on its oxidation by Co(III). It was shown[13] that Np(V) reacts with Co(III) about 150 times faster than Cr(III)·Np(V) does in 1 M $HClO_4$–1 M $LiClO_4$ at 25°. A more interesting observation is that reactions in which Cr(III)·Pu(V) is reduced by Pu(III) or Fe(II) are zero order in $[H^+]$ as well as being considerably faster than the corresponding reactions of Pu(V) which are first power in $[H^+]$. These observations lead to the plausible suggestion that Cr(III), in the complex, weakens and lengthens the Pu–O bonds, which are broken on reduction but shortened on oxidation. Electrostatic and steric effects can also contribute to the relative slowness of the oxidation of the complex by cations.

The reduction reactions of PuO_2^+ and other actinide-(V) ions usually show first-power $[H^+]$ dependences and may be interpreted to involve protonated species such as $HOPuO^{2+}$. Apparently Cr^{3+} plays a role similar to that of H^+ in these reactions. The relative effectiveness of these two ions may be seen by considering as an example the purely formal process $[HOPuOPu^{5+}]^* + Cr^{3+} = [CrOPuOPu^{7+}]^* + H^+$, where the formulas but not necessarily the structures of the activated complexes are implied. The "equilibrium" quotient for this process is $Q^* = k_{Cr}Q/k_H$, where k_{Cr} is the rate constant for the reduction of the complex by Pu(III), k_H is the rate constant for the $[H^+]$-dependent reduction of PuO_2^+, and Q is the association quotient for $CrOPuO^{4+}$ which for the corresponding Np complex is 2.6 ± 0.5 M^{-1} at 25° and $\mu = 8\ M$.[4] The values of k_{Cr} and k_H from Table II are 120 $M^{-1}\ \mathrm{sec}^{-1}$ and 0.05 $M^{-2}\ \mathrm{sec}^{-1}$ giving Q^* a value of about 2×10^3. The corresponding value for reduction by Fe(II) is about 200, if a reasonable ionic strength dependence is assumed for the reaction between Fe^{2+} and $CrOPuO^{4+}$. These rather large values for Q^* show that, *based on the aqueous ions*, Cr^{3+} is much more effective than H^+ in promoting the reduction of Pu(V) either by Pu(III) or by Fe(II).

Acknowledgments.—The authors gratefully acknowledge helpful discussions with Dr. J. C. Sullivan and with Dr. C. E. Holley, Jr., under whose general direction this work was done.

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Incomplete Conformational Averaging in Tris(ethylenediamine)platinum(IV) Ion

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The nmr spectra of tris(ethylenediamine)metal complexes provide evidence for a free energy difference between the δ and λ conformations of the coordinated ethylenediamine ligands.[1-4] The δ conformation is assumed to be more stable for the Λ configuration of the three ligands about the metal ion,[5,6] in accord with observed crystal structures,[7] conformational preferences of related propylenediamine complexes,[8] and calculations of nonbonded interactions within the complex.[5,9] About 60–75% of the ligands are in the δ conformation, estimated from the comparison of chemical shifts between propylenediamine and ethylenediamine complexes of ruthenium(II),[10] comparisons of vicinal coupling constants between tris(ethylenediamine)rhodium(III) ion and related molecules,[3] and observation of the temperature dependence of contact shifts in tris(ethylenediamine)nickel(II) ion.[1]

No evidence for a conformational preference in tris-(ethylenediamine)platinum(IV) ion appears to have been reported and arguments from optical activity data suggest that none exists.[11] The previously reported[2,12] 60-MHz nmr spectrum of N-deuterated $Pt(en)_3^{4+}$ consists of a single sharp peak of about 1-Hz width, together with equally sharp satellites due to coupling with ^{195}Pt. No chemical shift difference is observed which could be attributed to a conformational preference, although from comparison with the spectra of $Pt(pn)_3^{4+}$ any chemical shift difference is expected to be small.[10] At the higher magnetic field strength of the 220-MHz spectrum, however, a chemical shift difference is observed.

A chemical shift difference between protons in an optically inert tris-ethylenediamine complex does not necessarily indicate incomplete conformational averaging.[12] Even if there is no conformational preference and each ligand spends an equal amount of time in the δ and λ conformations, there exists in principle a chemical shift difference. The positions of the protons in the δ and λ conformations are not related by the symmetry of the complex due to the presence of the other two chelate rings. Consequently, an AA′BB′ spectrum is expected even if there is no conformational preference. The magnitude of the chemical shift difference arising from this inherent magnetic nonequivalence is unknown. A recent analysis of the spectrum of $Rh(en)_3^{3+}$ yields an indirect estimate of 0.02 ppm in that complex.[3] In the present work we suggest on the basis of observed differences in platinum–proton coupling constants that the chemical shift difference due to inherent magnetic nonequivalence is negligible in $Pt(en)_3^{4+}$ and that the observed chemical shift difference is better explained by incomplete conformational averaging.

