Conformational Analysis of Tris(ethylenediamine)ruthenium(II) Ion by Proton Magnetic Resonance

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Abstract: The multiplet structure of the methylene proton magnetic resonance spectrum of N-deuterated tris(ethylenediamine)ruthenium(II) ion has been analyzed as an AA′BB′ system. The parameters obtained from the 100-MHz spectrum (δ 0.23 ppm, $J_{\text{gem}} = -12.5$, $J_{\text{aa}} = 9.5$, $J_{\text{ae}} = 3.8$, and $J_{\text{ee}} = 5.5$ Hz) also fit the 60-MHz spectrum. Observation of a single AA′BB′ pattern implies either that each of the ethylenediamine ligands is in the same conformation or that there is no significant difference in the magnetic environments of the methylene protons between the δ and λ conformers in the complex.

The 100-MHz proton magnetic resonance spectrum of N-deuterated tris(ethylenediamine)ruthenium(II) ion consists of a well-resolved multiplet of at least 20 lines.[1] This spectrum is highly unusual, for the room-temperature spectra of the analogous N-deuterated trisethylenediamine complexes of Pt(IV),[2] Rh(III),[3] Zn(II),[3] and Cd(II)[2] consist of single sharp lines (with coupling observed with ^{195}Pt of 27 Hz[2]), while that of Co(III)[4] is a single broader line. A complex spectrum might be expected, however, if the conformation of the ethylenediamine ligands is considered.[5] Numerous crystal structures have revealed that coordinated ethylenediamine adopts a *gauche* conformation with distinct axial and equatorial protons.[6] A primitive conformational analysis has indicated that in the most stable form of Co(en)$_3{}^{3+}$ each ligand is in an identical *gauche* conformation designated δ for the Λ configuration of the complex.[7] A recent, more sophisticated analysis by Gollogy and Hawkins[8] suggests, on the other hand, that a wide range of conformations is possible for ethylenediamine in Co(en)$_3{}^{3+}$, with a low energy barrier between two energy minima, a result which is consistent with the absence of fine structure hitherto observed in the nmr spectra of these complexes.

We have now completed a detailed analysis which confirms our earlier assignment of the spectra observed for Ru(en)$_4{}^{2+}$ as an AA′BB′ system. Furthermore, the coupling constants obtained are entirely consistent with a *gauche* conformation, but with a considerably larger dihedral angle than those previously observed in the crystal structures of other complexes.

Experimental Section

Materials. [Ru(en)$_3$]Br$_2$ was prepared from the less soluble [Ru(en)$_3$]ZnBr$_4$ obtained by the method described by Meyer and Taube.[9] It was necessary to complex the zinc with EDTA in order to form the more soluble bromide. In a typical preparation 0.81 g of [Ru(en)$_3$]ZnBr$_4$, 0.52 g of Na$_2$H$_2$EDTA, and 0.27 g of NaOAc were placed in a flask with amalgamated zinc and the flask was deoxygenated with argon gas. About 7–8 ml of hot deoxygenated water was added by syringe and the mixture allowed to cool after complete dissolution had occurred. Addition of 2–3 ml of concentrated deoxygenated NaBr solution resulted in precipitation of the desired compound, which was collected by filtration and washed with ethanol and ether. The compound was dissolved in hot trifluoroacetic acid and reprecipitated from the cooled solution by addition of deoxygenated sodium bromide solution. *Anal.* Calcd for [Ru(en)$_3$]Br$_2$: C, 16.33; H, 5.48; Br, 36.22. Found: C, 16.24; H, 5.33; Br, 36.16. [Ru(en)$_3$]Br$_3$ was prepared as described earlier.[10]

N-Deuterated Ru(en)$_3{}^{2+}$ solutions were prepared expediently using the Ru(en)$_3{}^{3+}$-catalyzed exchange reaction. Solid samples of [Ru(en)$_3$]Br$_2$ and [Ru(en)$_3$]Br$_3$ were mixed in about a 12:1 mole ratio and placed in a flask with amalgamated zinc. After the flask was completely deoxygenated, previously deoxygenated D$_2$O was added and the solution allowed to stand several minutes before deoxygenated deuteriotrifluoroacetic acid was added. Reduction of Ru(III) to Ru(II) is complete in 20–30 min, after which the sample was transferred to the nmr tube. The final solution was 0.1 *M* in trifluoroacetic acid. Identical spectra were obtained with 0.1 *M* hydrobromic acid.

