

cured with *complete retention of configuration* (within the limits of the detection method used).

The chirality of the major acetolysis product, 3-homoadamantyl-4-*d* acetate (IX, R = D), was not determined directly. However, this product was rearranged to the thermodynamically more stable 1-adamantylcarbinyl-1'-*d* acetate (VI, R = D) by catalytic amounts of toluenesulfonic acid in acetic acid.¹ The optical purity of this rearranged ester was determined by saponification, conversion¹¹ to the O-methylmandelate, and nmr analysis. Again, only the δ 3.73 ppm band was observed. This indicates that both the conversion of VI (R = D) to IX (R = D) and the latter to VIII (R = D) had proceeded with optical integrity, both processes presumably involving inversion at the chiral center.

This evidence, along with that previously acquired,^{1,2i} strongly implicates bridged ion X as the intermediate in the reactions described.

According to our present view of solvolysis reactions,¹³ simple primary carbonium ions are energetically inaccessible in the usual solvents. Only two mechanistic routes are available for primary solvolysis: k_s (solvent assisted), which would lead only to unrearranged products and ester with inverted configuration, and k_A (neighboring group assisted). This is the only available mechanism which can lead to rearranged products. It follows then that the observation of *any* rearrangement accompanying the solvolysis of a simple, primary system can be taken as *prima facie* evidence for neighboring group participation. Thus, contrary to our former tentative conclusion,¹ the solvolysis of neopentyl tosylate must be assisted by methyl participation.

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Conformational Stability of Tris(ethylenediamine)ruthenium(II) Ion in Solution

Sir:

The possibility of conformational isomerism in chelated ethylenediamine ligands has long been recognized,¹ and a detailed analysis has been presented by Corey and Bailar.² They predicted that the most stable conformer of a Λ -tris(ethylenediamine)metal ion would have each ethylenediamine ligand in the δ conformation with the carbon-carbon axis of each

ligand parallel to the C_3 axis of the complex, in preference to the λ conformation in which the carbon-carbon bond forms an obtuse angle with the C_3 axis. This agrees with the observed crystal structures of $Co(en)_3^{3+}$ in several salts³⁻⁵ and with that of $[Ni(en)_3](NO_3)_2$.⁶ In each case the metal-ethylenediamine rings were observed to be *gauche* and in the $\delta\delta\delta$ conformation for a Λ configuration about the metal.

For both the δ and the λ conformations of the ethylenediamine ligand the hydrogens on both the amine nitrogen and methylene carbon atoms adopt approximately axial and equatorial positions and would be expected to produce a complex proton nmr spectrum. In particular, in the absence of coupling with the amine protons, which may be eliminated by deuteration, the methylene protons would be expected to produce an AA'BB' spectrum. Such complex spectra have not been observed, however, for the trisethylenediamine complexes of Pt(IV)⁷ or Rh(III),⁸ which exhibit single resonances only several cycles wide, or of Co(III) which gives a single broader line of 18 Hz width.⁹ The absence of the expected multiplets has been attributed to rapid conformational equilibration between the δ and λ forms during which the axial protons become equatorial, and *vice versa*, with the result that the methylene protons become equivalent.^{8,9} There have been several recent reports of nmr evidence from the amine proton spectra for distinct conformations of $Co(en)_3^{3+}$, but there seems to be no case of well-resolved fine structure for the methylene resonances of a trisethylenediamine complex.^{9,10}

The tris(ethylenediamine)ruthenium(II) ion in contrast has a methylene proton spectrum with very well resolved fine structure. Both the 60- and 100-MHz spectra of the deuterated complex, shown in Figure 1, have typical AA'BB' multiplet structures with the center of the band 2.55 ppm downfield from DSS. A detailed analysis of these spectra is in progress. In the spectrum of the nondeuterated complex two distinct broad amine proton resonances can be observed in the region 2.8-4.5 ppm downfield from DSS. Quite remarkably the multiplet structure of the methylene protons persists in 0.1 M trifluoroacetic acid solution up to 100°.

The bromide salt of $Ru(en)_3^{2+}$ used in this study was obtained from the less soluble $[Ru(en)_3]ZnCl_4$ or $[Ru(en)_3]ZnBr_4$ ¹¹ by dissolving the latter in an acetate-buffered solution of Na_2H_2EDTA and adding a concentrated solution of NaBr to effect precipitation. Previous studies of the optical activity¹² of $Ru(en)_3^{2+}$ and of its electron-exchange reaction^{11a} with $Ru(en)_3^{3+}$ indicate that the complex ion is monomeric and substitution inert, as are the trisethylenediamine complexes of Co(III), Rh(III), and Pt(IV). The facile air oxidation of $Ru(en)_3^{2+}$ was avoided by preparing solutions in an

