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Oxygen-17 Nuclear Magnetic Resonance Studies on the Hydration of Organometallic Cations[1]

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Oxygen-17 nmr spectra have been obtained for aqueous solutions containing $(CH_3)_3PtClO_4$, $(CH_3)_2AuClO_4$, $(NH_3)_2Pt(ClO_4)_2$, $(CH_3)_2GaClO_4$, $In(ClO_4)_3$, and $(CH_3)_2Sn(ClO_4)_2$. In most of the experiments, $Dy(ClO_4)_3$ was used to shift the bulk water resonance in order to search for a bound water resonance. At 29°, *only one* water resonance is observed for $(CH_3)_3PtClO_4$ solutions, but both bulk and bound water signals are recorded at 5°. Three water molecules are bound as determined by the molal shift method, and this cation is *cis*-triaquotrimethylplatinum(IV). The $(CH_3)_2AuClO_4$ solutions exhibit only a single oxygen-17 resonance even at 5°. In contrast, solutions containing the $(NH_3)_2Pt^{2+}$ ion give both bound and bulk water resonances even at 85°, and the ion binds two water molecules completing the square plane about platinum(II) as was determined by integration of the two signals. The water molecules bound to Ga(III) in $(CH_3)_2GaClO_4$ solutions exchange much more rapidly than is the case with Ga^{3+}, and it was not possible to determine the hydration numbers of this organogallium ion or of In^{3+} or $(CH_3)_2Sn^{2+}$. By comparison of the oxygen-17 line widths of these solutions with those of $Dy(ClO_4)_3$ solutions, the following lifetimes for the bound water molecules and activation energies for exchange were estimated for 25° using approximate equations: $(CH_3)_3Pt^+$, 8×10^{-5} sec, 9 ± 1 kcal/mol; $(CH_3)_2Au^+$, 2×10^{-5} sec, 8 ± 2 kcal/mol; $(NH_3)_2Pt^{2+}$, *ca.* 1 sec (based on rate of a precipitation reaction); $(CH_3)_2Ga^+$, 1×10^{-5} sec (30°); In^{3+}, 3×10^{-5} sec, 5 ± 1 kcal/mol; $(CH_3)_2Sn^{2+}$, 1×10^{-5} sec, 6 ± 1.5 kcal/mol. Coordinated methyl groups are very effective in reducing the charge and in labilizing the other ligands in the first coordination sphere of metal ions.

Introduction

Metal ions containing one or more σ-bonded organo groups in the first coordination sphere form many interesting coordination compounds. Many of these organometallic cations are stable in aqueous solution as simple aquated species. The chemistry of the ions formed from Pt(IV), Au(III), Hg(II), Tl(III), Pb(IV), and Sn(IV) has been reviewed.[3] Recently, stable transition metal derivatives have been synthesized in aqueous systems. These include pyridino derivatives of Cr(III)[4,5] and alkyl derivatives of Rh(III).[6] In addition, the aquocobalamins can be considered members of this class with one coordination site about Co(III) occupied by a carbanion ligand and the position *trans* to it filled by a rather labile water molecule.[7,8]

The carbanion ligands markedly affect the properties of the metals which are formally in rather high oxidation states. For example, the compounds formed by the dimethyl derivatives of Sn(IV), Pb(IV), and Tl(III) are generally much more like compounds of Sn(II), Pb(II), and Tl(I), respectively, than they are like other compounds where the metal is in the higher oxidation state.[3]

Reactions involving these organometallic compounds normally proceed quite rapidly even with the derivatives of Pt(IV) and Au(III). In a brief communication, we have noted the rapidity with which water molecules exchange between the bulk water and the first coordination sphere of the trimethylplatinum(IV) ion.[9] In order to characterize the first coordination spheres of these organometallic cations in aqueous solution and to obtain information on the lability of the coordinated water molecules, we have carried out oxygen-17 nmr studies on the solutions.

Since Jackson, Lemons, and Taube[10] first reported that a separate nmr signal could be observed for water coordinated to a diamagnetic metal ion, this method has been applied to the study of the hydration of Be-

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(II),[11,12] Al(III),[11-13] and Ga(III).[13,14] In some of our measurements we have determined the intensity ratio of the free and coordinated water to obtain hydration numbers as was done by Connick and Fiat.[11] In order to minimize the enrichment in oxygen-17 required, we have also employed the molal shift method of Alei and Jackson.[12] In a recent paper,[13b] Fiat and Connick have summarized the oxygen-17 nmr studies on metal ion solvation.

Experimental Section

Oxygen-17-Enriched Water.—Water enriched in oxygen-17 up to the extent of 10 atom % was obtained from the Weizmann Institute, Rehovoth, Israel, and from ICN, City of Industry, Calif. Samples were vacuum distilled and collected under a nitrogen atmosphere on a vacuum line. Transfers were made using capillary droppers.

Preparation of Compounds. Dysprosium(III) Perchlorate.—Dysprosium oxide, 99.99% D_2O_3, obtained from Michigan Chemical Co., St. Louis, Mich., was dried for 48 hr at 130°. Weighed amounts of the oxide were dissolved in weighed standard perchloric acid at 80°. Any weight loss was attributed to the evaporation of water, and the solution compositions were corrected accordingly. The solutions were analyzed by precipitation as the oxalate which was ignited to Dy_2O_3 at 950°.[15]

***cis*-Trimethylplatinum(IV) Perchlorate.**—Trimethylplatinum iodide[16,17] (6.5 g, 0.03 mol) dissolved in 200 ml of benzene was treated with thallous nitrate (8.0 g, 0.03 mol) dissolved in 120 ml of a 1:5 v/v acetone–water solution. The mixture was stirred vigorously for 48 hr, and the organic layer was separated. The aqueous solution was filtered, and an NaOH solution was added to pH of 7 at which point $[(CH_3)_3PtOH]_4$[18] precipitated. The solid which was yellow due to iodide impurity was dissolved in nitric acid, silver nitrate was added until no further precipitation occurred, and the solution was neutralized to pH 7 with NaOH. White trimethylplatinum(IV) hydroxide precipitated before the excess silver ion. *Anal.* Calcd for $C_3H_{10}OPt$: C, 14.0; H, 3.92; O, 6.22; Pt, 75.8. Found: C, 14.0; H, 3.79; O, 5.45; Pt, 75.9. The hydroxide was dissolved in weighed amounts of standard perchloric acid with heating on a steam bath. The solution was filtered to remove traces of undissolved hydroxide and platinum which resulted from decomposition. Based on a platinum analysis, this solid accounted for less than 2% of the starting material. The solutions were concentrated by evaporation in a stream of dry nitrogen, and the weight difference due to water loss was considered in the calculations of the solution composition.

