J. Am. Chem. Soc. 1986, 108, 3215–3218

^{195}Pt Shielding Tensors in Potassium Hexachloroplatinate(IV) and Potassium Tetrachloroplatinate(II)

S. W. Sparks[†] and P. D. Ellis[*]

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. Received November 4, 1985

Abstract: Platinum principal shielding tensor elements and directions are determined in the solid state for potassium hexachloroplatinate(IV) and potassium tetrachloroplatinate(II). The octahedral platinum(IV) complex exhibits isotropic shielding as required by site symmetry. The platinum(II) complex has an axially symmetric shielding tensor with the unique element along the crystallographic *c* direction. The tensor has a chemical shift anisotropy (CSA) of 10 414 ± 9 ppm with isotropic shift at −1 799 ± 35 ppm relative to K_2PtCl_6. Platinum line widths in both complexes are dominated by dipolar coupling to quadrupolar chlorine. The isotropic static powder line shape width of K_2PtCl_6, 34 ppm (1.5 kHz), is partly narrowed by magic angle spinning at 3 kHz. Single crystal line widths of K_2PtCl_4 vary from 16 ppm to more than 300 ppm with the angular dependence characteristic of this coupling. Chemical shielding of K_2PtCl_4 in dilute aqueous solution is largely unaffected by solvation. The platinum spin–lattice relaxation rate of 3 s^{-1} (4.7 T, 22 °C, 0.01 M) is consistent with picosecond rotational correlation times. These findings strongly indicate that CSA relaxation dominates spectral line shapes in solution studies of platinum(II) antitumor drugs.

During the past several years we have been examining ^{113}Cd shielding tensors in single crystals in an effort to gain a better understanding of the structural basis of ^{113}Cd chemical shifts and metal ion shifts in general.[1] Although this approach is a successful one, we have been hampered by the low symmetry of the cadmium complexes and the propensity for cadmium to engage in a variety of coordination environments. Further, the Cd^{2+} ion has a closed d shell, and hence the second order properties of this nucleus are not dominated by the mixing of a select number of orbitals into the ground state. A consequence of this is that it makes the quantum mechanical interpretation of the observed chemical shifts and coupling constants more difficult. For these reasons and our interest in the catalytic properties of platinum we have started to focus our attention on the shielding tensors of a variety of platinum compounds.

Recent solution state NMR studies of platinum complexes have revealed scalar coupling constants and line widths which depend on magnetic field strength.[2] These dependencies were attributed to the prominence of the chemical shift anisotropy (CSA) relaxation mechanism, a conclusion which is reasonable only when the anisotropy is on the order of several thousand ppm or greater.

Initial attempts to confirm the existence of these large anisotropies in Pt(II) and Pt(IV) complexes relied upon indirect methods. The method commonly used is estimation or measurement of the solution state reorientation correlation time and subsequent calculation of the platinum shielding anisotropy from platinum spin-lattice relaxation rates.[2,3] These techniques necessarily rely on pertinent assumptions concerning sample conditions and the applicability of simplified models of reorientation. Even when all assumptions are justified and parameter estimates are good, determination of CSA in solution ignores time averaging of the shielding tensor by ligand exchange. Resulting effective anisotropies can therefore be highly concentration and temperature dependent. Estimates of the CSA in one Pt(II) complex have ranged from 900 ppm to 7500 ppm.[2,4]

Doddrell et al. have circumvented several problems of solution state determinations by directly measuring platinum chemical shielding tensors in the solid state.[4] The two platinum(IV) compounds reported have anisotropies of 950 ppm and 1123 ppm. The investigators conclude shielding anisotropies may be considerably larger in the less symmetric tetra-coordinated platinum(II) complexes.

We report here the direct determination of chemical shielding tensor principal elements and orientation in solid state potassium hexachloroplatinate(IV) and potassium tetrachloroplatinate(II). The solid state ^{195}Pt powder and single-crystal NMR results are discussed with reference to platinum site symmetries obtained from previous X-ray diffraction studies. Consideration of solid state platinum(II) shielding anisotropy and the solution state isotropic resonance confirms the expectations of CSA dominated line shapes and relaxation rates in NMR studies of Pt(II) drug compounds.

Experimental Section

Materials. Potassium hexachloroplatinate(IV) was synthesized by neutralizing an aqueous solution of hydrogen hexachloroplatinate(IV) with aqueous potassium hydroxide. The finely divided, bright yellow precipitate was dried and used without further purification. Solid state static NMR powder spectra indicate contamination of product by starting material to be less than 0.1 mol %.