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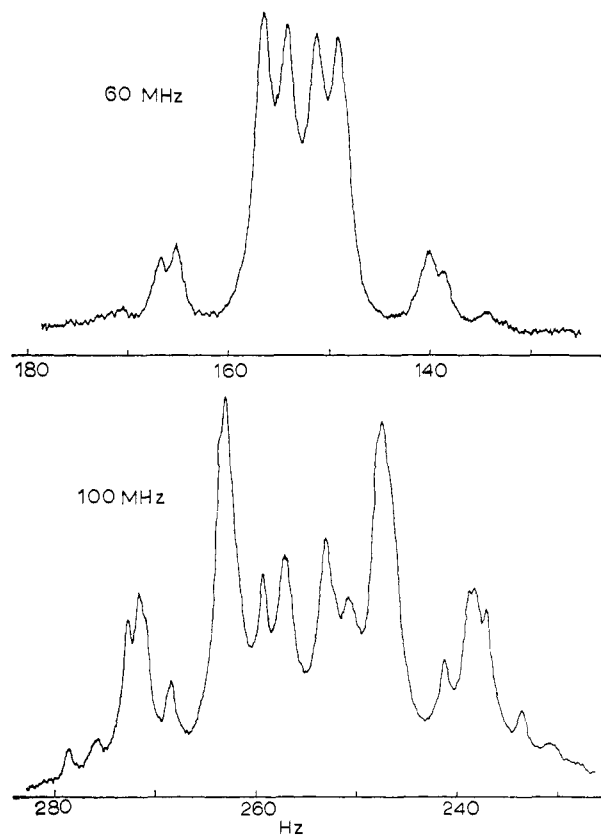


Figure 1. Proton nmr spectra (60 and 100 MHz) of $\text{Ru}(\text{en})_3^{2+}$ in D_2O solution of 0.1 M trifluoroacetic acid (frequencies in Hz relative to DSS).

inert atmosphere and sealing the nmr tubes under vacuum. The observed spectrum did not change with time for a given solution or with a change in medium from 0.1 M trifluoroacetic acid to 0.1 M hydrobromic acid.

The fine structure observed for the methylene protons of $\text{Ru}(\text{en})_3^{2+}$ may be explained in at least two possible ways. One explanation is that the ethylenediamine rings are strongly locked in one conformation resulting in distinct axial and equatorial protons. The activation energy required to convert to the other conformation is so large as to prohibit conformational interchange even at 100° . On the other hand, if one conformation, presumably the $\delta\delta\delta$ form for the Λ configuration, is strongly thermodynamically favored so that it is present in a very large excess, the observed spectra would result even though rapid conformational interchange occurs. In this case, the observed chemical shift for the axial proton would be a mole fraction average of the chemical shift of the axial proton of the stable conformer and the chemical shift of the equatorial proton of the unstable conformer. Similarly, the observed equatorial resonance would be a mole fraction average of the "stable equatorial shift" and the "unstable axial shift." If the two conformers differ sufficiently in energy so that the populations of the two states are extremely unequal, the observed axial and equatorial chemical shifts would not be the same and a single line resonance would not result even though rapid interconversion occurs. Collapse of the fine

structure would not be expected since the coupling between two given protons persists throughout the interconversion, and the coupling constant value may be a weighted average of the coupling constants for the two given protons in the two forms. The lack of temperature effects on the spectrum in this case would mean that energy difference for the two conformers is too large to allow a substantial shift in equilibrium population of the two states with changes within the accessible range of temperatures.

Our observations do not permit us to distinguish between these two possibilities for the $\text{Ru}(\text{en})_3^{2+}$ complex. The very narrow lines observed for the $\text{Rh}(\text{III})$ and $\text{Pt}(\text{IV})$ complexes, however, require both rapid interconversion and comparable energies for both forms for the methylene protons to become equivalent. For $\text{Co}(\text{en})_3^{3+}$, it has been estimated that 30% of the Λ complex is in the $\delta\delta\lambda$ form.¹ If rapid interconversion occurs between the conformers present in this ratio, the broad single line observed for the methylene protons may be due to the difference in the observed chemical shifts for the axial and equatorial protons being too small to yield resolved peaks. Since this chemical shift difference is greater for amine protons than for methylene protons, the two peaks are resolved for the amine protons. These nmr observations for the $\text{Pt}(\text{IV})$ and $\text{Co}(\text{III})$ complexes are consistent with those from a study of the influence of ring conformations on the optical activity of trisdiamine complexes; *i.e.*, the ethylenediamine chelate rings have a preferred conformation dependent upon the configuration of the chelate rings around the metal ion in the case of $\text{Co}(\text{III})$ but not for $\text{Pt}(\text{IV})$.^{13,14}

Raymond, Corfield, and Ibers have reported several crystal structures containing $\text{Cr}(\text{en})_3^{3+}$ in which the expected $\delta\delta\delta$ conformation for the Λ configuration is not observed.¹⁵ These authors suggest that "hydrogen bonding specifically favors the λ conformation relative to the more stable δ form." We would suggest as a tentative explanation that the observation of conformational stability in the $\text{Ru}(\text{II})$ ion is a result of its lower charge and consequent weaker hydrogen bonding relative to the $\text{Rh}(\text{III})$ and $\text{Pt}(\text{IV})$ complexes. For these latter ions the λ conformer is sufficiently stabilized by hydrogen bonding that at least the $\delta\delta\delta$ and $\delta\delta\lambda$ conformers are comparable in energy and rapid conformational interchange occurs. For the $\text{Ru}(\text{II})$ ion, on the other hand, the weaker hydrogen bonding does not lower the energy of the λ form enough to allow the conformational equilibrium necessary to make the methylene protons equivalent.

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