***cis*-Dimethylgold(III) Perchlorate.**—Dimethylgold(III) hydroxide[19] was dissolved in weighed quantities of standard perchloric acid at 0°. The hydroxide dissolved readily at this temperature.

***cis*-Diaquodiammineplatinum(II) Perchlorate.**—*cis*$PtCl_2(NH_3)_2$ was prepared from K_2PtCl_4 by the method of Kauffman and Cowan.[20] The crude product which contained several per cent of $[(NH_3)_4Pt][PtCl_4]$ was dissolved in hot dilute nitric acid, treated with excess silver perchlorate solution to precipitate all of the chloride, and digested for 15 min on a steam bath. The excess silver perchlorate precipitated the $PtCl_4^{2-}$ ion, since it was observed that the precipitate obtained by treating a solution of $K_2[PtCl_4]$ with excess $AgClO_4$ was pink and that the filtrate was colorless and contained no platinum. The excess silver ion was precipitated with sodium chloride solution until dichlorodiammineplatinum(II) just began to form. After filtration to remove the AgCl, excess NaCl solution was added to precipitate the yellow *cis*-dichlorodiammineplatinum(II); yield 21%. *Anal.* Calcd for $N_2H_6Cl_2Pt$: N, 9.34; H, 2.00; Cl, 23.6; Pt, 65.0. Found: N, 9.31; H, 2.60; Cl, 23.2; Pt, 64.8. *cis*-Dichlorodiammineplatinum(II) was dissolved in hot water, standard $AgClO_4$ was added to precipitate AgCl, and the solution was cooled to ice temperature and filtered. The filtrate was evaporated at 40° under a stream of nitrogen. The resulting translucent, slightly yellow crystals were dried under vacuum over P_4O_{10}. *Anal.* Calcd for $N_2H_{10}Cl_2O_{10}Pt$: N, 6.03; H, 2.17; Cl, 15.3; Pt, 42.0. Found: N, 5.48; H, 2.2; Cl, 15.2; Pt, 41.9.

Bis(perchlorato)diammineplatinum(II).—When *cis*-diaquodiammineplatinum(II) perchlorate was dried at 115° for 24 hr, a yellow-orange solid was obtained. The loss in weight corresponded to 2 mol of water/mol of platinum. When the compound was redissolved in water and treated with NaCl solution, the yellow $PtCl_2(NH_3)_2$ was precipitated. The anhydrous perchlorate is soluble in acetonitrile to about 0.8 *m* at room temperature. Both the hydrate and the anhydrous ammine exhibit the two infrared-active symmetric ammine deformations at 1364, 1345 and 1356, 1345 cm^{-1}, respectively, that are characteristic of *cis* isomers; *cf.* 1315, 1299 cm^{-1} for *cis* $(NH_3)_2PtCl_2$. In the anhydrous compound, the triply degenerate perchlorate vibrations ν_3, ν_4 are split and ν_1 is also weakly infrared active indicating a pronounced lowering of the perchlorate symmetry from that of the free ion.

Gallium(III) Perchlorate.—Gallium oxide, Ga_2O_3, was prepared by dissolving gallium metal, 99.999%, in nitric acid and adding aqueous ammonia to precipitate the hydroxide at pH 6. This product was washed with water, dried at 110° for 1 hr, and heated to 550° for 3 hr.[21] Weighed quantities of the oxide were dissolved in standard perchloric acid.

Dimethylgallium(III) Perchlorate.—Weighed quantities of dimethylgallium(III) hydroxide[22] were dissolved in standard perchloric acid at 0° under which conditions the hydroxide dissolves without decomposition.

Indium(III) Perchlorate.—Indium oxide, In_2O_3, was dissolved in standard perchloric acid on the steam bath over a period of 48 hr.

Dimethyltin(IV) Perchlorate.—Dimethyltin oxide, $(CH_3)_2SnO$, prepared by adding aqueous ammonia to an aqueous solution of $(CH_3)_2SnCl_2$ was washed free of chloride ion and dried for 48 hr in a vacuum oven at 75°. Weighed quantities of the oxide were added to standard perchloric acid at 0°.

Oxygen-17 Nuclear Magnetic Resonance. Spectrometer.—A Varian Associates V4200 wide-line line spectrometer operated at *ca.* 7.7 Mcps was used to obtain the spectra. The spectrometer included the following components: variable-frequency radiofrequency unit V4210A, electromagnet V2100B, magnetic field precession scanning unit V4280A, field modulation sweep unit V4250A, output control unit V4270A, 4–8-Mcps probe V4230B. A Hewlett-Packard audiooscillator 200AB and audiocounter 521C were employed when frequencies other than those available with the V4250A sweep unit were required. The radiofrequency was measured with a Hewlett-Packard 524D electronic counter. A Varian C1024 time-averaging computer was employed for signal enhancement during preliminary measurements. Because the magnetic field was slightly unstable over the long periods of time required for time averaging, accurate line-shape measurements could not be made by this procedure.

The radiofrequency field, H_1, was measured using the side-

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[12] M. Alei and J. A. Jackson, *ibid.*, **41**, 3402 (1964).

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[14] T. J. Swift, O. G. Fritz, Jr., and T. A. Stephenson, *J. Chem. Phys.*, **46**, 406 (1967).

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[21] See ref 15, Part I, Vol. 2, p 33.

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band method described by Anderson.[23] For line-width measurements, the radiofrequency field was set at 0.030 G. The magnetic field precession scanning unit V4280A was calibrated using absorption side bands.[23,24] A magnetic field modulation frequency greater than the line width was used, generating absorption side bands, and the center band was adjusted to zero amplitude with the phasing control of the V4270 phase-sensitive detector. The side bands are separated by the modulation frequency, ν_m, when the radiofrequency power is at a low value.[25] The modulation amplitude, H_m, was obtained from plots of the relative side-band intensity as a function of $\beta = |\gamma| H_m/\nu_m$, where γ is the magnetogyric ratio for oxygen-17. These plots were obtained by solving eq 2 of ref 24 with the CDC-1604 computer of the University of Minnesota. So long as the modulation frequency is kept constant, β is directly related to the amplitude of the modulation. This modulation power level was kept at $\beta < 1.0$ for line-width measurements and between 3 and 7 for magnetic field sweep calibration.

