water than either the disodium or the dipotassium salts. In order to obtain K_2ReH_9 from Na_2ReH_9, it is necessary first to convert the latter to $BaReH_9$ from which the dipotassium salt may be prepared by metathesis with K_2SO_4. The *d*-spacing data also show that Na_2ReH_9 and $NaKReH_9$ are not isomorphous with K_2ReH_9 or with each other.

An isolated ReH_9^{2-} ion (point group symmetry[2] D_{3h}) should give rise to three infrared-active ReH stretching frequencies, ν(ReH) ($2\,E' + A_2''$), and five infrared-active ReH bending frequencies, δ(ReH) ($3\,E' + 2\,A_2''$). Alkaline aqueous solutions of M_2ReH_9 (M_2 = Na_2, NaK, K_2, $((C_2H_5)_4N)_2$) have only a single rather broad ν(ReH) band at 1845 cm^{-1}. For $((C_2H_5)_4N)_2$-ReH_9 in acetonitrile solution, the ν(ReH) frequency is shifted to 1808 cm^{-1} and the band is still unresolved. The ν(ReH) and δ(ReH) frequencies in the solid state are listed in Table II; the most notable feature is the appreciable shift to lower frequencies of both the stretching and bending vibrations in the bis-tetraethylammonium salt.

TABLE II

SOLID-STATE INFRARED SPECTRA OF ENNEAHYDRIDORHENATE SALTS[a]

Compound	ν(ReH), cm^{-1}	δ(ReH), cm^{-1}
Na_2ReH_9	1835 s, br	745 s, ~720 sh, ~630 sh
$NaKReH_9$	~1950 sh, 1845 s, ~1700 sh	738 s
K_2ReH_9[b]	1931 w, sh, 1846 s, 1814 sh	735 s
$((C_2H_5)_4N)_2ReH_9$	1780 s, br	~720 sh, 675 s, ~610 sh

[a] Nujol oil mull spectra: s, strong; sh, shoulder; br, broad; w, weak. [b] From ref 1.

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Evidence of Ligand Motion in Tris(ethylenediamine)- and Tris(propylenediamine)cobalt(III) Complexes[1]

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The most difficult problem encountered in applying pmr spectroscopy to the study of cobalt(III) complexes is finding a suitable solvent. Clifton and Pratt[3] have shown that the pmr spectra of cobalt(III)–amine complexes could be obtained in acidified deuterium oxide solutions. Using this solvent, Spees, *et al.*,[4] observed the pmr spectra of several hexaminecobalt(III) complexes including those of ethylenediamine and propylenediamine. However, these spectra were not sufficiently well resolved to make unambiguous assignments of the different conformations of the individual chelate rings. Yoneda and Morimoto[5] have found that several acids could be used as solvents for pmr studies of these compounds. They were also able to relate the stereochemistry of $Co(en)_3^{3+}$ and $Co(tn)_3^{3+}$ complexes to the spectra obtained using trifluoroacetic acid (TFA) as a solvent.

The present investigation was undertaken to obtain a more complete understanding of the behavior of these complexes in solution. The dependence of the spectra on the nature of the solvent and temperature is reported herein.

Results and Discussion

The pmr spectrum of the $Co(en)_3^{3+}$ complex shows a marked dependence on the solvent. In TFA and 70% $HClO_4$, a broad doublet at lower fields and a broad singlet at higher field are observed. The chemical shift of the doublet changes greatly in different solvents while the singlet remains relatively fixed. When DMSO was employed as a solvent, only one peak, a broad singlet, was observed at lower fields. Since the sharpest lines were obtained, TFA appears to be the best solvent for this work.

The spectrum of this complex is easily understood by considering its stereochemistry. The X-ray structure of this compound, obtained by Nakatsu, *et al.*,[6] is shown in Figure 1A. The complex ion has a threefold axis about which the three ethylenediamine ligands have a nonplanar twisted structure. If the nitrogen atoms are assumed to have tetrahedral bonds, we can distinguish two kinds of $-NH_2$ protons, such that, of the six upper N–H hydrogens, three are directed upward from the N(I)–N(II)–N(III) plane and three outward, nearly perpendicular to the threefold axis.