Spectra were recorded on the Varian A-60 and HA-100 instruments.

Analysis of Spectra. The spectra were analyzed using the iterative programs NMRIT and NMREN 1 of Swalen and Reilly[11] which were adapted for the University of Illinois IBM OS/360 computer. Two unusual features of the spectrum, the crossover of line 8 through the midpoint and the unusual difference in separations of lines 3 and 4 compared with lines 1 and 2, frustrated attempts at preliminary assignments of the lines using the various frequency and intensity sum rules for AA′BB′ spectra. (The numbering used is that of Grant, Hirst, and Gutowsky.[12]) Assuming a chemically reasonable chemical shift difference and reasonable values for the coupling constants immediately gave good agreement with the observed spectra, however, and permitted the necessary line assignments to be made, from which the energy levels could be calculated.

Results

The definitions of coupling constants for the AA′BB′ system are

$$\begin{tikzcd}
\mathrm{A} \arrow[r, leftrightarrow, "J_{13}"] \arrow[d, leftrightarrow, "J_{12}"'] \arrow[dr, leftrightarrow, "J_{14}"] & \mathrm{B} \arrow[d, leftrightarrow, "J_{34}"] \\
\mathrm{A'} & \mathrm{B'}
\end{tikzcd}$$

The appearance of the spectrum depends only on the chemical shift difference $\nu_0\delta$ between nuclei A and B, the

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[1] H. Elsbernd and J. K. Beattie, *J. Amer. Chem. Soc.*, **91**, 4573 (1969).

[2] H. Elsbernd and J. K. Beattie, unpublished observations.

[3] D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 791 (1959).

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[5] A. M. Sargeson in "Transition Metal Chemistry," Vol. 3, R. Carlin, Ed., Marcel Dekker, Inc., New York, N. Y., 1966, pp 303–343.

[6] For a recent compilation, see literature cited in ref 8.

[7] E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

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[9] T. J. Meyer and H. Taube, *ibid.*, **7**, 2369 (1968).

[10] H. Elsbernd and J. K. Beattie, *ibid.*, **8**, 893 (1969).

[11] J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962); for a description of these programs see D. F. DeTar, Ed., "Computer Programs for Chemistry," Vol. I, W. A. Benjamin, Inc., New York, N. Y., 1968, p 54.

[12] D. M. Grant, R. C. Hirst, and H. S. Gutowsky, *J. Chem. Phys.*, **38**, 470 (1963).

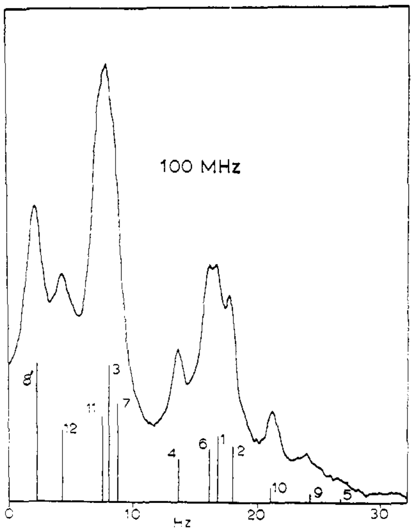

Figure 1. High-field half of 100-MHz spectrum of N-deuterated $Ru(en)_3^{2+}$ in D_2O with calculated spectrum and line assignments.

absolute magnitudes of the following four parameters, and the relative signs of N and K.[12]

$$N = J_{13} + J_{14} \qquad K = J_{12} + J_{34}$$

$$L = J_{13} - J_{14} \qquad M = J_{12} - J_{34}$$

From the analysis of the 100-MHz spectrum $N = \pm 8.7$, $K = \mp 15.0$, $L = \pm 16.3$, $M = \pm 40$, and $\nu_0\delta = 23.0$; *i.e.*, with K of opposite sign from N. Two sets of values of J's were found to reproduce the spectrum.