The absorption mode (V mode) was selected in all spectra. Resonance line positions and chemical shifts were measured by recording the absorption mode signals as derivatives. Intensity ratios of two signals were calculated by recording the absorption spectrum at ν_m = 400, 600, and 800 cps, $\beta \simeq 0.8$, and by measuring the signal areas with a Gelman planimeter.

Samples.—The cells used to hold the samples were blown from Pyrex glass and are illustrated in Figure 1.

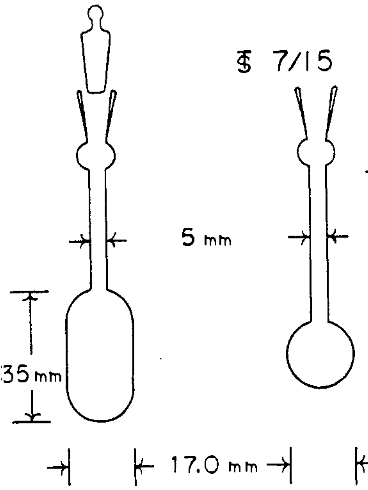

Figure 1.—Bulbs used to contain samples for oxygen-17 nmr.

Spectra were recorded at other than ambient temperatures by either cooling the sample bulb to ice temperature or heating it in a water bath, inserting it into the probe, tuning the radiofrequency, and scanning the signal within 30 sec. A temperature *vs.* time curve was constructed in a separate experiment with a thermocouple inserted into the sample. This procedure was repeated several times, and the data were averaged. The low-temperature measurements are believed to be accurate to ±2°, and the high-temperature measurements, to ±4°.

Results

Most of the studies of ion hydration numbers were made using the molal shift method employing Dy^{3+} as the indicating ion after Alei and Jackson.[12] Swift and Sayre[26] have shown that for a system of four nuclear environments, *e.g.*, H_2O–solvent, $M^{z+}(H_2O)_x$, H^+-$(H_2O)_y$, and $ClO_4^-(H_2O)_z$, where the exchange times between them are sufficiently short that only one resonance is observed, the chemical shift δ and line width $\delta\nu$ are weighted averages over all environments

$$\delta^{\text{soln}} = \textstyle\sum_i X_i \Delta\omega_i \tag{1}$$

Here X_i is the mole fraction of the solvent in the ith nuclear environment and $\Delta\omega_i$ is the chemical shift of the solvent in the ith environment. With solutions containing a single paramagnetic ion such as Dy^{3+}, $\Delta\omega_{Dy^{3+}}$ dominates the terms in the summation, and the shift measured from the ^{17}O resonance position of pure water is given to a very good approximation by

$$\delta_{H_2O}^{\text{soln}} = m_{Dy^{3+}} \Delta\omega_{Dy^{3+}} \tag{2}$$

There is no convenient way to measure the shifts $\delta_{H_2O}^{\text{soln}}$ directly from a pure water reference, and it is preferable to use an external, enriched water sample contained in a capillary immersed in the sample itself. The chemical shift measured in this manner $\delta_{H_2O,\text{ext}}^{\text{soln}}$ will differ from $\delta_{H_2O}^{\text{soln}}$ determined with a separate external water reference because of the susceptibility χ of the medium surrounding the capillary. If the apparent shift of the water reference in the capillary *vs.* the pure water resonance position is

$$\delta_{\text{app}} = \textstyle\sum_i m_i \chi_i \tag{3}$$

and one of the species in the solution surrounding the capillary is paramagnetic, *e.g.*, Dy^{3+}, the susceptibility of the paramagnetic ion will dominate the summation in (3). Consequently

$$\begin{aligned}\delta_{H_2O,\,\text{ext}}^{\text{soln}} &= \delta_{H_2O}^{\text{soln}} + m_{Dy^{3+}}\chi_{Dy^{3+}} = \\ &m_{Dy^{3+}}(\Delta\omega_{Dy^{3+}} + \chi_{Dy^{3+}}) = m_{Dy^{3+}}\Delta\omega'_{Dy^{3+}}\end{aligned} \tag{4}$$

With Dy^{3+}, the resultant chemical shift of the solution measured from a pure water sample contained in a capillary immersed in the solution will be larger than the shift measured from a separate pure water reference. The solution water resonance is shifted upfield with increasing concentration of Dy^{3+}, while the apparent shift of the capillary water reference is always downfield. Figure 2 illustrates the chemical shift of the solvent in $Dy(ClO_4)_3$ solutions measured *vs.* a pure water sample in a capillary immersed in the solution. The value of $\Delta\omega'_{Dy^{3+}}$ at 29° is 460 ppm m^{-1}. Figure 2 also illustrates shifts measured *vs.* the perchlorate resonance of the solution as an *internal* standard

$$\delta_{ClO_4^-}^{\text{soln}} - \delta_{ClO_4^-([Dy^{3+}]=0)}^{\text{soln}} = m_{Dy^{3+}}\Delta\omega_{Dy^{3+}} \tag{5}$$

The solvent chemical shift with reference to *internal* perchlorate where $[Dy^{3+}] = 0$ was taken with 5 m $NaClO_4$ and had the value 288 ppm. The value $\Delta\omega_{Dy^{3+}}$ calculated, 370 ppm m^{-1}, may be compared to the value obtained by Alei and Jackson[12] using a separate pure water sample, 368 ppm m^{-1}. The data for the shifts of water in the $Dy(ClO_4)_3$ solutions are collected in Table I.

When a diamagnetic ion which holds back water is introduced into the solutions, the ion hydration num-

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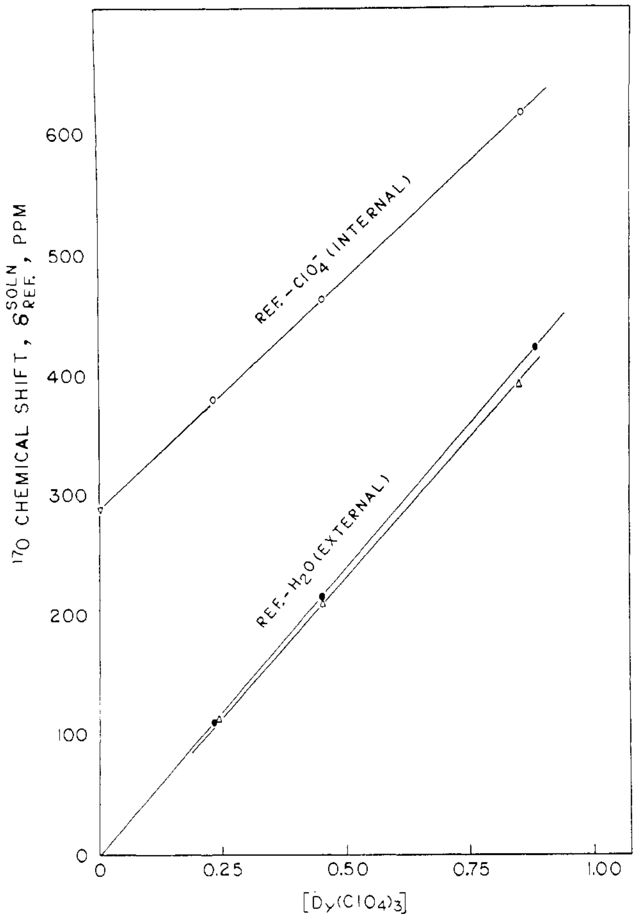

