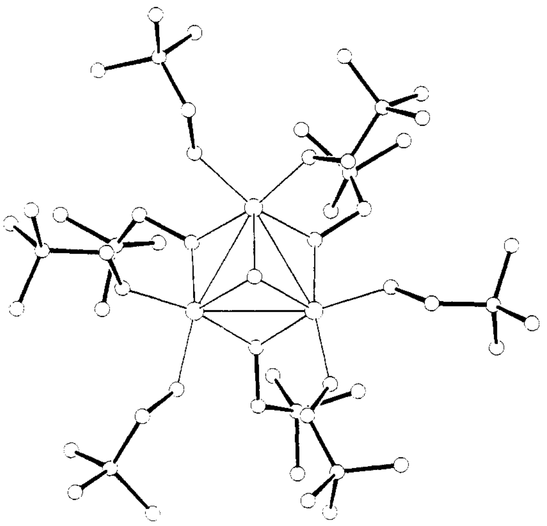

Figure 1. A ball-and-stick drawing of the $W_3(\mu_3\text{-}P)(\mu\text{-}OCH_2\text{-}t\text{-}Bu)_3(OCH_2\text{-}t\text{-}Bu)_6$ molecule. Pertinent bond distances and angles are given in the text. The molecule has a crystallographically imposed C_3 axis of symmetry.

In the space group R_3, there are two independent $W_3(\mu_3\text{-}P)(\mu\text{-}OCH_2\text{-}t\text{-}Bu)_3(OCH_2\text{-}t\text{-}Bu)_6$ molecules in the unit cell. Each molecule has crystallographically imposed C_3 symmetry, and the two molecules are virtually superimposable, differing so little that all parameters are virtually equivalent within the criteria of 3σ. A view of one of the molecules is given in Figure 1.

Each tungsten atom is in a square-based-pyramidal coordination geometry with the W-P bond occupying the axial site; W-P = 2.365(4) Å. The W-W distance is 2.757 (1) Å, and the angles within the distorted W_3P tetrahedron are W-W-W = 60°, W-P-W = 71.3 (1)°, and P-W-W = 54.3 (1)°. the W-O(terminal) and W-O(bridging) distances are 1.92 (1) and 2.05 (2) Å (average), respectively. Structurally and electronically the clusters $W_3(\mu_3\text{-}X)(\mu\text{-}OR)_3(OR)_6$ where X = CMe[9] and P are closely related. Of course, RC and P are isolobal,[10] and we have previously reported the characterization of $W_2(\mu\text{-}X_2)(OR)_6(py)_n$ compounds where n = 1 or 2 and X = CH[11] and P.[12] Also, the $(\eta^3\text{-}C_3R_3)$ moiety seen in the molecular structure of $(Me_2NCH_2CH_2NMe_2)Cl_3W(\eta^3\text{-}C_3Me_2(t\text{-}Bu))$[13] is isolobal with the $(\eta^3\text{-}P_3)$ moiety in $(HNMe_2)(t\text{-}BuCH_2O)_3W(\eta^3\text{-}P_3)$. Given the extensive chemistry of $(RO)_3W{\equiv}CR'$ compounds[14] and to a lesser extent $(RO)_3W{\equiv}N$ compounds,[15] we suggest a similar chemistry for $(RO)_3W{\equiv}P$.[16] In particular, the formation of $W_3(\mu_3\text{-}P)(OCH_2\text{-}t\text{-}Bu)_9$ in eq 1 could well follow the reaction scheme outlined in eq 2.

$$W_2(OR)_6 + P_4 \xrightarrow{\text{slow}} W_2(OR)_6(P_4) \quad (2a)$$

$$W_2(OR)_6(P_4) \xrightarrow{\text{fast}} (RO)_3W(\eta^3\text{-}P_3) + (RO)_3W{\equiv}P \quad (2b)$$

$$W_2(OR)_6 + (RO)_3W{\equiv}P \xrightarrow{\text{fast}} W_3(\mu_3\text{-}P)(\mu\text{-}OR)_3(OR)_6 \quad (2c)$$

