in locating a signal. A knowledge of the ^{195}Pt solution-state chemical shift is a considerable advantage in most cases and therefore the solubility of a solid can be an important factor in the search for a platinum resonance. The multitude of spinning sidebands, usually present, reduces the intensity of the centreband and so

Table. Platinum-195 shielding tensor parameters[a]

Compound	Spinning speed/Hz	$\Delta\sigma_{iso.}$	$\Delta\sigma_{33}$[b]	$\Delta\sigma_{22}$[b]	$\Delta\sigma_{11}$[b]	$\beth$[b]	η[b]	Solution δ/p.p.m.	Solvent
				p.p.m.					
$K_2[Pt(OH)_6]$	3 200	−3 476[d]	−3 218	−3 567[c]	−3 643[c]	258	0.29	3 290[e]	1 mol dm^{-3} KOH
	1 907		−3 222	−3 574[c]	−3 632[c]	254	0.23		
cis-$[PtMe_2(PEt_3)_2]$	3 000	4 654[d]	5 058	4 649	4 256	404	0.97	−4 653[f]	CD_3CN
	2 500		5 054	4 639	4 267	400	0.93		
$[Pt(en)_3]Cl_4{\cdot}2H_2O$	3 000	943[g]	585	1 070	1 174	−358	0.29	Insoluble	
	2 600		622	1 022	1 186	−322	0.51		
cis-$[PtCl_4(NH_3)_2]$	2 620	237[g]	367	209	134	130	0.58	−145[h]	H_2O
$Na_2[PtCl_6]{\cdot}6H_2O$	3 000	−85[g]				*i*		0[j]	D_2O

[a] The shielding values are measured in p.p.m. relative to $[PtCl_6]^{2-}$ in D_2O. For chemical shifts on the δ scale the signs should be reversed. [b] As discussed in the text the data, strictly speaking, refer to effective average tensors which may be affected, *inter alia*, by heteronuclear dipolar interactions as well as shielding anisotropy. [c] For discussion of the distinction between $\Delta\sigma_{22}$ and $\Delta\sigma_{11}$ for $K_2[Pt(OH)_6]$ see text. [d] Measurement accuracy ±1 p.p.m. [e] T. G. Appleton, J. R. Hall, S. F. Ralph, and C. M. Thompson, *Inorg. Chem.*, 1984, **23**, 3521. [f] This work. Digitization rate 5 Hz per point. [g] Measurement accuracy ±2 p.p.m. [h] I. M. Ismail and P. G. Sadler, *ACS Symp. Ser.*, 1983, **209**, 171. [i] Small (see text). [j] By definition.

increases location difficulty. The accuracy of setting the magic angle plays a crucial role in obtaining high-resolution ^{195}Pt spectra; a slightly off-set angle can considerably broaden lines because of a large anisotropy. The observation of spinning sidebands in the ^{79}Br n.m.r. (at 50.14 MHz) of solid KBr was used for angle adjustments.[10] For sufficiently accurate setting of the magic angle (that is, to obtain minimum linewidths) as much as half a rotor of KBr is required; this of course decreases the sensitivity for the observation of a platinum signal. Fine adjustments of the angle were made by slight alteration of the spinning rate while observing the ^{79}Br free-induction decay (f.i.d.). When the optimum speed is obtained, small sharp spikes appear superimposed on the regular cosine decay of the f.i.d.

Shielding Tensor Evaluation.—In theory, shielding tensor components may be measured from powder bandshapes.[11] However, this tends to be difficult in practice as the signal-to-noise ratio may be very poor when the bands are broad (as is common), and a computer bandshape fit is often required. Alternative methods have been proposed by Maricq and Waugh[2] and Herzfeld and Berger.[3] Both use spinning sideband intensities, such as are usually observed in the m.a.r. ^{195}Pt spectra. In the present work, the method of Maricq and Waugh led to the most consistent results.