Figure 2.—Oxygen-17 chemical shifts of $Dy(ClO_4)_3$ solutions from an external capillary water reference (●, no $NaClO_4$; △, 8.3–8.4 *M* $NaClO_4$) and from perchlorate ion as an internal standard (○, 8.3–8.4 *M* $NaClO_4$) *vs.* the molal concentration of $Dy(ClO_4)_3$.

Table I

Oxygen-17 Nmr Chemical Shift Data for Dysprosium(III) Solutions at 27° and 7.648 Mcps

$[Dy(ClO_4)_3]$, *m*	$[HClO_4]$, *m*	$[NaClO_4]$, *m*	$\delta^{soln}_{H_2O, ext}$, ppm	$\delta^{soln}_{ClO_4^-}$, ppm
0.230	0.490	...	110 ± 2	...
0.453	0.464	...	213 ± 4	...
0.887	0.376	...	420 ± 4	...
0.231	0.530	8.44	112 ± 4	378 ± 4
0.455	0.490	8.32	209 ± 4	461 ± 4
0.851	0.490	8.32	388 ± 4	614 ± 6
0.357	0.399	...	154 ± 4[a]	415 ± 4[a]
0.692	0.861	...	309 ± 4[b]	540 ± 6[b]
...	23.92	...	...	279 ± 3
...	...	5.03	...	288 ± 2

[a] Solution is also 2.122 *m* in $(CH_3)_2Sn(ClO_4)_2$. [b] Solution is also 1.793 *m* in $(CH_3)_2Sn(ClO_4)_2$.

ber, *n*, can be obtained from the solvent chemical shift data using the expression

$$n = \frac{55.5}{[M^{z+}]}\left(1 - \frac{(\delta/[Dy^{3+}])_{ref}}{(\delta/[Dy^{3+}])_{sample}}\right) \qquad (6)$$

This is the relation employed in ref 9.

For the $Dy(ClO_4)_3$ solutions where rapid exchange leads to only a single solvent resonance, the half-line-width at half-maximum intensity is given by a relation analogous to (1)[26]

$$\delta\nu_{1/2,1/2} = \sum_i X_i/T_{2i} \qquad (7)$$

where T_{2i} is the relaxation time in the *i*th nuclear environment and X_i is the mole fraction of solvent in the *i*th environment. The effect of the paramagnetic Dy^{3+} ion will again dominate, since the acidity of the solution has little effect on line width for pH <5.[27,28] Eigen[29] has estimated that the first-order rate constant for exchange of water in and out of the first coordination sphere of Dy^{3+} is of the order of 10^7 sec^{-1}. If to the $Dy(ClO_4)_3$ solution is added a salt containing a diamagnetic cation which exchanges solvent with a rate constant appreciably less than 10^7 sec^{-1}, the oxygen-17 resonance for water will be broadened. If the rate for exchange is less than *ca.* 10^4 sec^{-1}, resonances will be observed for both bound and bulk solvent. By measuring the line broadening of a solution containing $Dy(ClO_4)_3$ and the more slowly exchanging cation relative to a solution containing only $Dy(ClO_4)_3$, information can be obtained on the rate with which the diamagnetic cation exchanges water. The equations derived for two site systems can be employed.[30] One site is at the diamagnetic ion while the other is the average of the H_2O–Dy^{3+}, H_2O–H^+, and H_2O–ClO_4^- environments.

The $Dy(ClO_4)_3$ solution line widths, W'', were obtained from plots of W'' *vs.* concentration; see Figure 3. The data for this figure are given in Table II. These spectra were obtained at the same time and with the same spectrometer settings as the spectra of the solutions containing the diamagnetic cation. The plots are linear except for the most concentrated solution at 5° where there may be exchange broadening if the lifetime of bound water molecules, $\tau_{H_2O,bound}$, for $Dy^{3+} \simeq 4 \times 10^{-8}$ sec or where there may be viscosity broadening or both. The values of $\delta\nu$, the difference in frequency of the two water resonances in the absence of exchange, are believed to be within ±5% of the true values, and in cases where the $Cl^{17}O_4^-$ signal was observed providing an internal standard, it was found to be well within this limit. Within the experimental error, the dysprosium molal shift was found to vary as $1/T$. This variation was used to calculate $\delta\nu$ for solutions containing exchanging diamagnetic cations at temperatures other than 29°.

Trimethylplatinum(IV) Ion.—Chemical shifts and line widths were measured at three temperatures for solutions of trimethylplatinum(IV) perchlorate both with and without $Dy(ClO_4)_3$. The solutions were *ca.* 4.5 atom % in oxygen-17. At 29°, only a single oxygen-17 water resonance was recorded, but at 5° both bound and bulk water resonances were observed. The chemical shift of the bound water resonance with respect to the ^{17}O resonance of a separate pure water reference was 15 ± 6 ppm upfield determined using the perchlorate

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(30) See, for example, A. Allerhand, H. S. Gutowsky, R. A. Meinzer, and J. Jonas, *J. Am. Chem. Soc.*, **88**, 3185 (1966), and references cited therein.