Potassium tetrachloroplatinate(II) was obtained commercially and used for powder spectra without purification. Solid state MAS and TOSS[5] NMR powder spectra indicate contamination by potassium hexachloroplatinate(IV) at 0.5 mol %.

Crystal Growth. Crystals of potassium tetrachloroplatinate(II) were grown from aqueous solutions by slow evaporation at ambient conditions. Average crystallization times from initial saturated solutions were 10–20 days. Crystals harvested from neutral solution preferred a thick columnar habit with unavoidable twinning. Mild acidification (0.5 molar HCl) encouraged growth of crystals with a flattened habit and lessened tendency to twinning. A single crystal was harvested from acidified solution after one reseeding, mechanically trimmed to dimensions 2 × 3.5 × 4 mm, mounted in an orthogonal alumina cube, and used for all single-crystal experiments.[1] X-ray diffraction results indicate crystal repeat distances of $a = 7.05 \pm 0.33$ and $c = 4.14 \pm 0.02$ Å, in agreement with literature values of 6.99 and 4.13 Å, respectively.[6,7]

NMR Experiments. NMR spectra were obtained using a modified Bruker WP-200 system at 43.02 MHz (4.7 T).[8] Spectra of both anhydrous compounds were obtained by Bloch decay; 6.7 μs 90° pulse at 64 W power, 5–300 s recycle delay. MAS experiments were performed with a nominal 3 KHz spinning rate. Solution chemical shifts were determined for 0.01 and 0.004 molar aqueous K_2PtCl_4 and the spin–

[†] Present address: National Institutes of Health, Building 30, Room 106, NIDR, Bethesda, MD 20892.

(1) (a) Honkonen, R. S.; Doty, F. D.; Ellis, P. D. *J. Am. Chem. Soc.* **1983**, *105*, 4163. (b) Honkonen, R. S.; Ellis, P. D. *Ibid.* **1984**, *106*, 5488. (c) Marchetti, P. S.; Honkonen, R. S.; Ellis, P. D. *Ibid.*, in press.

(2) Lallemand, J.-Y.; Soulie, J.; Chottard, J.-C. *J. Chem. Soc., Chem. Commun.* **1980**, 436.

(3) Dechter, J. J.; Kowalewski, J. *J. Magn. Reson.* **1984**, *59*, 146.

(4) Doddrell, D. M.; Barron, P. F.; Clegg, D. E.; Bower, C. *J. Chem. Soc., Chem. Commun.* **1982**, 575.

(5) Dixon, W. T. *J. Chem. Phys.* **1982**, *77*, 1800.

(6) Wyckoff, R. W. G. *Crystal Structures*, 2nd ed.; Interscience: 1965; Vol. 3, p 339–340.

(7) Wyckoff, R. W. G. *Crystal Structures*, 2nd ed.; Interscience: 1965; Vol. 3, p 69–70.

(8) Inners, R. R.; Doty, F. D.; Garber, A. R.; Ellis, P. D. *J. Magn. Reson.* **1981**, *45*, 503.

0002-7863/86/1508-3215$01.50/0

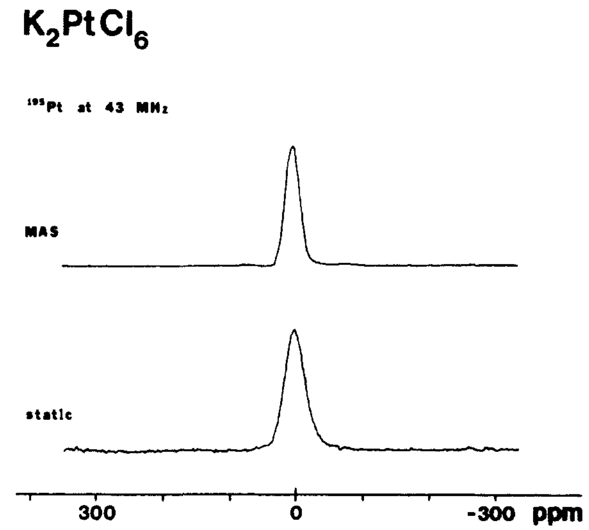

Figure 1. The ^{195}Pt static and powder spectra of anhydrous potassium hexachloroplatinate(IV) are shown. Each spectrum represents 1024 acquisitions, 84 min, by using a 90° pulse of 9.6 μs. One ppm of line broadening was applied to natural line widths of 34 ± 1 ppm for static and MAS cases, respectively. The MAS rate was approximately 3 KHz.