If this rigid structure is present in solution, we would expect to observe two distinct chemically shifted NH_2 protons. If the complex is not rigid in solution, with a flipping of the NH_2 groups taking place, the magnetic environment of these protons would be time averaged to a single chemical shift. The nitrogen quadrupole moment and the electric field asymmetry around the nitrogen would cause neighboring proton resonances to be broadened. Various unresolved spin–spin splittings would also cause the spectrum to appear broad.

The room-temperature spectra of $Co(en)_3^{3+}$ dissolved in TFA or 70% $HClO_4$ are consistent with the predictions for a rigid structure. The low-field doublet can be assigned to the NH_2 protons and the broad singlet to the $-CH_2-$ protons. The spectrum obtained in DMSO indicates that the complex is no longer rigid.

In some solvents a variation of the spectrum at different temperatures is observed. The spectrum of $Co(en)_3^{3+}$ in TFA is independent of the temperature

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(1) Presented in part at the 9th International Conference on Coordination Chemistry, Zurich, Switzerland, 1966.

(2) University of Hawaii Hilo Campus, Hilo, Hawaii 96720.

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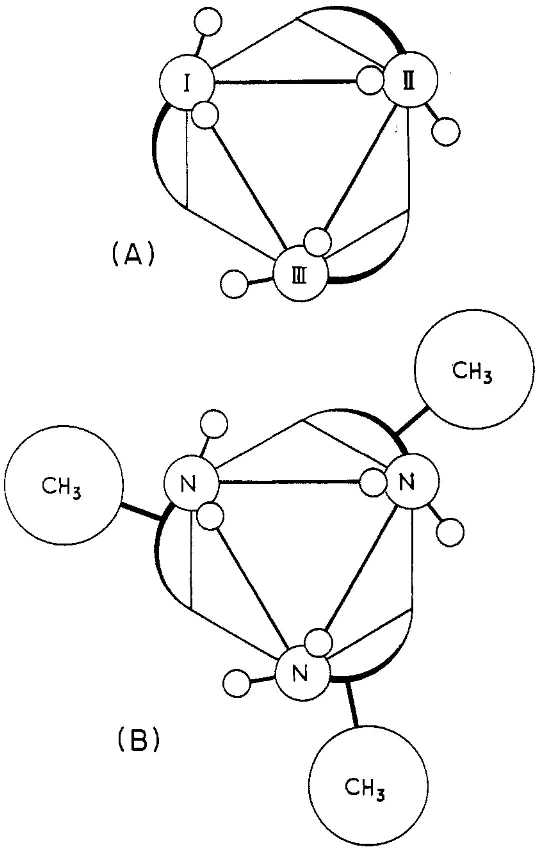

Figure 1.—Structures of (A) $Co(en)_3^{3+}$ and (B) $Co(pn)_3^{3+}$.

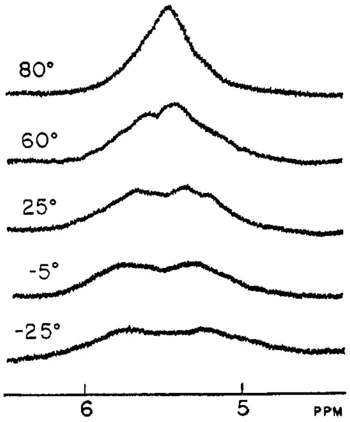

Figure 2.—NH_2 signals of $[Co(en)_3](CH_3CO_2)_3$ dissolved in isobutyric acid at several temperatures.

up to the boiling point of the solvent. However, the marked temperature dependence shown in Figure 2 is observed using isobutyric acid as a solvent. The broad NH_2 doublet, obtained at low temperatures, coalesces into a singlet above 80°. The observed line shapes are those expected when the magnetic environment averaging becomes more rapid[7] and indicate that the complex is becoming less rigid with more mobile NH_2 groups at elevated temperatures.