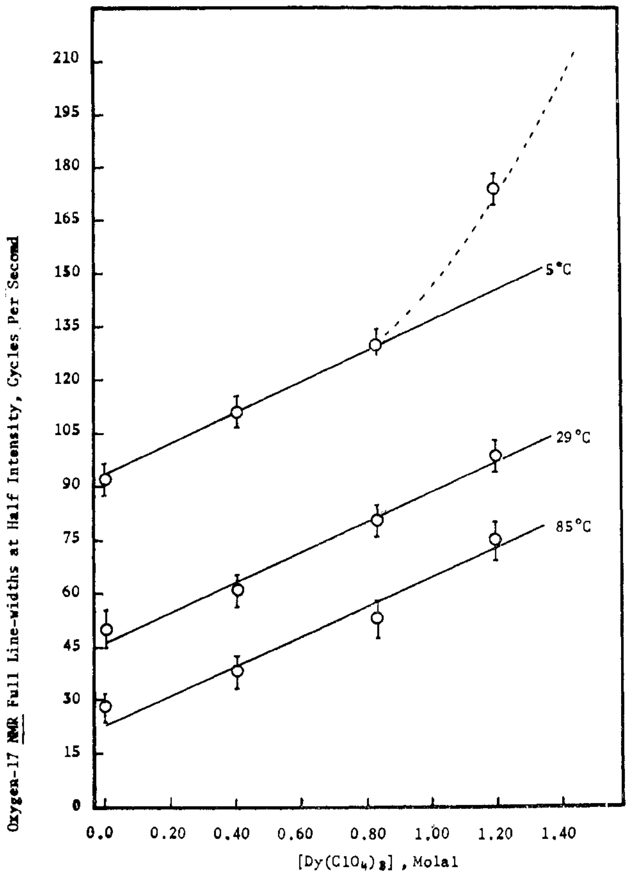

Figure 3.—Oxygen-17 water resonance line widths *vs.* the molal concentration of $Dy(ClO_4)_3$.

resonance as an internal standard. The large uncertainty was mainly a result of uncertainty in the location of the weak perchlorate resonance.

From the chemical shift data for 5° given in Table II, the hydration number was determined to be 3. This has been reported in a preliminary communication. The data for the line widths of the water resonances of the $(CH_3)_3PtClO_4$-$Dy(ClO_4)_3$ solutions and of the $Dy(ClO_4)_3$ solutions measured under identical conditions are also tabulated in Table II.[31]

A plot of log $(1/\tau_{H_2O,mean})$ *vs.* $1/T$ gives a value of 9.4 ± 1 kcal mol^{-1} for the activation energy for exchange. A value of $\tau_{H_2O,mean}$ for 25° was obtained from this plot, and this corresponds to a value for the lifetime of the ^{17}O of water molecules coordinated to platinum, $\tau_{H_2O,bound}$, of 8.0×10^{-5} sec.

Dimethylgold(III) Ion.—The exchange between coordinated and solvent water molecules was found to be rapid by molal shift measurements. Data for the oxygen-17 nmr measurements are given in Table III.

The energy of activation for exchange was estimated to be 8.4 ± 1.8 kcal mol^{-1} from the plot of log $(1/\tau_{H_2O,mean})$ *vs.* $1/T$. From this plot a value of $\tau_{H_2O,bound} = 2.2 \times 10^{-5}$ sec was estimated for the lifetime of water molecules bound to gold.

Diammineplatinum(II) Perchlorate.—The diammineplatinum(II) moiety was examined, since it is isoelectronic and isostructural with the dimethylgold(III) species. This platinum complex exchanges coordinated water slowly with the solvent as expected, and the hydration number was found to be 1.9 ± 0.1 by integrating the oxygen-17 absorption side bands of free and bound water signals. The data are listed in Table IV, and Figure 4 shows the absorption signal and its derivative.

The bound water resonance is shifted 93 ppm upfield measured from the solvent water resonance position. This shift was, within the experimental error, independent of temperature over the range 29–85°. At high temperatures, where the spectrum was nearing natural line widths unbroadened by viscosity, the bound water signal exhibited a non-Lorentzian, symmetrical line shape suggesting unresolved platinum–oxygen coupling. Further enrichment would be required to resolve this point. Diammineplatinum(II) perchlorate has also been observed to coordinate two solvent molecules in acetonitrile solution.[32]

Dimethylgallium(III) Perchlorate.—At the beginning of this work, the hydration number of gallium(III) was determined to be 5.9 ± 0.4 from measurements on perchlorate solutions. Water with the natural abundance of oxygen-17 was employed, and the signal:noise ratio was improved by accumulating up to 16 scans with the CAT. The results are in satisfactory agreement with the values of 5.9 ± 0.1 found by Swift and coworkers[14] and of 5.89 ± 0.20 and 6.28 ± 0.26 found by Fiat and Connick.[13]

As is to be expected, coordination of methyl groups to Ga(III) and the consequent charge reduction leads to a labilization of the remaining water molecules in the first coordination sphere. The oxygen-17 nmr spectra of solutions of dimethylgallium(III) perchlorate showed no resonance assignable to bound water. The data for the dimethylgallium(III) solutions are given in Table V. From the data at 30°, the lifetime for water molecules coordinated to gallium was estimated to be $\tau_{H_2O,bound} = 1.1 \times 10^{-5}$ sec. In this calculation, two coordinated water molecules are assumed, since Raman studies on these solutions have shown the dimethylgallium(III) moiety to be bent with a structure similar to that found in the hydroxide.[33]

Indium(III) Perchlorate.—Indium(III) was studied for comparison with gallium(III), and molal shift measurements indicated that all water molecules were in rapid exchange among the different sites. The data are collected in Table VI. The line-width measurements indicated a value of $\tau_{H_2O,bound} = 2.5 \times 10^{-5}$ sec at 25° and an activation energy for exchange of 4.6 ± 1 kcal mol^{-1}. In view of this rather low value obtained for the activation energy, the solution viscosity may have influenced the line widths and therefore the value of $\tau_{H_2O,bound}$ may only be an upper limit; *i.e.*, exchange may actually be even faster.

Dimethyltin(IV) Perchlorate.—The dimethyltin(IV) ion was also found to exchange its coordinated water

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[31] L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, **30**, 899 (1959).

[32] J. F. O'Brien, G. E. Glass, and W. L. Reynolds, *Inorg. Chem.*, **7**, 1664 (1968).

[33] R. S. Tobias, M. J. Sprague, and G. E. Glass, *ibid.*, **7**, 1714 1968).