$$J_{12} = -5.5 \qquad J_{12} = +5.5$$

$$J_{13} = +12.5 \qquad J_{13} = +3.8$$

$$J_{14} = -3.8 \qquad J_{14} = -12.5$$

$$J_{34} = -9.5 \qquad J_{34} = +9.5$$

These differ only in the signs of the coupling constants and the (arbitrary) labeling of nuclei 3 and 4. These values fit the observed 100-MHz spectrum as shown in Figure 1 with an average deviation of 0.15 Hz for the positions of all 24 lines, with the largest deviations appearing in the uncertain positions of lines 5 and 9 in the wings of the spectrum and in the position of the overlapped line 11. In addition the 60-MHz spectrum illustrated in Figure 2 is also reproduced quite well with these values, as are the relative intensities of the lines in both spectra, further confirmations of a correct assignment.

This "complete" analysis of the spectrum still does not permit identification of which protons in the ligand have the smaller (A,A′) or larger (B,B′) chemical shifts and consequently precludes identification of the various coupling constants with particular interactions between the axial and equatorial protons. Two additional pieces of information are used to make these assignments. The first is that one of the observed coupling constants of |12.5| Hz is that usually observed for geminal coupling constants, for which the sign is probably negative.[13] This indicates that protons 1,3 and 2,4 are geminal pairs. Secondly, it is generally observed that vicinal coupling is largest between protons related by dihedral angles near 0 or 180° and is very small for dihedral angles near 90°.[14] Consequently the coupling constant of $J_{34} = 9.5$ Hz is assigned to the *trans*-axial axial protons. This permits the complete assignment of coupling constants and signs as illustrated in Figure 3: $J_{gem} = -12.5$, $J_{aa} = 9.5$, $J_{ae} = 3.8$, $J_{ee} = 5.5$.

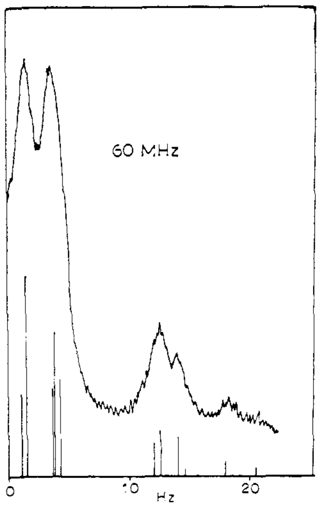

Figure 2. High-field half of 60-MHz spectrum of N-deuterated $Ru(en)_3^{2+}$ in D_2O with calculated spectrum.

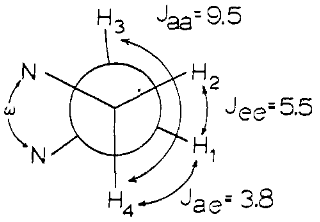

Figure 3. Assignments of coupling constants (Hz) for coordinated ethylenediamine in N-deuterated $Ru(en)_3^{2+}$.

The axial protons 3 and 4 are found at 0.23 ppm higher than the equatorial protons, an assignment consistent with those of some organic systems, such as cyclohexane-d_{11} in which the chemical shift of the axial proton is 0.47 ppm greater than that of the equatorial proton.[15]

Discussion

The most important result of this work is the confirmation of the AA′BB′ character of the spectra which indicates a *gauche* conformation for the coordinated ethylenediamine in solution. The coupling constants indicate that geminal coupling occurs between protons with different chemical shifts (between A and B and A′ and B′) corresponding to the axial and equatorial protons of each methylene group. The symmetry of the spectrum (AA′BB′ instead of ABCD) indicates that the two axial protons have the same chemical shift, as do the two equatorial protons, which requires that the ligand is symmetric with respect to the magnetic environments of the methylene groups. This does not

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(13) M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, **85**, 1901 (1963); *Advan. Magn. Resonance*, **1**, 149 (1965).