It should be noted that (1) P_4 metal-containing compounds are known,[17] (2) asymmetric cleavage of $(RO)_3M{\equiv}M(OR)_3$ compounds,[18] as well as $Cp(CO)_2M{\equiv}M(CO)_2Cp$ compounds[19] (M = Mo, W), is well documented, and (3) the comproportionation reaction, reaction 2c, has ample precedent in the preparation of $W_3(\mu_3\text{-}CR')(OR)_9$,[20] $W_3(\mu_3\text{-}O)(OR)_{10}$,[21] and $W_3(\mu_3\text{-}NH)(OR)_{10}$ compounds.[22] Also, given the existence of phosphaalkyne compounds,[23] $RC{\equiv}P$, and the propensity, perhaps above all other metals, for tunsten to form $W{\equiv}CR$ bonds, we believe the quest for compounds containing $W{\equiv}P$ bonds will shortly be fulfilled.[24]

Registry No. $W_2(OCH_2\text{-}t\text{-}Bu)_6(HNMe_2)_2$, 83437-02-9; P_4, 12185-10-3; $W_3(P)(OCH_2\text{-}t\text{-}Bu)_9$, 115436-98-1.

Supplementary Material Available: A complete listing of atomic coordinates for $W_3(\mu_3\text{-}P)(\mu\text{-}OCH_2\text{-}t\text{-}Bu)_3(OCH_2\text{-}t\text{-}Bu)_6$ (3 pages). Ordering information is given on any current masthead page.

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Experimental Determination of the ^{27}Al NMR Quadrupole Coupling Constant of the Hexaaquoaluminum Ion in Aqueous Perchloric Acid and Mixed Acetone-Aqueous Perchloric Acid Solution

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The ^{27}Al nucleus is quadrupolar, having a nuclear spin, I, of $^5/_2$ and a quadrupole moment, Q, of 0.149×10^{-24} cm^2. Interaction of the quadrupole moment with local electric field gradients couple the nucleus to molecular motions, thereby giving rise to an efficient magnetic relaxation mechanism.[1] Electric field gradients are generated or imposed about the ^{27}Al nucleus by the ligand field asymmetry of ligands or solvent molecules bound to the aluminum(III) metal ion. In the limit of fast motion, nuclear spin quadrupolar relaxation is governed by eq 1, where T_Q, T_1,

$$\frac{1}{T_Q} = \frac{1}{T_1} = \frac{1}{T_2} = \frac{3}{40}\left[\frac{2I+3}{I^2(2I-1)}\right]\left(\frac{\eta^2}{3} + 1\right)\left(\frac{e^2qQ}{\hbar}\right)^2 \tau_c \quad (1)$$

and T_2 are the quadrupolar, spin-lattice, and spin-spin relaxation

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Table I. ^{27}Al NMR Line Width and Spin–Spin Relaxation Rate of the Hexaaquoaluminum Ion in Aqueous Perchloric Acid and Mixed Acetone/Aqueous Perchloric Acid Solution[a]

pt no.	mole fraction of acetone, X_{Me_2CO}	T, K	$\Delta\nu_{1/2}$, Hz[b]	$1/T_2$, s^{-1} [c]	viscosity, cP[d]	$10^{10}\tau_c$, s[e]	δ_{Al}[f]
1	0.00	334	1.18	3.71	0.5395	0.364	0.45
2	0.00	320	1.40	4.40	0.6184	0.435	0.27
3	0.00	310	1.93	6.06	0.7500	0.545	0.19
4	0.00	295	2.46	7.73	0.9342	0.714[g]	0.0
5	0.05	295	3.33	10.46	1.338	1.022	−0.07
6	0.07	295	4.30	13.51	1.469	1.122	−0.11
7	0.10	295	4.48	14.07	1.562	1.193	−0.13