TABLE II

OXYGEN-17 NMR DATA FOR TRIMETHYLPLATINUM(IV) PERCHLORATE SOLUTIONS AT 7.661 MCPS

Soln no.	$[(CH_3)_3PtClO_4]$, *m*	$[Dy(ClO_4)_3]$, *m*	$[HClO_4]$, *m*	$\delta_{H_2O,\ ext}^{soln}$, ppm		$\delta_{H_2O,\ ext}^{soln}/[Dy^{3+}]$, ppm m^{-1}		Line widths, cps		
				5°	29°	5°	29°	5°	29°	85°
1	2.400	...	0.558	...	...	...	...	210	101	39
2	2.167	0.434	0.520	...	212 ± 2	...	488	286	277	57
3	1.969	0.802	0.486	449 ± 1	397 ± 2	560[a]	495	290[b]	444	76[d]
4	1.758	1.196	0.451	661 ± 2	585 ± 2	552[a]	489	349[b]	533[c]	120[d]
5	...	0.406	0.051	...	188 ± 2	...	463	111	61	38
6	...	0.829	0.033	413 ± 1	380 ± 2	498[a]	458	130	80	53
7	...	1.194	0.043	599 ± 1	547 ± 2	502[a]	458	174	98	75
8	...	...	...	0	0	...	...	92	50	28

[a] Hydration number, *n*, calculated with eq 6 is 3.1 ± 0.1 (solutions 3 and 6) and 2.9 ± 0.1 (solutions 4 and 7). [b] The exchange rates $10^{-4}/\tau_{H_2O,mean}$ (radian sec^{-1}) are 0.47 and 0.51 for solutions 3 and 4, respectively, at 5°. These values were calculated using the expression for slow exchange[31]

$$1/\tau_m = \frac{\pi(W^*_a - W''_a)}{1 - P_a} \tag{a}$$

τ_m is the mean lifetime of an exchanging species in seconds (*i.e.*, seconds radian^{-1}), W^* is the *full* line width at half-intensity of an exchange-broadened signal in cycles per second, and W'' is the *full* line width at half-intensity of the unbroadened signal calculated using Figure 3 in cycles per second, P_a and P_b are the fractional populations of the sites such that $P_a + P_b = 1$. The lifetime of an exchanging species, τ_a, in a particular site a is $\tau_a = \tau_m/P_b$ since $\tau_a/P_a = \tau_b/P_b$ and $1/\tau_m = (1/\tau_a) + (1/\tau_b)$. Lifetimes are quoted as having units of seconds but are calculated in terms of seconds radians^{-1}. Radians being unitless are omitted. The values used in this calculation are $W'' = 131$ and 195 cps; $P_a = 0.894$ and 0.905, the mole fractions of water in "solvent" calculated on the basis of three water molecules bound per $(CH_3)_3Pt^+$ ion; $\delta\nu = 2750$ and 4050 cps calculated for this concentration of Dy(III) not counting those water molecules bound to platinum. The value estimated earlier[9] differs from those reported here by the factor 2π. [c] The exchange rate $10^{-4}/\tau_{H_2O,mean}$ is 1.6 radian sec^{-1} at 29° approximated by the coalescence formula[30]

$$1/\tau_m \approx \sqrt{2}\pi\delta\nu \tag{b}$$

$\delta\nu$ is the separation in cycles per second of the resonances of the two sites in the absence of exchange, 3510 cps. The extreme width of the ^{17}O resonance prompted this mode of estimation. [d] The exchange rates $10^{-4}/\tau_{H_2O,mean}$ are 22.7 and 19.7 radians sec^{-1} for solutions 3 and 4, respectively, at 85°, calculated using the expression for fast exchange[30]

$$1/\tau_m = \frac{4\pi(P_aP_b)(\delta\nu)^2}{W^* - W''} \tag{c}$$

The values used in this calculation are $W'' = 55$ and 72 cps, calculated using Figure 3, and $\delta\nu = 2000$ and 2960 cps.

TABLE III

OXYGEN-17 NMR DATA FOR DIMETHYLGOLD(III) PERCHLORATE SOLUTIONS AT 7.680 MCPS

Chemical Shifts

Soln no.	$[(CH_3)_2AuClO_4]$, *m*	$[Dy(ClO_4)_3]$, *m*	$[HClO_4]$, *m*	$\delta_{H_2O,ext}^{soln}$,[a] ppm	$\delta_{H_2O,ext}^{soln}/[Dy^{3+}]$, ppm m^{-1}	$\delta_{ClO_4^-}^{soln}$,[a] ppm	$[\delta_{ClO_4^-}^{soln} - (\delta_{ClO_4^-([Dy^{3+}]=0)}^{soln})]/[Dy^{3+}]$, ppm m^{-1}
1	6.586	0.680	2.524	298 ± 4	438 ± 6	545 ± 4	378 ± 6
2	4.210	0.809	0.925	362 ± 2	447 ± 4	593 ± 4	377 ± 6
3	5.137	...	1.094	...	...	290 ± 2	...
4	...	0.757	8.859	337 ± 4	445 ± 6	563 ± 4	363 ± 6
5	...	...	6.891	...	...	278 ± 2	...

Line Widths

Soln. no.	W^*, cps			W'', cps			$\delta\nu$, cps			$10^{-4}/\tau_{H_2O,mean}$,[c] radians, sec^{-1}			
	5°	29°	50°	5°	29°	50°	5°	29°	50°	P_{H_2O}[b]	5°	29°	50°
2	300	154	92	129	80	69	3240	2970	2510	0.848	6.1	12	34
3	200	99	...										
5				84	55	...							

[a] Chemical shifts measured at 29°. [b] Calculated assuming two molecules of water bound per $(CH_3)_2Au^+$. [c] Calculated using the expression for fast exchange, eq c, footnote *d* of Table II.

TABLE IV

OXYGEN-17 NMR OF *cis*-DIAMMINEPLATINUM(II) PERCHLORATE SOLUTIONS AT 7.673 MCPS[a]

$[(NH_3)_2Pt(ClO_4)_2]$, *m*	$[Dy(ClO_4)_3]$, *m*	$[HClO_4]$, *m*	Area integral ratio, free:bound	$\delta_{ClO_4^-}^{soln} - \delta_{ClO_4^-([Dy^{3+}]=0)}^{soln}$, ppm	$\delta_{H_2O,solvent}^{H_2O,bound}$, ppm	*n*[b]	*n*[c]
3.80 ± 0.6	0.57	0.80	7.9 ± 0.3	95 ± 5	...	1.8 ± 1.3	1.6 ± 0.3
9.45	0	0	2.09 ± 0.06	...	92.6 ± 1.0	...	1.9 ± 0.1

[a] Chemical shifts measured at 29°. [b] Hydration numbers calculated by the molal shifts method, eq 6. [c] Hydration numbers calculated from the signal integrals

$$n = \frac{55.5/[(\text{integral ratio, free:bound}) + 1]}{[(NH_3)_2Pt(ClO_4)_2]}$$