In principle the static spectra, and hence the spinning sideband manifolds, may be influenced by a number of anisotropic interactions. For the compounds studied here, the major effect is likely to arise from the shielding tensor. High-power proton decoupling was used to remove the influence of (Pt,H) dipolar (and indirect) coupling interactions. The atoms directly bonded to platinum are C, O, N, P, and Cl. The major isotopes of carbon and oxygen have zero spin and therefore can be discounted. Calculations based on typical Pt–X distances give values for the relevant dipolar interaction constants, $(\mu_0/4\pi)\gamma_{Pt}\gamma_X(\hbar/2\pi)r_{PtX}^{-3}$ of 144, 868, and 203 Hz respectively, for X = ^{14}N, ^{31}P, and ^{35}Cl. These values are substantially less than the observed static bandwidths. We have, therefore, for simplicity, assumed that the effective tensor components which we derive are those for the platinum shielding only. It is probable that the effect of dipolar interactions is to cause the shielding anisotropy to be slightly overestimated when N or Cl are directly bonded to Pt.

Splittings are observed for *cis*-$[PtMe_2(PEt_3)_2]$ arising from scalar isotropic (Pt,P) coupling, and these are taken into account in our analysis. No splittings are observed due to (Pt,N) or (Pt,Cl) scalar coupling. Either there is fast Cl and N spin-lattice relaxation or the coupling constants are less than the linewidths. There appear to be no data in the literature for the relevant anisotropies in indirect (scalar) coupling constants in the systems used, or for closely-related compounds.

First-moment calculations, together with experiments at variable rotation rate, show that the centrebands of the spectra are as indicated in the Figures. These yield the values of the isotropic shifts listed in the Table. Measurements of the second and third moments of the spectra gave[2] data on the principal components of the shielding tensor. The results for *cis*-$[PtMe_2(PEt_3)_2]$ were obtained for the central component of the triplet caused by (Pt,P) coupling (see below). We have used the Haeberlen convention,[11] $|\sigma_{33} - \sigma_{iso.}| > |\sigma_{11} - \sigma_{iso.}| > |\sigma_{22} - \sigma_{iso.}|$, for the tensor components, which are also reported in the Table. In three cases the consistency of these results was checked by experiments at different spinning speeds. For two of the compounds the consistency was impressive (agreement to within 14 p.p.m., when $|\sigma_{33} - \sigma_{11}|$ is *ca.* 400 p.p.m. in one case and *ca.* 800 p.p.m. in the other). In the other case, agreement is not so good (37, 48, and 12 p.p.m. for the three components). Of course, the accuracy of the Maricq and Waugh method[2] is heavily dependent on the sidebands towards the extreme of the envelope, where the signal-to-noise ratio is at its poorest. Spectra at slower spinning rates are likely to yield the more accurate results, since they are closer to reconstructing the envelope of the powder pattern, though, in compensation, the signal-to-noise ratio decreases as the number of sidebands increases.

Shielding anisotropies, $\sigma_{33} - \sigma_{iso.}$ (written as $\beth$ rather than δ to avoid confusion with the chemical shift scale), and asymmetries, $\eta = (\sigma_{22} - \sigma_{11})/\beth$, have also been calculated and are reported in the Table. As for the individual shielding tensor components, results at two different spinning speeds are consistent for $K_2[Pt(OH)_6]$ and *cis*-$[PtMe_2(PEt_3)_2]$, but the variations for $[Pt(en)_3]Cl_4{\cdot}2H_2O$ are considerable, particularly for η.

Discussion

Isotropic Shifts.—All the compounds studied showed a single isotropic chemical shift for the solid state. This could indicate that the crystal structures have only equivalent sites for Pt in their respective unit cells. This is, indeed, known[12] to be true for $K_2[Pt(OH)_6]$ (see below), and our *X*-ray results indicate this is the case for *cis*-$[PtMe_2(PEt_3)_2]$ also. However, it is possible that in the other cases the substantial linewidths could conceal small splittings from crystallographic non-equivalence, though the sensitivity of Pt chemical shifts to chemical effects suggests non-equivalence should give rise to substantial shift differences.