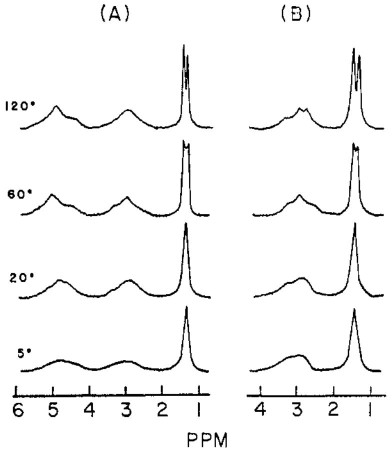

Figure 3.—Pmr spectra of D-$[Co((+)pn)_3]Cl_3$ in TFA at several temperatures: (A) amino-protonated complex; (B) amino-deuterated complex.

Further evidence for mobility of the ligands is obtained from the temperature dependence of the spectrum of D-$[Co((+)pn)_3]Cl_3$[8] dissolved in TFA. As is seen in Figure 3A, the $-CH_3$ signal is a broad singlet at lower temperatures and begins to split into a doublet at 60°. The lines become sharper, and this splitting is more pronounced at higher temperatures. Paralleling this change, the downfield part of the NH_2 signal is a very broad band at room temperature and becomes sharper at higher temperatures. The upfield half remains unchanged. The spectrum of the amino-deuterated complex exhibits a similar temperature dependence as shown in Figure 3B; the $-CH_3$ signal is a broad singlet at room temperature and begins to sharpen into a doublet at 60°. This immediately indicates that the NH_2 protons are not primarily responsible for the broadening of the $-CH_3$ resonance.

Figure 1B shows the structure of D-$Co((+)pn)_3^{3+}$ obtained by Iwasaki and Saito.[9] The observed temperature dependence of the spectra can be explained if we postulate that, as the temperature is increased, one of the $-NH_2$ groups (probably the one adjacent of the CH– group) starts a rocking motion which is accompanied by a twisting of the C–C axis. This twisting motion would result in an averaging of the spin–spin couplings between the $-CH_2-$ and $-CH_3$ groups, thus producing a decrease in the magnitude of the long-range coupling constants which were responsible for the broadening of the $-CH_2-$ and $-CH_3$ signals. This decreased coupling results in a sharpening of both the $-CH_2-$ and $-CH_3$ resonances on increasing the temperature. Thus, the splitting of the $-CH_3$ signal into a doublet by the adjacent bridgehead hydrogen becomes observable. Similarly, we would expect the $-CH_2-$ resonance to sharpen into a doublet in the spectrum of the amino-deuterated compound where the larger NH_2 proton coupling is greatly reduced by the substitution of deuterium for the NH_2 hydrogens.

These predictions are in complete agreement with the observed spectra shown in Figure 3A and 3B. We

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(7) C. E. Looney, W. D. Phillips, and E. L. Reilly, *J. Am. Chem. Soc.*, **79**, 6136 (1957).

(8) The optically active complex was used in place of the more easily obtained *rac*-$Co(pn)_3^{3+}$ to avoid the confusion caused by having to consider the various chelate conformations.

(9) H. Iawasaki and Y. Saito, *Bull. Chem. Soc. Japan*, **39**, 92 (1966).

observe a partially resolved doublet[10] adjacent to the methyl resonance in the spectrum of the deuterated compound at 120°. Obviously, this doublet arises from the $-CH_2-$ protons and confirms the arguments proposed above. Therefore, we conclude that the ligands undergo a rocking and twisting motion at elevated temperatures. This would also explain the observed temperature dependence of the $Co(en)_3^{3+}$ complex spectra.

Experimental Section

Compounds used in this study were the chloride, sulfate, nitrate, and acetate salts of the $Co(en)_3^{3+}$ complex[11] and D-$[Co((+)pn)_3]Cl_3$.[12,13] The pmr spectra were obtained on a Varian A-60 spectrometer equipped with a variable-temperature probe. The samples were degassed and sealed under vacuum to eliminate any possibility of line broadening by dissolved oxygen. Tetramethylsilane was used throughout as an internal standard.