[a] Line width of $Al(H_2O)_6^{3+}$ resonance measured instrumentally with a JEOL Model FX-90Q spectrometer equipped with a 5-mm omnitunable probe and a JEOL Model NM-TVS temperature controller: w_0 = 23.348 MHz; spectral width 110 Hz. $[HClO_4]$ = 1.0 M and $[Al(NO_3)_3]$ = 0.10 M for all samples. The temperature inside the probe was calibrated to within ±0.5 °C by using the proton shift (in Hz) for a sample of ethylene glycol. [b] Multiple measurements on single samples and single measurements on multiple samples indicate an uncertainty in $\Delta\nu_{1/2}$ data of ±5%. [c] Calculated from the relation $\pi(\Delta\nu_{1/2}) = 1/T_2$, by using $\Delta\nu_{1/2}$ data in this table. [d] Viscosity data in centipoises for 1 M aqueous perchloric acid solutions were extrapolated from data taken from ref 5. Viscosity data in centipoises for acetone/H_2O mixtures were extrapolated from data taken from ref 6. [e] Calculated from the Gierer–Wirtz formula, $\tau_c = f4\pi r^3\eta/3k_BT$, where η is the viscosity of aqueous perchloric acid or the acetone/H_2O mixture, r is the molecular radius of $Al(H_2O)_6^{3+}$ (5.05 Å) as reported by Fong and Grunwald,[7] f is the microviscosity correction factor $(=[6(a_s/a) + (1 + a_s/a)^{-3}]^{-1} = 0.5767)$ associated with the Gierer–Wirtz model[9] where a_s/a was taken to be 0.96 Å/5.05 Å = 0.1901 for this system, T is the absolute temperature, and k_B is Boltzmann's constant. [f] Positive shifts are downfield, and negative shifts are upfield from an $Al(H_2O)_6^{3+}$ reference standard at 22 °C (295 K) in 1.0 M aqueous perchloric acid solution. [g] Although values of τ_c are influenced by the value of r used, this value of τ_c for $Al(H_2O)_6^{3+}$ at 22 °C in 1.0 M $HClO_4$(aq) is very reasonable compared to that reported for $Al(H_2O)_6^{3+}$ in neat H_2O at 25 °C of (5.3 ± 1.3) × 10^{-11} s.[10]

times, respectively, I is the nuclear spin, eQ is the electric quadrupole moment, eq is the electric field gradient, n is the deviation of the electric field gradient from axial symmetry, $\hbar$ is Plank's constant divided by 2π, and τ_c is the rotational correlation time.[2]

The extent to which the electric quadrupole moment (eQ) is coupled to electric field gradients present in a given complex is known as the quadrupole coupling constant (QCC) and can be expressed quantitatively by eq 2. Due to its highly symmetric,

$$\mathrm{QCC} = \left(\frac{n^2}{3} + 1\right)^{1/2}\left(\frac{e^2qQ}{\hbar}\right) \qquad (2)$$

octahedral arrangement of H_2O molecules, the hexaaquo ion $Al(H_2O)_6^{3+}$ relaxes very slowly, gives rise to very narrow ^{27}Al NMR resonances, and would be expected to possess a vanishingly small value of QCC. Haraguchi and Fujiwara[3] have reported a value of QCC for $Al(H_2O)_6^{3+}$ of 1 MHz by using an experimental line width of 40 Hz for the $Al(H_2O)_6^{3+}$ resonance in aqueous acid solution at 25 °C and estimating the rotational correlation time of a rigid sphere with a radius of 3 Å as 5 × 10^{-11} s. Takahashi[4] has treated the internal rotations of coordinated water molecules about their C_2 axes using a jump model involving two overall configurations of T_h and C_{2v} symmetries for which $eq = 0$ and $eq = 1.97 \times 10^{13}$ erg/(esu·cm^2), respectively. From the latter value of eq we calculate a value of QCC of 1.3 MHz for $Al(H_2O)_6^{3+}$. These values of QCC for $Al(H_2O)_6^{3+}$ are reasonable, but to our knowledge an experimental confirmation has not been reported.

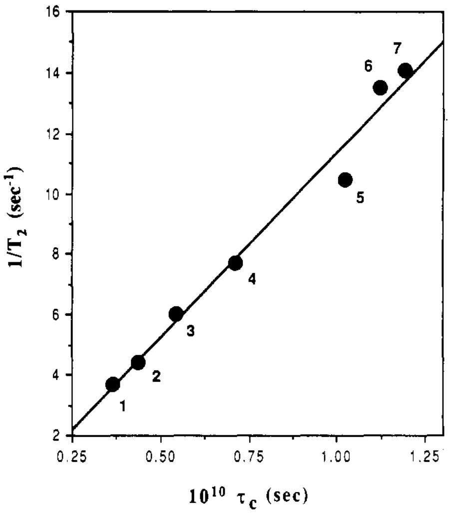

Figure 1. Plot of $1/T_2$ (s^{-1}) as a function of τ_c (s) for the hexaaquoaluminum ion. Data point numbers correspond to Table I. Slope of the line defined by points 1–4 equals 1.17 (0.08) × 10^{11} s^{-2} (intercept −0.5691 (0.4003); R = 0.922); see text.