The solution-to-solid chemical shift change is negligible for

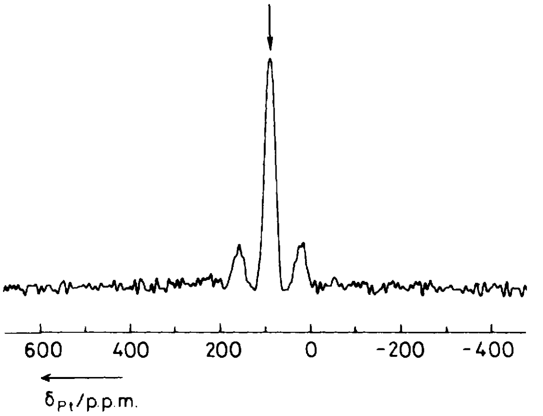

Figure 1. 43.022-MHz ^{195}Pt-{^{1}H} c.p./m.a.r. spectrum of $Na_2[PtCl_6]\cdot 6H_2O$, with the centreband indicated by an arrow. Spinning speed = 3 kHz, number of transients = 1 000, recycle delay = 5 s, contact time = 5 ms, spectral width = 50 kHz, offset = 12 kHz

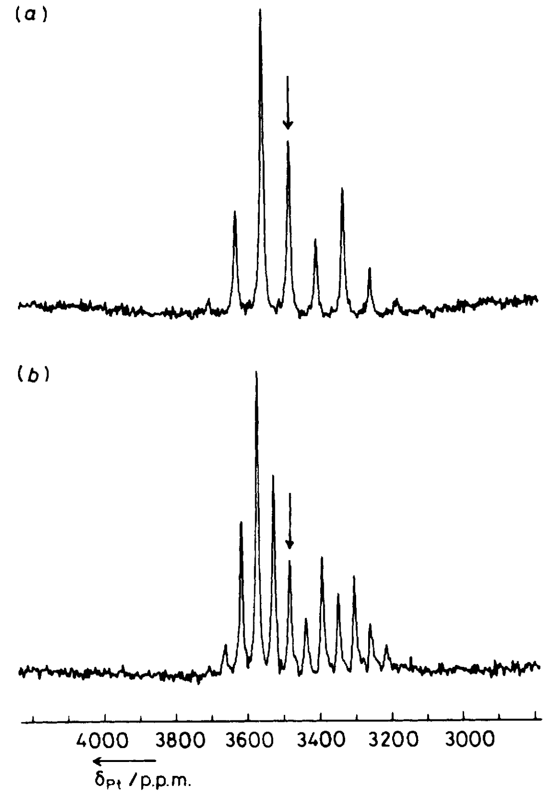

Figure 2. 43.022-MHz ^{195}Pt-{^{1}H} c.p./m.a.r. spectrum of solid $K_2[Pt(OH)_6]$, with the centreband indicated by an arrow. (*a*) Spinning speed 3 200 Hz, number of transients = 8 140, recycle delay = 2 s, contact time = 1 ms, spectral width = 62.5 kHz, offset = 160 kHz; (*b*) as for (*a*) but with spinning speed = 1 907 Hz and number of transients = 8 200

cis-$[PtMe_2(PtEt_3)_2]$ and is undetermined for $[Pt(en)_3]Cl_4\cdot 2H_2O$. For $Na_2[PtCl_6]\cdot 6H_2O$ the magnitude of the difference is 85 p.p.m., while for *cis*-$[PtCl_4(NH_3)_2]$ it is 92 p.p.m. In view[4] of the large chemical shift range for ^{195}Pt and the established influence of solvent, these effects of the phase change must be regarded as only modest. For $K_2[Pt(OH)_6]$ the shift difference on changing phase is somewhat larger (186 p.p.m.) but it should be noted that the medium used for the solution-state measurement (namely 1 mol dm^{-3} KOH) is an aggressive one.

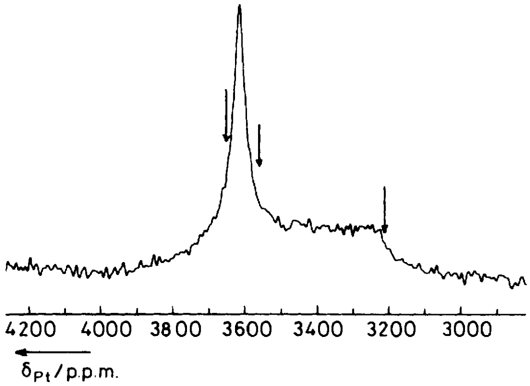

Figure 3. Static ^{195}Pt-{^{1}H} bandshape for $K_2[Pt(OH)_6]$ at 43.022 MHz. The vertical arrows mark the positions of σ_{11}, σ_{22}, and σ_{33} as deduced from the spinning sideband analysis. Number of transients = 11 000, recycle delay = 3 s, contact time = 1 ms, spectral width = 62.5 kHz, offset = 160 kHz