Experimental Section

Tris(ethylenediamine)platinum(IV) chloride was prepared as

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described in the literature.[13] Solutions for the nmr spectra were obtained by dissolving $[Pt(en)_3]Cl_4$ in D_2O, using the sodium salt of 3-(trimethylsilyl)propanesulfonic acid (DSS) as an internal reference. The spectra were recorded using Varian A-60-A, HA-100, and HR-220 spectrometers at the ambient probe temperatures (42, 28, and 23°, respectively). The spectra were analyzed using the computer program NMRIT[14] and simulated with a CALCOMP plotter using natural line widths of 1.0 and 2.0 Hz for the 100- and 220-MHz spectra, respectively. The frequencies used in the CALCOMP program were obtained from the NMRIT calculation with and without coupling to ^{195}Pt, and the intensities were adjusted for the 33.8% natural abundance of ^{195}Pt.

Results

The 100- and 220-MHz spectra of N-deuterated $Pt(en)_3^{4+}$ in D_2O are presented in Figure 1. The average chemical shift is 3.30 ppm downfield from DSS and the average platinum–proton coupling constant is 27 Hz as previously reported from the 60-MHz spectrum.[2,12] Three observations can be made immediately from these spectra. (1) There is a small chemical shift difference between the axial and equatorial ligand protons as observed in the poorly resolved doublet of the central peak of the 220-MHz spectrum. (2) Each of the ligand protons is coupled to the platinum nucleus in those complexes containing ^{195}Pt ($I = ^1/_2$) since the relative intensities of the peaks are in the ratio 1:4:1, reflecting the 33% natural abundance of ^{195}Pt. (3) There is a small difference in the platinum–proton coupling constants between the protons of different chemical shifts, leading to the unequal line widths of the satellite peaks observed in each spectrum.

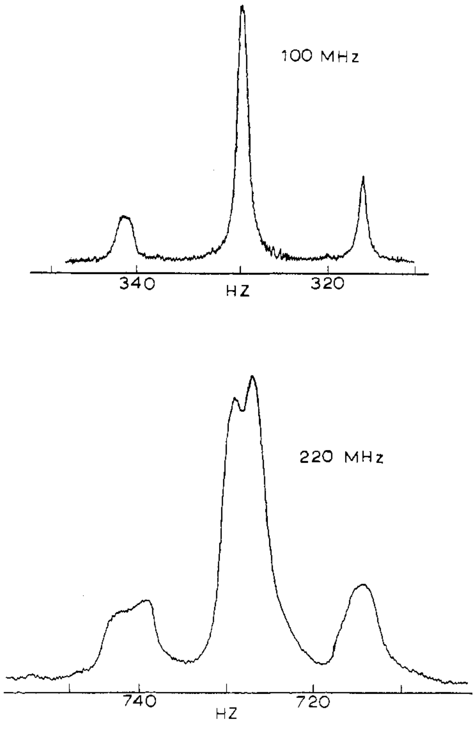

Figure 1.—The 100- and 220-MHz spectra of N-deuterated $Pt(en)_3^{4+}$ in D_2O.

Because the chemical shift difference is small compared with the intraligand proton–proton coupling constants of ethylenediamine, it was necessary to calculate the complete AA'BB' spectrum of the parent peak and the AA'BB'X spectrum of the satellites in order to evaluate the chemical shift and coupling constant differences. Fortunately, the complete 100-MHz spectrum and the parent peak of the 220-MHz spectrum are insensitive to substantial changes (±4 Hz) in the intraligand coupling constants, enabling evaluation of the chemical shift difference and the platinum–proton coupling constant difference. The satellite peaks of the 220-MHz spectrum are very sensitive to the natural line width, the chemical shift difference, and the platinum–proton coupling constant difference as well as to the intraligand coupling constants. Consequently, the intraligand coupling constants could not be determined accurately and provide no information about the ligand conformation. From previous work[2,10] the following intraligand proton–proton coupling constants were assumed: $J_{\text{gem}} = 12.5$, $J_{\text{aa}} = 8.4$, $J_{\text{ee}} = 6.6$, and $J_{\text{ae}} = 4.0$ Hz.

A good fit of both the 100- and 220-MHz spectra was obtained using the above values of the intraligand proton–proton coupling constants, a chemical shift difference of 0.04 ± 0.01 ppm, and a platinum–proton coupling constant difference of 6.0 ± 1.0 Hz. The spectra are slightly temperature dependent with the line widths decreased somewhat at 80°.

Discussion

There are two possible origins of the chemical shift difference observed in the spectra of $Pt(en)_3^{4+}$: incomplete conformational averaging and/or the inherent magnetic asymmetry of the ethylenediamine ligand in a tris complex. There appears to be no way to assess directly the relative contribution of each of these to the observed chemical shift difference of 0.04 ppm. The observation that there is also a difference in the coupling constants with platinum between the protons possessing different chemical shifts, however, strongly indicates that a conformational preference exists in $Pt(en)_3^{4+}$.