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necessarily imply that the ligand is geometrically symmetric, however, since the effect of slightly different geometries on the chemical shifts is unknown and rapid exchange between symmetric and unsymmetric geometries *of one conformation*, which preserves the difference between axial and equatorial protons, could lead to the observed chemical shift difference.

The observation of a *single* AA′BB′ pattern implies either that each ethylenediamine ligand is in the same conformation, and consequently related to the other two ligands by the C_3 axis of the complex, or that there is no significant interaction between the ligands so that the δ and λ conformers of each ligand are magnetically equivalent.

The spectrum of a *gauche* conformation of ethylenediamine is invariant with respect to inversion to its enantiomeric conformation, say δ to λ. Consequently if the two conformations δ and λ are magnetically enantiomeric in a trisethylenediamine complex, *i.e.,* if there is no significant interaction between the ligands, mixtures of δ and λ conformations will lead to identical coupling constants. Only when the rate of exchange between δ and λ forms is on the order of the chemical shift difference between axial and equatorial protons will significant changes in the spectrum be observed. In the present case the observed chemical shift difference of 0.23 ppm is similar to that of 0.28 ppm observed for $Pd(pn)_2^{2+}$, which is believed to be in a single conformation with the C-methyl group equatorial.[16] It thus appears from the chemical shift difference and observed coupling constants that the ethylenediamine rings in $Ru(en)_3^{2+}$ are in stable *gauche* conformations, but it is not possible to determine whether each ligand in the complex is in a single, say δ, conformation, or whether a mixture of δ and λ forms occurs. In other words, it is still impossible to determine whether one conformer, say, $\delta\delta\delta$, is sufficiently thermodynamically more stable to account for the observed spectrum or whether the barrier to inversion is sufficiently high so that the rate of exchange between δ and λ conformers is low.

A second important result is a prediction of the dihedral angle ω between the N_1–C–C and N_2–C–C planes as illustrated in Figure 3. Vicinal coupling constants are generally related to the dihedral angle between the two coupled protons by the Karplus equation

$$J_{ab} = J_0 \cos^2 \phi_{ab} - C$$

where J_{ab} is the observed coupling constant between vicinal protons H_a and H_b, J_0 is a constant for dihedral angles ϕ of 0–90° between C–H_a and C–H_b, and C is a constant.[14,17] The constant C is generally small and will be ignored in this application in order to obtain an estimate of ω using the two *gauche* coupling constants J_{ae} and J_{ee}. The simplified Karplus equation is believed to yield values of dihedral angles within about ±5°. Applying the relation to the two coupling constants J_{ae} and J_{ee} defined in Figure 3 in order to eliminate the parameter J_0 gives a value for the dihedral angle ω of 63°. This value is significantly larger than those observed in the solid state for various trisethylenediamine complexes, which are generally in the range 45–55°.[8] Extrapolation from the solid state to properties in solution is admittedly hazardous, especially in the present case involving charged ions with amine protons capable of hydrogen bonding with the solvent, and prediction of a dihedral angle from the Karplus equation is necessarily crude. Nevertheless it is attractive to speculate that the anomalous nmr spectrum of $Ru(en)_3^{2+}$ may be due to an unusually large dihedral angle ω, which results in a large barrier to inversion between conformers. It will be interesting to determine whether the conformational analysis recently proposed by Gollogly and Hawkins,[8] which predicted a dihedral angle of somewhat less than 60° and a low barrier to inversion for $Co(en)_3^{3+}$, will yield substantially different results when the parameters appropriate to $Ru(en)_3^{2+}$ are employed.

The increased metal–nitrogen distance in $Ru(en)_3^{2+}$ relative to other trisethylenediamine complexes cannot be the only factor responsible for the observed spectrum, however, for the methylene resonance of N-deuterated $Co(en)_3^{3+}$ has a line width of about 18 Hz whereas that of N-deuterated $Rh(en)_3^{3+}$ is less than 3 Hz wide.[3] Partially resolved multiplets are also observed for *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ whereas *cis*-$[Co(en)_2(NH_3)_2]^{3+}$ displays only a single symmetric resonance[5] which indicates, as suggested earlier, that hydrogen bond effects may be important.

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