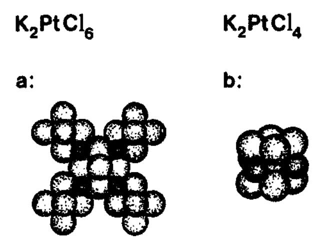

Figure 2. Packing drawings of K_2PtCl_6 and K_2PtCl_4 are shown. Chlorine atoms are represented by spheres with light shading; potassium cations by heavier shading. Platinum is obscured (a) by surrounding chlorine octahedra and (b) by the tetrachloro plane. The structures are redrawn from 6, 7.

lattice relaxation rate by inversion-recovery at 0.01 molar. All experiments were performed at ambient temperature.

Results and Discussion

Platinum(IV). The static and magic angle spinning (MAS) ^{195}Pt NMR powder spectra of potassium hexachloroplatinate(IV) are shown in Figure 1. The static line width of 34 ppm (1.5 KHz), relatively narrow by solid state platinum NMR standards, has been narrowed to 24 ppm by magic angle spinning at 3 KHz. The source of the 10 ppm line width contribution suppressed by MAS in K_2PtCl_6 is restricted by group symmetry arguments based on the known crystal structure.[6]

As shown in Figure 2a, each platinum nucleus is surrounded by a regular octahedron of six chlorine nuclei. Potassium cations are spaced equidistantly from 12 chlorine nuclei, three from each of four surrounding $(PtCl_6)^{2-}$ octahedra. Four molecules are therefore required per unit cell.[6] The extreme regularity in crystal structure, however, allows each of the four platinum nuclei to be translated to the cell origin with complete regeneration of the original crystal lattice.[9] Group theoretical arguments therefore require the four platinum shielding tensors to be fully degenerate. In addition, the platinum sites take on the full symmetry of the crystal point, O_h.[7,10] The octahedral site symmetry of the platinum nucleus constrains the ^{195}Pt shielding tensor to be isotropic.[11] The line narrowing seen in Figure 1, then, is not due to suppression of chemical shift anisotropy but to another influence having similar angular dependence.

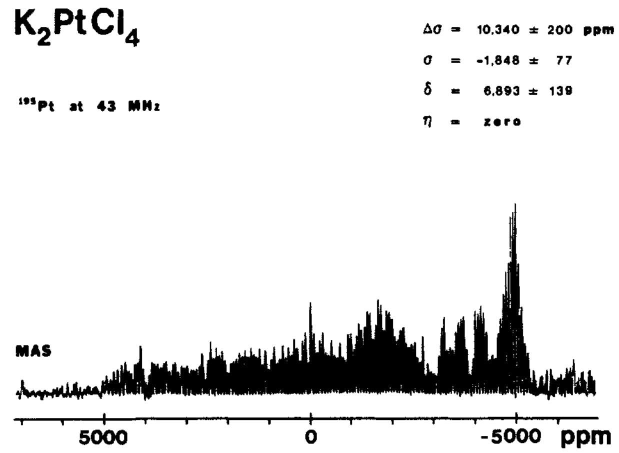

Figure 3. A composite ^{195}Pt MAS spectrum of anhydrous potassium tetrachloroplatinate(II) is shown. The composite spectrum is composed of seven overlapping 100-KHz (2324-ppm) spectra taken with nominal spinning rate of 3 kHz, 90° pulse (9.6 μs), 5-s recycle time. Modulation of sideband intensity results from Nyquist folding and filter attenuation. The base line is artificially flattened. The intense sideband at zero ppm is from K_2PtCl_6 impurity.

Dipolar coupling of spin 1/2 platinum to neighboring quadrupolar chlorine nuclei is an expected source of line broadening in these compounds. For a single platinum–chlorine coupling through a bond possessing an axially symmetric electric field gradient, the line width about the isotropic frequency is given by[12]

$$\Delta\omega = \frac{\gamma_I \gamma_S \hbar}{r^3}\left\{\langle S_z\rangle(3\cos^2\theta - 1) + \frac{3}{2}\langle S_x\rangle \sin(2\theta)\right\} \quad (1)$$

where θ is the angle between the internuclear vector and the static magnetic field, r is the magnitude of the internuclear vector, and $\langle S_{x,z}\rangle = \langle\phi|S_{x,z}|\phi\rangle$ determines the quantization axes of quadrupolar spin S in its eigenstates $|\phi\rangle$.