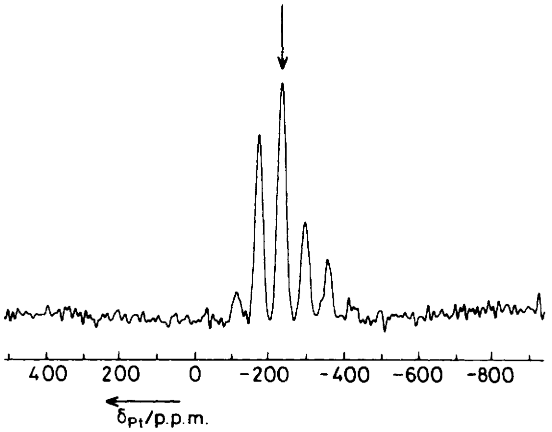

Figure 4. 43.022-MHz ^{195}Pt-{^{1}H} c.p./m.a.r. spectrum of *cis*-$[PtCl_4(NH_3)_2]$, with the centreband indicated by an arrow. Spinning speed = 2 620 Hz, number of transients = 7 140, recycle delay = 7 s, contact time = 5 ms, spectral width = 62.5 kHz, offset = 0.0

The variation in isotropic chemical shifts is, as expected, quite large. The factors affecting the chemical shifts of heavy metal nuclei are many and varied.[4,13] The electronegativity of the substituents attached directly to the platinum atom is known[13] to be of importance in this respect. For the small number of Pt^{IV} complexes studied here, the chemical shift increases monotonically with increasing electronegativity (O > Cl > N), as expected from solution-state data, *i.e.* δ/p.p.m. for $K_2[Pt(OH)_6]$ > $Na_2[PtCl_6]\cdot 6H_2O$ > *cis*-$[PtCl_4(NH_3)_2]$ > $[Pt(en)_3]Cl_4\cdot 2H_2O$.

Sodium Hexachloroplatinate(IV) *Hexahydrate*.—The ^{195}Pt spectrum (Figure 1) of $Na_2[PtCl_6]\cdot 6H_2O$ gives rise to a single resonance with two weak spinning sidebands, indicating the presence of only a small anisotropy. This is to be expected when considering the molecular symmetry of the compound, but the crystal structure has not been reported.

Potassium Hexahydroxyplatinate(IV).—The spectrum (Figure 2) of $K_2[Pt(OH)_6]$ might be expected to show a similar sideband pattern. However, in this case the observed shielding

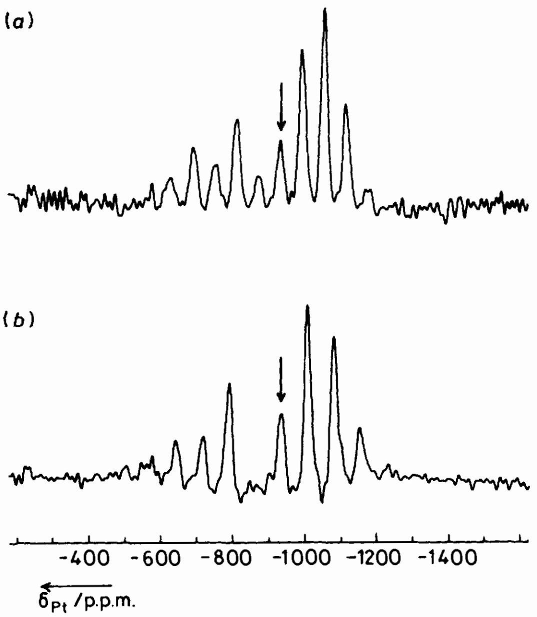

Figure 5. 43.022-MHz $^{195}Pt-\{^1H\}$ c.p./m.a.r. spectrum of $[Pt(en)_3]Cl_4 \cdot 2H_2O$, with the centreband indicated by an arrow. (*a*) Spinning speed = 2 600 Hz, number of transients = 3 540, recycle delay = 2 s, contact time = 1 ms, spectral width = 62.5 kHz, offset = -30 kHz; (*b*) as for (*a*) but with spinning speed = 3 000 Hz and number of transients = 20 000