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[10] The bridgehead proton, which we expect to givean unresolved multiplet, can now be assigned to the broad resonance that is visible as a shoulder on the low-field side of the methylene doublet in the 120° spectrum.

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Lanthanide 2-Hydroxy-2-methylbutanoate Chelate Stabilities[1]

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In an earlier note[2] it was proposed that the picolinate anion bonds to lanthanons in a purely bidentate manner. This conclusion was reached through an application of Bjerrum's theory[3] that ratios of successive step formation constants depend principally upon individual formation and decomposition statistics relating to the AB_{n-1} and AB_n chelate species. Bjerrum's theory can be expressed generally as $*P = *K_{n-1}/*K_n = SRT$, where $*P$ is the observed ratio of true thermodynamic step formation constants (at infinite dilution or zero ionic strength), S is the purely statistical contribution, T is the electrostatic factor, and R is a general "rest" or "everthing else" factor (which includes ligand asymmetry and steric effects).[3]

At ionic strength other than zero, the observed ratio P depends upon the ionic strength as well as the factors S, R, and T

$$P = K_{n-1}/K_n = (*K_{n-1}/*K_n)f(\mu) = *Pf(\mu) = SRTf(\mu) \quad (1)$$

In the case of the lanthanide picolinate species,[2] it was shown that the K_1/K_2 ratio at $\mu = 0.1$ was essentially constant at about 4. Thus, the observed values of P fell between the purely statistical values of 3.27 and 4.92 which one predicts from the supposition that picolinate anion functions bidentately or tridentately, respectively, in its associations with nine-coordinate lanthanons (in aqueous media). T has been estimated[4] to be about 1.5 and $f(0.1)$ is about 0.67. Thus, since it is difficult to imagine anything giving rise to an R factor less than unity, it is clear that picolinate *does not* bond tridentately through the nitrogen atom and both carboxyl oxygen atoms.

Although it has been suspected for some time,[5] the following stability constant data (for the first time) clearly demonstrate that homologs of the glycolate anion (substituted α-hydroxycarboxylate ligands) can function either bidentately or tridentately, depending on the ionic radius of the presumably nine-coordinate aquated lanthanide cation. (The short nonbonded distance between the two carboxyl oxygen atoms dictates that they do not simultaneously occupy coordination sites on a regular nine- or ten-coordinated lanthanon. It is suggested that tridentate ligancy in this instance involves attachment of the second carboxyl oxygen atom to a hydrogen atom of a coordinated water molecule *via* a hydrogen bond to give a –Ln–O–H–O–C–O– ring rather than –Ln–O–C–O–.) These data in no way discredit the likelihood that the coordination number of the lighter (larger) cations of the series (La^{3+}–Nd^{3+}) may be 10 rather than 9. At least one regular ten-coordinate array (Archimedean antiprism + 2) leads to the same predicted S value (4.92) as the nine-coordinate (trigonal prism + 3) array of sites in its associations with tridentate ligands.[2,5] Indeed, it is even likely that a change from nine- to ten-coordination is the factor that permits accommodation of the α-hydroxycarboxylate ligand as a nominally tridentate entity.

Experimental Section

2-Hydroxy-2-methylbutanoic Acid Buffer.—Reagent grade 2-hydroxy-2-methylbutanoic acid was obtained commercially and purified further by recrystallization from hot carbon tetrachloride. The purified product (mp 72–73°) was used to prepare buffer stock solutions, 0.1 N in HL and 0.1 N in KL, in which the precise concentrations of acid and salt were determined by standard stoichiometric techniques.

Ionization Constants of the Acid.—Series of 20–25 individual dilutions of the buffer (all adjusted to 0.10 M ionic strength by appropriate additions of KNO_3) were prepared. The volumetric flasks were carefully equilibrated in a 25° water bath and the pH_c of each was read to a precision of 0.0002 unit, using the

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2522.

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