For K_2PtCl_6 with internuclear distance of 2.341 Å,[6] the interaction strength of eq 1 is found to be 95 Hz. The magnitude of the remaining factors in this equation depend upon the strength of chlorine quadrupole coupling and upon crystallite orientation in the magnetic field. Quantitative analysis is hampered by the presence of six couplings to either of two quadrupolar chlorine nuclei: 75% abundant ^{35}Cl or 25% abundant ^{37}Cl. The two line width data of Figure 1 are sufficient to determine approximate magnitudes of the two terms if other contributions to line width are not large.[13]

The 10-ppm (430-Hz) reduction to the residual line width of 24 ppm (1032 Hz) limits $\langle S_z\rangle$ to a value between 0.65 and 2.26. By like calculation, $\langle S_x\rangle$ has a maximum value of 11.56 and a minimum value determined by other contributions to line width. The relative magnitudes of terms indicate that platinum–chlorine dipolar couplings in single-crystal K_2PtCl_6 or similar chloro–platinum compounds line widths will be dominated by effects having minimum influence for perpendicular or parallel orientation of the chlorine–platinum bond in the magnetic field, maximum for the intermediate orientation. In particular, single-crystal line widths of square planar K_2PtCl_4 may be expected to vary between a minimum of ten(s) of ppm for parallel or perpendicular orientation of the chlorine plane to a maximum of tens or hundreds of ppm when $\theta = 45°$.

---

(9) *International Tables for Crystallography*, Hahn, T. Ed.; Space-Group Symmetry; D. Reidel: 1983; Vol. A, pp 678–681.

(10) Weil, J. A.; Buch, T.; Clapp, J. E. *Advances in Magnetic Resonance*; "Crystal Point Group Symmetry and Microscopic Tensor Properties in Magnetic Resonance Spectroscopy"; 1973; Vol. 6, pp 200–206m.

(11) (a) Buckingham, A. D.; Malm, S. M. *Mol. Phys.* **1971**, *22*, 1127–30. (b) Nye, J. F. *Physical Properties of Crystals*; Oxford University: 1967; pp 22–24. (c) Bhagavantam, S. *Crystal Symmetry and Crystal Properties*; Academic Press: 1966; pp 72–78.

(12) VanderHart, D. L.; Gutowsky, H. S.; Farrar, T. C. *J. Am. Chem. Soc.* **1967**, *89*, 5056.

(13) Another possible contribution to the observed ^{195}Pt line width that would remain invariant to MAS methods is the indirect scalar coupling to the six chlorines. Such a coupling is not expected to be large, and the value of the coupling should be independent of orientation of the $PtCl_6$ with respect to the field. However, the number of magnetically nonequivalent chlorines will not be independent of the direction of the field.