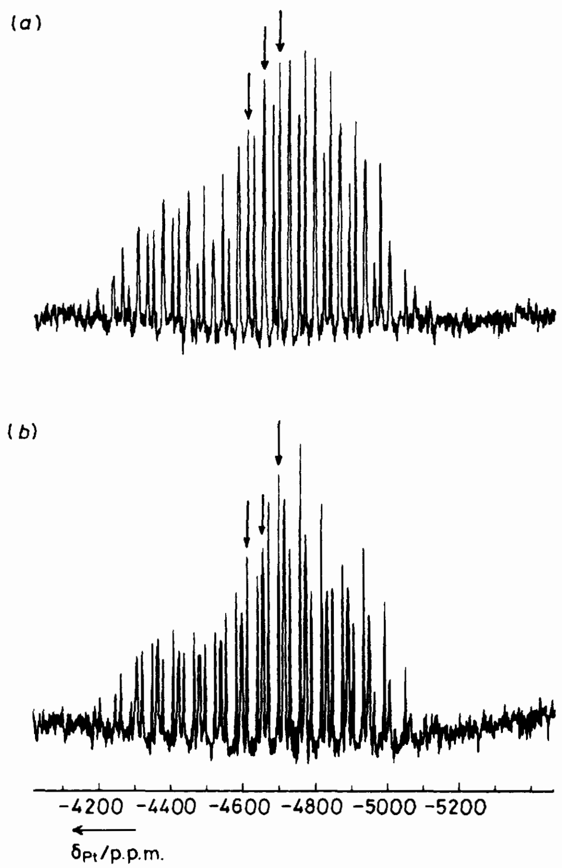

Figure 6. 43.022-MHz $^{195}Pt-\{^1H\}$ c.p./m.a.r. spectrum of *cis*-$[PtMe_2(PEt_3)_2]$, with the centrebands indicated by arrows. (*a*) Spinning speed = 3 000 Hz, number of transients = 26 000, recycle delay = 2 s, contact time = 2 ms, spectral width = 62.5 kHz, offset = -195 kHz; (*b*) as for (*a*) but with spinning speed = 2 500 Hz and number of transients = 17 230

anisotropy is, at first sight, surprisingly substantial, especially as there can be little contribution to the proton-decoupled static bandshape from dipolar interactions, since the dominant isotope of oxygen is non-magnetic and the potassium ions are relatively distant from platinum. The crystal structure obtained[12] for this compound shows that it belongs to the rhombohedral system (space group $R\bar{3}$). The platinum atom is surrounded by six equidistant oxygen atoms (2.016 Å). One would therefore expect to see a very small shielding anisotropy for the platinum, giving rise to few (if any) spinning sidebands in the ^{195}Pt spectrum. The observed anisotropy is, however, consistent with the existence of a $\bar{3}$ axis at Pt in the crystal structure.[12] Potassium ions are positioned around the platinum atoms in the form of a bicapped trigonal antiprism. Such *axial* symmetry in the platinum environment should lead to a zero asymmetry factor in the ^{195}Pt shielding, contrary to the results given in the Table. We have checked our calculations, using both methods[2,3] of deriving shielding tensor components from spinning sidebands, and consistently obtain $\eta \sim 0.25$, though it is difficult to estimate the experimental errors involved and there was considerable divergence between the two values obtained using the Herzfeld and Berger method.[3] Moreover, the difficulty of measuring second and third moments accurately (necessary for the Maricq and Waugh method[2]) is well known. Furthermore, the spinning sideband calculations are not very sensitive to the asymmetry parameter in conditions of nearly axial symmetry. We have also obtained the static ^{195}Pt spectrum for $K_2[Pt(OH)_6]$, which is illustrated in Figure 3. This appears to indicate axial symmetry, though the bandshape is somewhat distorted by dead-time problems. It is possible that the appearance may be consistent with a small non-zero asymmetry in σ if there is substantial line-broadening. The value of $\Delta\sigma_{33}$ given by the turning point in the static bandshape is in good agreement with that obtained from the spinning sideband calculations. The results for $\Delta\sigma_{22}$ and $\Delta\sigma_{11}$ derived from the spinning sidebands bracket the marked maximum in the static bandshape. There would appear to be three possible explanations for these results. The first and most likely is that the n.m.r. results (including the sideband analysis) may be consistent with axial symmetry within experimental error. Secondly, the *X*-ray results may be misleading in that the platinum environment may not be axially symmetric. The latter possibility arises either because the protons (not accurately located by the *X*-ray study) may not provide complete axial symmetry around platinum, or because there may be some disorder in the structure undetected by *X*-ray work. It should be recalled that n.m.r. shifts reflect the local environment with great sensitivity, whereas *X*-rays respond to relatively long-range order. The authors of the *X*-ray study[12] believe there are hydrogen bridges between neighbouring PtO_6 octahedra, and this may be a source of structural disorder. The third possibility, though regarded as unlikely, is that motional processes (*e.g.* of the H-bond protons) may cause averaging of σ_{11} and σ_{22} for the static bandshape but that magic-angle rotation modulates this process, leading to the reappearance of distinguishable tensor components in the analysis of the m.a.r. spectrum. It may be noted that the rotation rate is of the same order of magnitude as $|\sigma_{22} - \sigma_{11}|$ expressed in Hz.