Herein, we report an indirect experimental determination of QCC for $Al(H_2O)_6^{3+}$ in aqueous perchloric acid solution over the temperature range 22–61 °C. We also show that QCC at 22 °C does not change in acetone/H_2O mixtures having a limiting acetone mole fraction (X) of 0.10. This latter observation serves as an independent confirmation that acetone does not coordinate to the Al^{3+}(aq) cation at these acetone mole fractions.

^{27}Al NMR line width data (Table I) for a 0.1 M aluminum nitrate solution in 1.0 M aqueous perchloric acid show a sharpening of the $Al(H_2O)_6^{3+}$ resonance upon increasing temperature. The chemical shift of the $Al(H_2O)_6^{3+}$ resonance is also temperature-dependent as evidenced by a downfield shift upon going from 22 to 61 °C (Table I). Sharpening of the $Al(H_2O)_6^{3+}$ resonance upon going to higher temperatures is interpreted as being due to the effect of the correlation time (τ_c) on the quadrupolar relaxation rate ($1/T_Q$) of the ^{27}Al nucleus at the center of the complex ion. Table I summarizes the temperature dependence of the ^{27}Al NMR line width ($\Delta\nu_{1/2}$), spin–spin relaxation rate ($1/T_2$), correlation time (τ_c), and ^{27}Al NMR chemical shift (δ_{Al}) data for the hexaaquoaluminum ion in aqueous perchloric acid solution.

A plot of $1/T_2$ (s^{-1}) as a function of τ_c (s) over the temperature range from 22 to 61 °C (points 1–4 in Table I) yields the straight line shown in Figure 1 having a slope of 1.17 (0.08) × 10^{11} s^{-2}. Due to the relatively large error associated with the intercept, this line essentially passes through the origin, given the experimental uncertainty in $\Delta\nu_{1/2}$ of ±5%. Setting the slope of this line equal to the term $\{3(2I + 3)/40[I^2(2I - 1)]\}(\mathrm{QCC})^2$ in eq 1 gives a value of the quadrupole coupling constant (QCC) of 1.6 (0.1) MHz for the hexaaquoaluminum ion in 1.0 M aqueous perchloric acid solution. Since QCC ∝ $\Delta\nu_{1/2}$, it should be pointed out that the precision of QCC is no better than the precision of the $\Delta\nu_{1/2}$ measurements. Furthermore, viscosity values were determined indirectly by extrapolation (exponential curve fitting) of existing data for $HClO_4$(aq) solutions.[5]

Even after consideration of empirical limitations, our determination of QCC is in reasonable agreement with both the value of 1 MHz estimated by Haraguchi and Fujiwara[3] and the value of 1.3 MHz that we calculate from the eq value reported by Takahashi.[4] As a result, our experimentally determined value of QCC confirms previously reported estimated and calculated values, which, in turn, supports the interpretation that sharpening of the $Al(H_2O)_6^{3+}$ resonance upon increasing temperature is due to quadrupolar relaxation effects.

The experimental results for a series of 0.1 M aluminum nitrate solutions in 1.0 M $HClO_4$(aq) at 22 °C that contained increasing

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mole fractions of acetone are also summarized in Table I (points 4–7). In light of the discussion above, the increased line width of the $Al(H_2O)_6^{3+}$ resonance upon addition of acetone is interpreted as being due to a decrease in the molecular tumbling rate (increased correlation time) of the hexaaquoaluminum ion in a more viscous solvent medium. The viscosity of these mixtures increases to a maximum at an acetone mole fraction of 0.15 and then decreases steadily until it reaches a minimum at an acetone mole fraction of 1.0.[6] These experimental data have been included in Figure 1 (points 4–7) to show that, up to an acetone mole fraction of 0.10, the data obtained in acetone/aqueous acid fall along the same line as those obtained in aqueous acid solution. The slope of the plot of $1/T_2$ (s^{-1}) versus τ_c (s) shown in Figure 1 does not change (within experimental error) from that when only points 1–4 are plotted. Therefore, there is no change in QCC upon addition of acetone, which indicates that the integrity of the $Al(H_2O)_6^{3+}$ complex is preserved at acetone mole fractions of 0.10 or less.