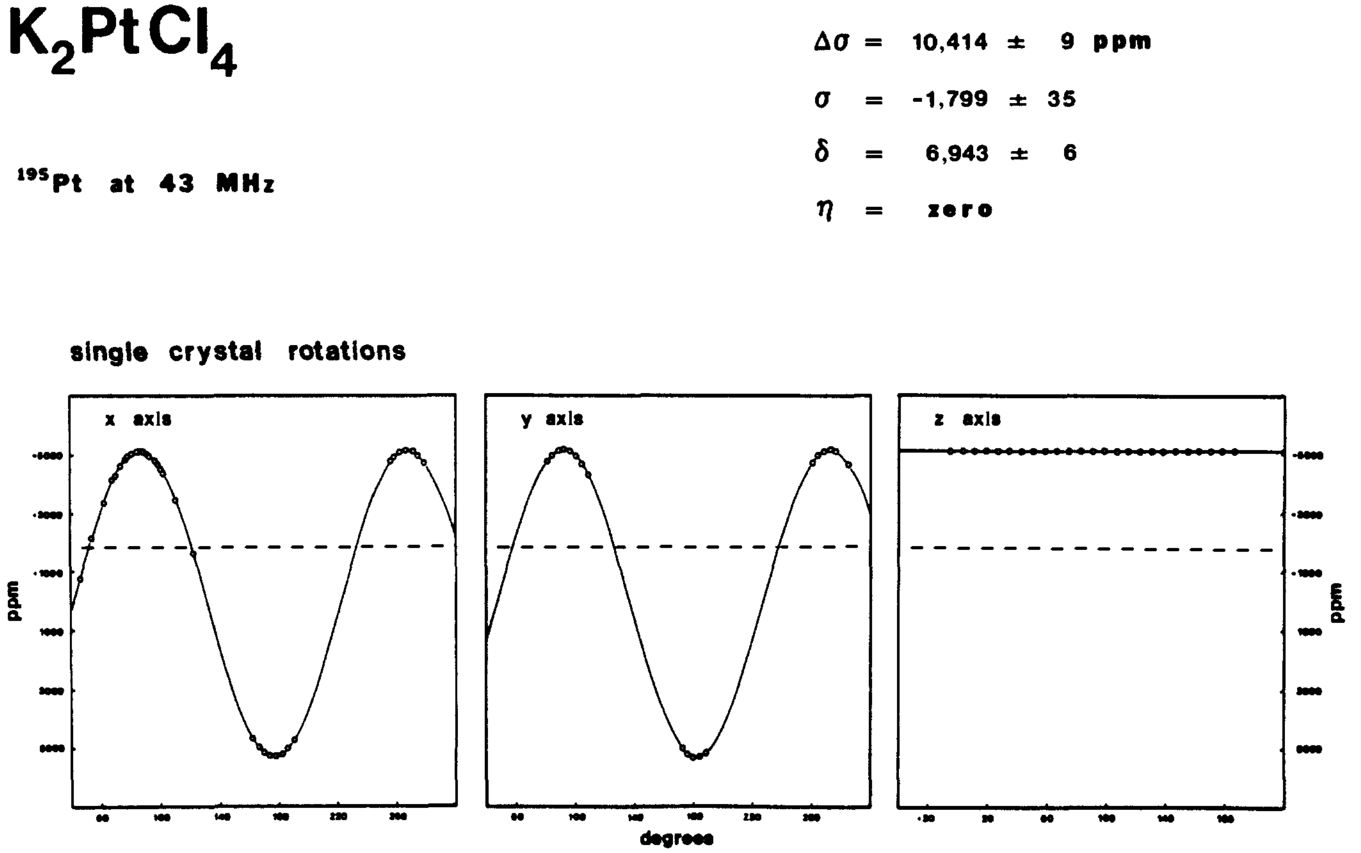

Figure 4. Chemical shift vs. goniometer angle is plotted for three orthogonal rotations of single crystal K_2PtCl_4. The X and Y rotation data are clustered about certain goniometer angles for sensitivity reasons, as discussed in text. The dashed line indicates the isotropic shielding frequency.

The simplicity of isotropically shielded K_2PtCl_6, then, allows separation and magnitude estimates of mechanisms important in other chloro-platinum compounds. In addition, the complete lack of chemical shift anisotropy, relatively narrow line width, chemical stability, and high signal intensity attainable with K_2PtCl_6 make this an attractive chemical shift reference and will be employed as such in the following discussion of divalent platinum in K_2PtCl_4.

Platinum(II). Platinum in its square planar coordination arrangement is exemplified by potassium tetrachloroplatinate(II). This compound crystallizes in the tetragonal system with the atomic arrangement illustrated by the packing drawing of Figure 2b. Each unit cell contains one molecule.[7] Platinum nuclei are surrounded by four chlorine atoms, arranged in a plane. Potassium cations, each having eight chlorine neighbors, bridge the ($PtCl_4^{2-}$) groups. With platinum in special position at the origin, the platinum site symmetry again coincides with the crystal point group, in this case D_{4h}.[1,7] The symmetry constraints on the ^{195}Pt shielding tensor require axial symmetry.[11]

The MAS powder spectrum of anhydrous K_2PtCl_4 is shown in Figure 3. This spectrum is a composite of seven individual overlapping 2324-ppm (100-KHz) spectra. The composite spectrum is subject to sideband intensity modulation due to folding of sidebands about the Nyquist frequency in individual spectra and to filter attenuation at spectra edges. The composite spectrum and crystal group symmetry arguments together establish unique and nonunique shielding elements respectively of +5045 ppm and −5295 ppm, the unique axis coincident with the crystallographic *c* direction. The 10340-ppm shift anisotropy, approximately 1% of the static field strength, is the largest yet determined for ^{195}Pt in either the 2+ or 4+ valence state.[14]