There is ample evidence from other studies that vicinal platinum–proton coupling constants are strongly dependent on the dihedral angle between the bonds connecting the coupled nuclei in a fashion analogous to the Karplus relation for coupling constants between protons.[15] In these coordinated ligands, protons occupying axial positions with dihedral angles to platinum of approximately 60° possess much smaller coupling constants than protons occupying equatorial positions with dihedral angles of approximately 180°. There is also substantial evidence that protons in axial positions resonate at higher fields than protons in equatorial positions.[2,3,10] Consequently, if conformational averaging is incomplete, those protons which are more often in axial than in equatorial positions will resonate at a higher field and possess a smaller coupling constant with platinum than those protons more often in equatorial positions. This accounts qualitatively for the observed spectra, as depicted schematically in Figure 2. The simultaneous difference in chemical shifts and in coupling constants between protons incompletely averaged between axial and equatorial positions leads

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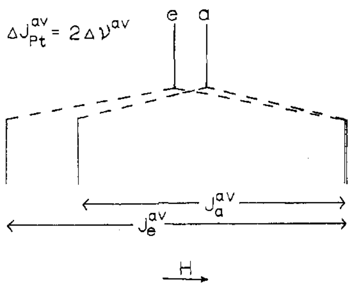

Figure 2.—Schematic explanation for the difference in satellite peak line widths in the particular case that the difference in coupling constants is exactly twice the chemical shift difference.

to a narrow satellite peak at high field and a broad satellite peak at low field.

Were conformational averaging complete and the chemical shift difference due solely to the inherent magnetic nonequivalence of the tris complex, a substantial difference in coupling constants to platinum would not be expected. If each ligand populated the δ and λ conformations equally, then each proton would possess an identical geometric relationship with the platinum. In this model a chemical shift difference arises from the magnetic effects of the other two chelate rings in the complex, not from their effects on the geometry of the ligand. The distribution of the ligands about the platinum is not expected to influence the scalar coupling through the Pt–N–C–H bonds. Neither is through-space dipole–dipole coupling expected. Dipole–dipole coupling is averaged to zero by rapid tumbling in solution except when the nuclei are in an anisotropic environment. The metal ion in a tris-diamine octahedral complex is nearly isotropic as indicated by the absence of effective nuclear quadrupole relaxation in Co(en)$_3{}^{3+}$.[16] The observed difference in coupling constants is therefore more likely the consequence of incomplete conformational averaging than the result of the asymmetry of the complex.

To determine the extent of conformational averaging, one additional assumption is necessary. Either the intrinsic chemical shift difference between an axial and an equatorial proton in a fixed conformation or the intrinsic coupling constants between platinum and the axial and equatorial protons in a single conformation are required. We chose to assume that the chemical shift difference between the axial and equatorial methylene protons observed in tris(propylenediamine)platinum(IV) ion[10] is appropriate for a single conformation of ethylenediamine. Using the value of $\Delta\nu^0$ of 13 ± 2 Hz for the intrinsic chemical shift difference,[10] the averaged chemical shift difference of 4 ± 1 Hz implies that 65 ± 5% of the ethylenediamine ligands are in the more stable conformation and 35 ∓ 5% in the less stable conformation.

The intrinsic platinum–proton coupling constant can now be calculated from this result together with the observed difference in the averaged coupling constants ($\Delta J_{Pt}{}^{av}$ = 6 ± 1 Hz) and the sum of the averaged coupling constants (54 Hz, determined from the separation of the satellite peaks). The platinum–equatorial proton coupling constant is calculated to be 40 ± 5 Hz, and the platinum–axial proton coupling constant, 15 ∓ 5 Hz. These values are in accord with other observations[15] that the equatorial proton is more strongly coupled to the metal ion than is the axial proton and thus support the assumptions made in evaluating them.

We conclude that conformational preferences exist for the ethylenediamine ligands in Pt(en)$_3{}^{4+}$ in solution since complete conformational averaging does not account for the differences in platinum–proton coupling constants. Since incomplete conformational averaging of the coupling constants is needed to explain the asymmetry of the satellite peaks, this effect must also be included in explaining the chemical shift difference. Assuming only incomplete conformational averaging effects, the spectra can be fit and reasonable values of the ^{195}Pt coupling constants calculated; hence the inherent magnetic nonequivalence of an ethylenediamine ligand in a tris complex must not contribute significantly to the observed chemical shift difference.

The extent of conformational averaging is comparable to that found for Ru(en)$_3{}^{2+}$ [10] and Ni(en)$_3{}^{2+}$,[1] which suggests that the charge on the complex does not substantially alter the conformational energies. The relatively narrow lines of the Pt(en)$_3{}^{4+}$ spectra compared with those of Ru(en)$_3{}^{2+}$ and Rh(en)$_3{}^{3+}$ are better explained[9,10] in terms of the relatively small intrinsic chemical shift difference between the axial and equatorial protons, probably a consequence of the high oxidation state of the metal.

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Preparation of Salts of the Bis(triphenylphosphine oxide)hydrogen(I) Cation

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Collamati[1] has reported the reformulation of the compound HAuCl$_4\cdot$2(C$_6$H$_5$)$_3$PO as {[(C$_6$H$_5$)$_3$PO]$_2$H}AuCl$_4$. Potts[2] has recently extended the work to include other protonic complexes of oxo ligands with HAuCl$_4$. During studies of the chemistry of triphenylphosphine oxide with several metal salts, additional examples of

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