TABLE V

OXYGEN-17 NMR DATA FOR DIMETHYLGALLIUM(III) PERCHLORATE SOLUTIONS AT 7.658 MCPS

Chemical Shifts

Soln no.	$[(CH_3)_2GaClO_4]$, m	$[Dy(ClO_4)_3]$, m	$[HClO_4]$, m	$\delta^{soln}_{H_2O,ext}$,[a] ppm	$\delta^{soln}_{H_2O,ext}/[Dy^{3+}]$, ppm m^{-1}	$\delta^{soln}_{ClO_4^-}$,[a] ppm	$[\delta^{soln}_{ClO_4^-} - (\delta^{soln}_{ClO_4^-([Dy^{3+}]=0)}]/[Dy^{3+}]$, ppm m^{-1}
1	. . .	0.901	6.839	389 ± 3	432	609 ± 5	356
2	5.194	0.816	1.004	345 ± 3	423	581 ± 5	359
3	5.073	0.798	0.981	339 ± 3	425	569 ± 5	352

Line Widths

Soln no.	W^*,[b] cps	W'',[b] cps	$\delta\nu$,[c] cps	P_{H_2O},[d]	$10^{-4}\tau_{H_2O,mean}$,[e] radians sec^{-1}
3	230	155	2150	0.816	9.1

[a] Chemical shifts measured at 29°. [b] Line widths were measured at 30°. [c] Approximated by $\delta^{soln}_{ClO_4^-} - \delta^{soln}_{ClO_4^-([Dy^{3+}]=0)} = (\delta^{soln}_{ClO_4^-} - 288 \text{ ppm})(7.658 \text{ cps/ppm})$. [d] Calculated assuming 2 molecules of water bound per $(CH_3)_2Ga^+$. [e] Obtained using the expression for fast exchange, eq c, footnote *d* of Table II.

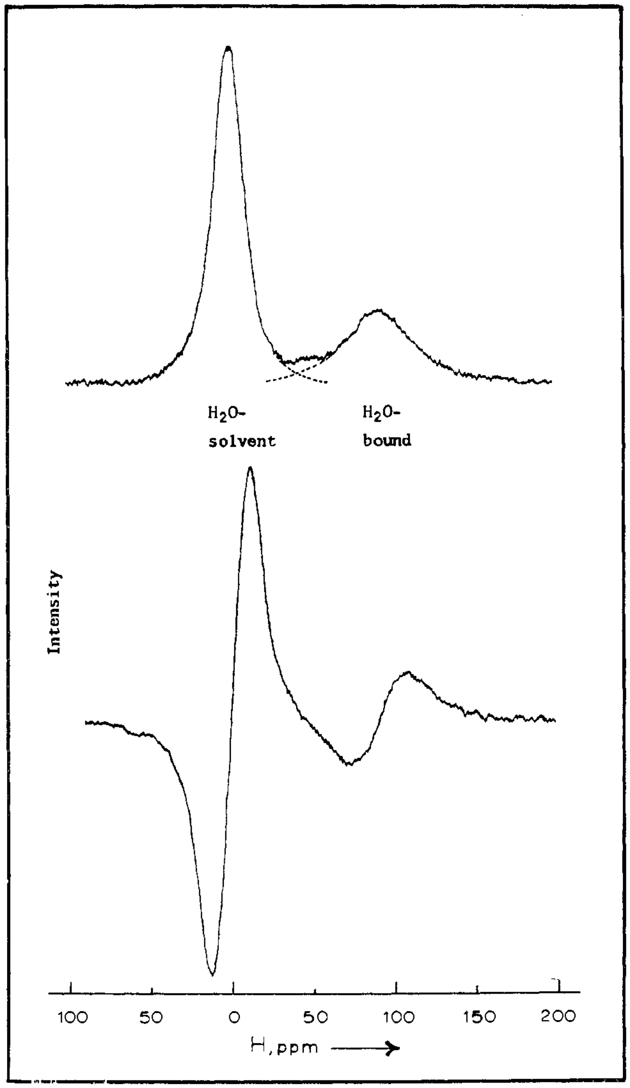

Figure 4.—Oxygen-17 nmr spectrum for an aqueous solution of $(NH_3)_2Pt(ClO_4)_2$, 9.45 *m*, at 60°.

molecules rapidly with the bulk solvent. The data for the chemical shifts and line widths are tabulated in Table VII. The line-width data for the solution 5.05 *m* in $(CH_3)_2Sn(ClO_4)_2$ were influenced by the solution viscosity, since the slopes of the two Arrhenius plots were significantly different. From the data for the more dilute solution, the activation energy for exchange was estimated to be 6.2 ± 1.5 kcal mol^{-1}, and an upper limit to $\tau_{H_2O,bound}$ can be set at 1.2×10^{-5} sec at 25°.

Discussion

Experience in the past few years has shown that most aquo ions exchange their bound water molecules with the bulk solvent at rates which are "fast" on the oxygen-17 nmr time scale. Previously, hydration numbers of diamagnetic ions have only been reported for Be^{2+}, Al^{3+}, and Ga^{3+} using this method.

The trimethylplatinum(IV) ion is assigned the *fac* structure because the pmr spectrum in aqueous solution exhibits only a single sharp resonance for methyl protons.[34] In addition, the platinum-195–methyl proton coupling constant is identical with that found for the hydroxide where the methyl groups should all be *cis*.[18] At 29°, this ion also undergoes exchange at a rate which is rapid on the oxygen-17 nmr time scale. However, at 5° the rate is slowed to the point where both bulk and bound water resonances are observed. The hydration number was found to be 3, so a well-defined *fac*-triaquotrimethylplatinum(IV) cation exists in aqueous solutions. Recently, the trimethylplatinum(IV) cation was found to coordinate up to three pyridine molecules in aqueous pyridine solutions.[35] The labilizing effect of the methyl groups situated *trans* to the aquo groups leads to the unusual situation where an octahedral platinum(IV) (d^6) complex has three very labile ligands. The lifetimes in seconds (*i.e.*, sec radian^{-1}), $\tau_{H_2O,bound}$, for water molecules bound to platinum are obtained from $\tau_{H_2O,mean}$ by dividing by the fractional population of "solvent" water. The pseudo-first-order rate constant, k_1, for chemical exchange is $n/\tau_{H_2O,bound}$ where n is the ion hydration number. For $(CH_3)_3Pt(H_2O)_3^+$ at 25°, $\tau_{H_2O,bound} = 8.0 \times 10^{-5}$ sec and $k_{1H_2O,bound} = 3.8 \times 10^4$ sec^{-1}.

The other methyl derivative of a transition metal, the dimethylgold(III) cation (d^8), still exchanges coordinated water rapidly at 5° on the oxygen-17 nmr time scale. At 25°, $\tau_{H_2O,bound}$ was estimated to be 2.2×10^{-5} sec. In contrast, the isoelectronic diammineplatinum(II) ion which is presumably also iso-

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[34] K. Kite, J. A. S. Smith, and E. J. Wilkins, *J. Chem. Soc., A*, 1744 (1966).