Results of the single-crystal study, shown in Figure 4, confirm the presence of a single shielding tensor and serve to refine the anisotropy determination to 10414 ± 9 ppm. The unique axis of the shielding tensor is nearly coincident with the *z* axis of the cube frame as evidenced by the linearity of the *z* rotation chemical shift data. Rotation of the crystal about this axis leaves the platinum-chlorine plane oriented parallel to the field. In this rotation, the platinum line width varies little from its 24 ± 3 ppm minimum. In contrast, rotation about *x* or *y* axes causes line width changes of several hundred ppm. Representative line widths are 21 and 31 ppm for parallel ($\theta = 90°$) and perpendicular ($\theta = 0°$, 180°) orientations, respectively. Intermediate orientations are associated with extreme broadening, as shown in Figure 5. Interpolation indicates a maximum line width of 340 ppm at θ = 45 and 135°.

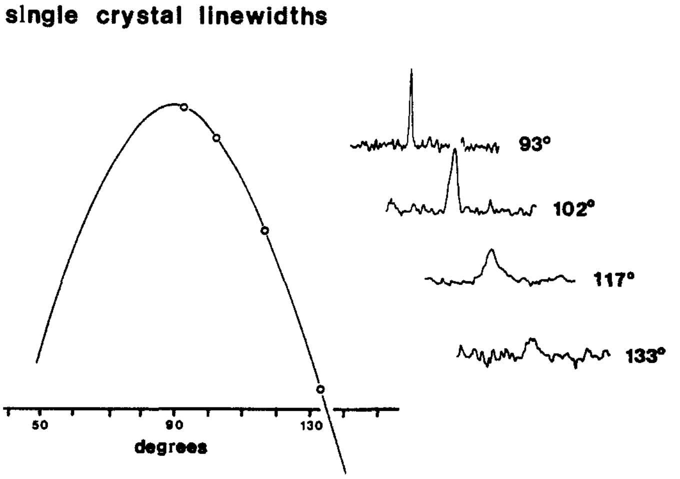

Figure 5. Single-crystal line widths of ^{195}Pt in K_2PtCl_4 are shown. Line widths are most narrow for parallel and perpendicular orientations of the platinum-chlorine bonds, about 20 ppm, and reach an interpolated value of 340 ppm between. Broadening is a sinusoidal function of twice the goniometer angle. Representative spectra are shown from both X and Y rotation experiments.

This loss of signal-to-noise is compounded by relaxation effects. The spin-lattice relaxation time, T_1, is 5.9 ± 0.4 s for parallel orientation of the chlorine-platinum plane, increasing to 21.0 ±

---

[14] Sparks, S. W.; Ellis, P. D., unpublished results.

1.4 s when tilted 28° away. T_1 measurement at the 45° orientation was not feasible, the long relaxation time and broad line shapes combining to make acquisition of single-crystal platinum spectra prohibitive. In Figure 5, the narrow resonance at 93° required 2.3 min acquisition time; the broad resonance at 133°, 1.7 h. For practical reasons, then, we have used platinum chemical shift data clustered about specific crystal orientations to define the phase and amplitude of the single-crystal rotation curves.

Solution. Potassium tetrachloroplatinate(II) provides an important test case for ^{195}Pt solution NMR spectra. In dilute solution, K_2PtCl_4 exists as K^+ and $(PtCl_4)^{2-}$ ions. Hydration of the tetrachloro–platinum anion does not appreciably disturb the platinum–chloride bonds or their symmetry. In this special case, the shielding elements lying in the platinum–chloride plane will be little affected by weak solvation. The solution state CSA can therefore be calculated from the known shielding elements lying in the platinum–chloride plane, −5270 ppm, and the solution isotropic resonance. In 0.01 and 0.004 molar aqueous solution, the solution peak appears at −1735 ± 39 ppm, shifted only 64 ppm from its value in the solid. The unique shielding element is calculated to be +5255 ppm and the anisotropy 10485 ppm.

Such a large anisotropy allows the CSA relaxation mechanism to dominate many platinum NMR characteristics. In 0.01 M solution and at 4.7 T, the platinum relaxation rate is 3 s^{-1}. Reorientation of the chloroplatinum anion, to a very good approximation, may be considered isotropic. Simple calculation shows that correlation times of 2–3 ps completely account for observed relaxation.