These results demonstrate that the increased line width of the $Al(H_2O)_6^{3+}$ resonance upon going from an aqueous perchloric acid solution to an acetone–aqueous perchloric acid solution ($X_{Me_2CO} \leq 0.10$) cannot be attributed to coordination of the Al^{3+}(aq) cation by acetone or to acetone/H_2O exchange on $Al(H_2O)_6^{3+}$. Solvation studies in water/acetone mixtures[11–14] have shown that acetone is unable to coordinate the Al^{3+}(aq) cation and that there is a direct correlation between solvent basicity and coordinating ability.

Through experiments similar to those just described for $Al(H_2O)_6^{3+}$, we have also determined QCC over the temperature range 4–96 °C for tris(acetohydroxamato)aluminum(III) ($Al(CH_3C(O)N(O))_3$) in aqueous solution to be 28.1 (2.2) MHz. Comparison of QCC for $Al(CH_3C(O)N(O))_3$ with that for $Al(H_2O)_6^{3+}$ (28 MHz versus 1.6 MHz, respectively) follows the reduction in molecular symmetry from C_{2v} in the case of $Al(H_2O)_6^{3+}$ to C_3 in the case of $Al(CH_3C(O)N(O))_3$. The aluminum nucleus at the center of the $Al(CH_3C(O)N(O))_3$ complex is clearly sensing the loss of purely octahedral symmetry due to the structural constraints imposed by hydroxamate coordination, which also includes the possibility of a mixed population of facial and meridional isomers.

Llinâs and DeMarco[15] have proposed that electric field gradients present in the alumichromes (aluminum(III) complexes of cyclic tris(hydroxamic acid) siderophores) originate mainly from coordination by the hydroxamate moiety and that the peptide chain of the alumichromes has little or no effect upon symmetry distortions. Comparison of the QCC values of $Al(CH_3C(O)N(O))_3$ and alumichrome C[15] with that of $Al(H_2O)_6^{3+}$ (28 and 34 MHz versus 1.6 MHz, respectively) suggests that appreciable ligand field asymmetry exists in a simple tris(hydroxamate) complex of aluminum(III). This observation is consistent with the conclusions of Llinâs and DeMarco.[15]

The QCC value of tris(acetylacetonato)aluminum(III), $Al(acac)_3$, has been determined to be 0.49 MHz by Dechter and co-workers.[16] If we consider that $Al(acac)_3$ possesses D_3 symmetry, comparison of the QCC values of $Al(acac)_3$ and $Al(CH_3C(O)N(O))_3$ (0.49 MHz versus 28 MHz) indicates that the six-membered ring of the acetylacetonate complex accommodates octahedral coordination better than the more constrained five-membered ring of the hydroxamate complex. Our experimentally determined value of QCC for $Al(H_2O)_6^{3+}$ is consistent with the Takahashi[4] jump model, which shows that $Al(H_2O)_6^{3+}$ relaxes only when in a C_{2v} configuration. It is then reasonable that $Al(acac)_3$ exhibits a smaller value of QCC than does $Al(H_2O)_6^{3+}$ by virtue of its higher symmetry.

This study experimentally confirms estimated and calculated values of QCC for $Al(H_2O)_6^{3+}$. Data in mixed acetone/water solvent mixtures indicate that the integrity of $Al(H_2O)_6^{3+}$ is preserved and acetone does not compete effectively with H_2O for coordination sites on the Al^{3+}(aq) cation when $X_{Me_2CO} \leq 0.10$. Our value of QCC for $Al(H_2O)_6^{3+}$ of 1.6 MHz compares favorably with the QCC values of other aluminum(III) complexes,[15,16] when differences in ligand field asymmetry are considered. These observations serve to illustrate the use of ^{27}Al NMR as a probe for the ligand field asymmetry in aluminum(III) complexes.

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Registry No. $Al(H_2O)_6^{3+}$, 15453-67-5; $HClO_4$, 7601-90-3.

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