[35] D. E. Clegg and J. R. Hall, *Australian J. Chem.*, **20**, 2025 (1967).

TABLE VI

OXYGEN-17 NMR DATA FOR INDIUM(III) PERCHLORATE SOLUTIONS AT 7.661 MCPS

Chemical Shifts

Soln no.	$[\mathrm{In(ClO_4)_3}]$, *m*	$[\mathrm{Dy(ClO_4)_3}]$, *m*	$[\mathrm{HClO_4}]$, *m*	$\delta^{\mathrm{soln}}_{\mathrm{H_2O,ext}}$,[a] ppm	$\delta^{\mathrm{soln}}_{\mathrm{ClO_4^-}}$,[a] ppm	$[\delta^{\mathrm{soln}}_{\mathrm{ClO_4^-}} - \delta^{\mathrm{soln}}_{\mathrm{ClO_4^-([Dy^{3+}]\to 0)}}]/[\mathrm{Dy^{3+}}]$, ppm m^{-1}
1	2.369	0.726	0.574	. . .	560 ± 4	375 ± 6
2	1.865	0.571	0.832	251 ± 3	500 ± 4	371 ± 6

Line Widths

	W^*, cps			W'', cps			$\delta\nu$,[b] cps				$10^{-4}/\tau_{\mathrm{H_2O,mean}}$,[d] radians sec^{-1}		
Soln no.	5°	29°	85°	5°	29°	85°	5°	29°	85°	$P_{\mathrm{H_2O}}$[c]	5°	29°	85°
2	344 ± 20	168 ± 10	66 ± 5	117	69	44	1760	1620	1370	0.789	2.7_6	5.3_6	$17._3$

[a] Chemical shifts measured at 29°. [b] Obtained by measuring the chemical shift of the solution *vs.* perchlorate as an internal standard. [c] Mole fraction computed assuming six bound water molecules per In(III). [d] Calculated using the expression for rapid exchange, eq c, footnote *d* of Table II.

TABLE VII

OXYGEN-17 NMR DATA FOR DIMETHYLTIN(IV) PERCHLORATE SOLUTIONS AT 7.661 MCPS

Chemical Shifts

Soln no.	$[\mathrm{(CH_3)_2Sn(ClO_4)_2}]$, *m*	$[\mathrm{Dy(ClO_4)_3}]$, *m*	$[\mathrm{HClO_4}]$, *m*	$\delta^{\mathrm{soln}}_{\mathrm{H_2O,ext}}$,[a] ppm	$\delta^{\mathrm{soln}}_{\mathrm{ClO_4^-}}$,[a] ppm	$\delta^{\mathrm{soln}}_{\mathrm{ClO_4^-}} - \delta^{\mathrm{soln}}_{\mathrm{ClO_4^-([Dy^{3+}]\to 0)}}]/[\mathrm{Dy^{3+}}]$, ppm m^{-1}
1	5.05	0.582	0.49	236 ± 2	492 ± 2	351
2	2.43	1.039	0.04	451 ± 2	675 ± 3	372

Line Widths

	W^*, cps			W'', cps			$\delta\nu$, cps				$10^{-4}/\tau_{\mathrm{H_2O,mean}}$,[c] radians sec^{-1}		
Soln no.	5°	29°	85°	5°	29°	85°	5°	29°	85°	$P_{\mathrm{H_2O}}$[b]	5°	29°	85°
1	470 ± 30	240 ± 10	86 ± 5	119	69	49	1710	1570	1330	0.636	2.4_4	4.1_9	$13._9$
2	340 ± 20	150 ± 10	78 ± 5	137	91	68	3240	2970	2510	0.825	9.5_0	$26._4$	$11._4$

[a] Chemical shifts measured at 29°. [b] Mole fraction computed assuming four bound water molecules per $(\mathrm{CH_3})_2\mathrm{Sn^{IV}}$. [c] Calculated with the expression for fast exchange, eq c, footnote *d* of Table II.

structural is very inert, and the spectrum still shows separate bound and bulk water resonances at 85°. Only two water molecules were found to be bound strongly to the diammineplatinum(II) cation, logically those completing the square plane about platinum(II). Any axially bound water molecules must exchange much more rapidly, and there is no indication of a facile equatorial–axial interchange. A comparison between $(\mathrm{CH_3})_2\mathrm{Au^+}$ and $(\mathrm{NH_3})_2\mathrm{Pt^{2+}}$ indicates the extreme charge-reducing effect of $\mathrm{CH_3^-}$ and the general labilizing effect exerted by methyl groups on the other ligands in the first coordination sphere.

Addition of chloride ion to solutions containing *cis*-diaquodiammineplatinum(II) ion leads to precipitation of insoluble *cis*-$\mathrm{PtCl_2(NH_3)_2}$. The formation of the first traces of the yellow precipitate is not instantaneous and was observed to require several seconds depending upon the concentrations employed. This rate is probably of the order of the aquo exchange rate, and consequently $\tau_{\mathrm{H_2O,bound}}$ is of the order of 1 sec. This observation agrees with the estimate of Belluco, *et al.*,[36] for $k_{1\mathrm{H_2O}}(\mathrm{Pt(dien)H_2O^{2+}}) = 0.4\ \mathrm{sec^{-1}}$ (dien = $(\mathrm{H_2NCH_2CH_2})_2\mathrm{NH}$).

Since the organometallic cations derived from Pt(IV) and Au(III) have exceedingly labile coordinated water, it is not surprising that ions derived from post-transition metals, *e.g.*, $(\mathrm{CH_3})_2\mathrm{Ga^+}$ and $(\mathrm{CH_3})_2\mathrm{Sn^{2+}}$, also have very labile water molecules in the first coordination sphere; $\tau_{\mathrm{H_2O,bound}} = 1.1 \times 10^{-5}$ (30°) and 1.2×10^{-1} (25°) sec. While the acidity of the aquo ions $\mathrm{Be^{2+}}$ and $(\mathrm{CH_3})_2\mathrm{Sn^{2+}}$ is similar indicating that the cations polarize the coordinated water molecules to about the same extent, the exchange rates of the organometallic cations are 30–50 times faster. However, Hunt[37] has pointed out that there is no simple correlation between aquo exchange rates and hydrolysis constants.

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(36) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).

(37) J. P. Hunt, "Metal Ions in Aqueous Solution," W. A. Benjamin, Inc., New York, N. Y., 1963, p 82.