Conclusion. Shielding tensor elements and anisotropies have been determined for potassium tetrachloroplatinate(II) in both solid and solution and for potassium hexachloroplatinate(IV) in the solid state. These measurements constitute the first direct evidence of 10000-ppm anisotropies in solid- and solution-state platinum compounds. This has important implications in platinum NMR studies.

In the solid state, K_2PtCl_4 and K_2PtCl_6 possess simplified shielding tensors due to crystal symmetry. It is generally not the case that all platinum nuclei will have a single shielding tensor or degenerate tensors. As a rule, static and MAS platinum spectra will consist of superimposed line shapes spanning several thousand ppm. Single-crystal rotation experiments, particularly in conjunction with known X-ray crystal structures, are shown to circumvent the difficulty of extracting reliable information.

In single-crystal chloroplatinum compounds, strong dipolar coupling to quadrupolar chlorine dominates platinum line widths. While this results in some difficulty in measurement, the angular dependence of the broadening provides information on shielding tensor orientation independent of X-ray studies or symmetry arguments. In K_2PtCl_4, line broadening alone allows complete determination of the orientation of the shielding tensor. In compounds of lower symmetry, this information will allow assignment of shielding tensors to nonequivalent platinum nuclei.

In solution, parts per thousand and part per hundred anisotropies cause relaxation to be dominated by the CSA mechanism for all reasonable values of correlation times at even moderate field strengths. In the dinucleoside monophosphate platinate(II) model systems of platinum antitumor drugs, slow correlation times make CSA relaxation much more effective. The broadening of platinum resonances and the decoupling of platinum from other spin $^1/_2$ nuclei observed in these model systems arises from platinum(II) chemical shift anisotropy.

Acknowledgment. We thank the National Science Foundation through Grants CHE 83-06580 and CHE 8207445. The latter in support of the RIF in NMR spectroscopy at the University of South Carolina.

Elucidation of the Mechanism and Kinetics of the Si, Al Ordering Process in Synthetic Magnesium Cordierite by ^{29}Si Magic Angle Spinning NMR Spectroscopy

Colin A. Fyfe,*† Gian C. Gobbi,† and Andrew Putnis‡

Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada, and the Department of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, England.

Received June 19, 1985

Abstract: The course of Si, Al ordering in synthetic magnesium cordierite was determined from the high-field (9.4 T) ^{29}Si MAS NMR spectra of samples annealed from the glass precursor at 1185 °C for various periods of time. The results indicate that the driving force of the ordering process is the establishment of Loewenstein's aluminum avoidance principle in the structure of orthorhombic cordierite and that the hexagonal-orthorhombic ordering transformation takes place by an apparently continuous mechanism via a sequence of intermediate structural states. The Si, Al ordering process was found to be approximately linear with log time, consistent with the continuous transformation mechanism proposed previously, and involves a net migration of silicon from rings to chains within the structure and rearrangements within the rings via a series of $Si^{T_2} \rightleftharpoons Al^{T_1}$ and $Si^{T_2} \rightleftharpoons Al^{T_2}$ exchanges.

Magnesium cordierite, $Mg_2Al_4Si_5O_{18}$, occurs in two polymorphic forms. In the high-temperature hexagonal structure, space group *P*6/*mcc*, stable above ~1450 °C.[1,2] the Al and Si atoms are distributed over two sets of tetrahedral sites—three T_1 and six T_2 sites per formula unit, with Mg in octahedral coordination. In a structure refinement of indialite, the naturally occurring hexagonal polymorph of magnesium cordierite, it was suggested[3] that the Al, Si distribution involved 2.2 Al and 0.8 Si atoms disordered over the T_1 sites and 1.8 Al and 4.2 Si disordered over the T_2 sites. In the slightly distorted, low-temperature (<1450 °C) orthorhombic polymorph, space group *Cccm*, the T_1 sites are

---

† University of Guelph.

‡ University of Cambridge.

(1) Schreyer, W.; Schairer, J. F. *J. Petrol.* **1961**, *2*, 324.

(2) Putnis, A. *Contrib. Mineral. Petrol.* **1980**, *74*, 135.

(3) Meagher, E. P.; Gibbs, G. V. *Can. Mineral.*, **1977**, *15*, 43.