cis-*Diamminetetrachloroplatinum*(IV).—No single-crystal *X*-ray diffraction study of *cis*-$[PtCl_4(NH_3)_2]$ has been reported to our knowledge, which is surprising in view of its close relation to *cis*-$[PtCl_2(NH_3)_2]$, the anti-cancer drug. The solid-state ^{195}Pt spectrum (Figure 4) indicates the presence of a single crystallographic site for Pt and shows that the shielding anisotropy is of a modest magnitude.

Tris(ethylenediamine)platinum(IV) *Tetrachloride–Dihydrate.*—The solid-state n.m.r. spectrum of $[Pt(en)_3]Cl_4 \cdot 2H_2O$ is shown in Figure 5. As for $K_2[Pt(OH)_6]$, the atoms directly bonded to Pt in $[Pt(en)_3]Cl_4 \cdot 2H_2O$ are all the same, so a small shielding anisotropy is to be expected. However, the observed anisotropy is substantial (*ca.* 350 p.p.m.), and this must arise from a lack of symmetry in the environment more than one bond removed from platinum. For octahedral tris(ethylenediamine) metal complexes there are[14] two enantiomorphous ways of orienting the chelate rings about the metal atom. Moreover, since the ethylenediamine chelate rings are themselves puckered, and therefore chiral, there are, in principle, four enantiomorphous pairs of diastereomers. The n.m.r. spectrum suggests that only one crystallographic site is present. However, this does not necessarily mean that there is a single enantiomer, since (*a*) it is possible that the observed linewidth contains unresolved splittings, and (*b*) if the space group of the unit cell contains a mirror plane, two enantiomers could be present in the unit cell, related by symmetry and therefore crystallographically equivalent, giving rise to a single ^{195}Pt resonance. The ring puckering effect, as well as hydrogen bonding and other intermolecular interactions, could account for the large anisotropy seen.

cis-*Dimethylbis(triethylphosphine)platinum*(II).—The ^{195}Pt spectrum (Figure 6) of *cis*-$[PtMe_2(PEt_3)_2]$ gives rise to a multitude of sidebands and illustrates several features of chemical interest. There are three centrebands, situated at −4 610, −4 654, and −4 698 p.p.m., relative to $[PtCl_6]^{2-}$ in D_2O. The broad centreband at −4 654 p.p.m. is found to have twice the linewidth of the outer lines, and the ratio of the total intensities for the three sideband manifolds is 1:2:1. The three centrebands are equally separated, with a spacing of 1 893 Hz, which undoubtedly represents $|^1J(PtP)|$, though the width of the central component suggests there may be two different values for this parameter. Indeed, some of the spinning sidebands of the central resonance show an incipient splitting. The solution-state ^{195}Pt spectrum of *cis*-$[PtMe_2(PEt_3)_2]$ exhibits a triplet pattern because of coupling of two equivalent phosphorus nuclei, the magnitude of the coupling constant being 1 860 Hz (measured with a digitisation rate of 17 Hz per point).

Information has already been obtained on this compound from the solid-state ^{31}P spectrum.[15] This shows two central peaks at 11.7 and 10.3 p.p.m. (relative to 85% H_3PO_4), flanked by platinum satellites with $|^1J(PtP)|$ equal to 1 827 and 1 905 Hz. The two phosphorus resonances could be due to two non-equivalent crystallographic sites for the molecule as a whole or to a molecular site symmetry which is lower than the molecular symmetry, *i.e.* the effect may be intermolecular or intramolecular in origin. The fact that there is only a single ^{195}Pt chemical shift in the solid-state spectrum is unequivocal evidence for the presence of only one crystallographic site for the molecule in the unit cell. Therefore the lack of symmetry is intramolecular in origin. *X*-Ray analysis confirms the n.m.r. results and shows that the asymmetric unit is one complete molecule. The space group is $P2_1/n$, and the triethylphosphine groups have different conformations.

Since the middle centreband of the ^{195}Pt spectrum is unresolved, the system may be treated as a three-spin AX_2 case. Three tensor properties need to be taken into account when analysing the sideband manifolds, namely (*a*) indirect (^{195}Pt, ^{31}P) coupling (J); (*b*) dipolar (Pt,P) coupling (D); and (*c*) ^{195}Pt shielding (σ). The interplay of these tensors has been recently illustrated for both AX and AX_2 systems.[6,16,17] The AX_2 case has the advantage that the middle manifold of sidebands corresponds to a zero total spin component of the phosphorus nuclei. Its effective anisotropy is uninfluenced by (Pt,P) coupling of either type, and therefore an analysis of this manifold gives the principal component of the ^{195}Pt shielding tensor unambiguously (see the Table), thus reducing the number of unknowns. Detailed analysis of the outer sidebands for an AX_2 case requires development of theory, which we are currently undertaking. However, in the present case, detailed examination of the spectra reveals a similar spread of frequency for the two outer sideband manifolds, which indicates that there is only a small coupling contribution to anisotropy.

Linewidths.—As well as shielding anisotropies and chemical shifts, the linewidths of the different compounds vary considerably. Thus, the width for *cis*-$[PtMe_2(PEt_3)_2]$ is *ca.* 100 Hz, whereas for $K_2[Pt(OH)_6]$ it is *ca.* 400 Hz and becomes *ca.* 1 kHz for $[Pt(en)_3]Cl_4 \cdot 2H_2O$, *cis*-$[PtCl_4(NH_3)_2]$, and $Na_2[PtCl_6] \cdot 6H_2O$. It is perhaps not surprising that the three last-mentioned platinum complexes exhibit the broadest linewidths, as in each case there are quadrupolar nuclei directly bonded to the platinum. Thus unresolved splittings due to isotropic indirect (scalar) (^{195}Pt, ^{14}N), (^{195}Pt, ^{35}Cl), and (^{195}Pt, ^{37}Cl) coupling will probably contribute to the linewidths. Moreover, although the first-order quadrupolar interaction is eliminated by m.a.r., there is a second-order interaction which is merely reduced by m.a.r. and therefore may contribute to the linewidth[18–22] of coupled spin $\frac{1}{2}$ nuclei. One would, however, expect for $K_2[Pt(OH)_6]$ a linewidth similar to that of the *cis*-$[PtMe_2(PEt_3)_2]$ because there are no quadrupolar nuclei bonded to Pt in either case.

Broad lines may also be expected when the shielding anisotropy is large, as a slightly off-set angle for the rotation axis (or some instability in this angle) would then cause considerable line broadening. For the limited number of Pt^{II} and Pt^{IV} complexes already studied,[7,8] the Pt^{II} complexes have the greater values of the shielding anisotropy. This probably explains the reason for our failure to observe spectra for other Pt^{II} complexes in the solid state {*e.g.*, $[Pt^{II}(acac)_2]$, $\Delta\sigma \sim 10\,000$ p.p.m.[8]}.

Conclusions

Our work demonstrates the feasibility of high-resolution solid-state ^{195}Pt n.m.r., and shows the type of information that may be obtained. As well as being invaluable for platinum compounds which are insoluble, or whose chemical structures are altered by dissolution, solid-state spectra have the advantage over those in solution in that they yield information on the anisotropy of n.m.r. parameters (particularly the shielding tensor). Correlations with single-crystal *X*-ray data are useful, but in cases of compounds which are amorphous or otherwise unsuitable for *X*-ray work, solid-state n.m.r. can still provide structural (and even some crystallographic) data.

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