The insolubility of $Mo(acac)_2Cl_2$ in even fairly polar organic solvents suggested that a polymeric structure for these complexes may be possible even though a monomeric structure seemed most likely. Because of its low solubility, molecular weight studies could not be carried out on $Mo(acac)_2Cl_2$; however, determinations were made on some other representative compounds including $Mo(hpd)_2Cl_2$, $Mo(dpm)_2Cl_2$, $Mo(nhpd)_2Cl_2$, and $Mo(dibm)_2Cl_2$. With the exception of $Mo(hpd)_2Cl_2$, the values obtained by both the freezing point depression and the vapor pressure depression methods were in excellent agreement with the calculated values for monomeric species.

The reason for the insolubility of $Mo(acac)_2Cl_2$ is not known but there is a graduated increase in the solubility of the complex with the size and number of organic substituents on the diketonate ligands. Since all the complexes whose molecular weights were measured are monomeric, including $Mo(hpd)_2Cl_2$ whose steric interactions are only slightly more severe than $Mo(acac)_2Cl_2$, it seems most likely that all the complexes in this series, including $Mo(acac)_2Cl_2$, are also monomeric and that the postulate of Larson and Moore[14] regarding the polymeric nature of $Mo(acac)_2Cl_2$ may be incorrect. The low solubility of $Mo(acac)_2Cl_2$ does not seem to be irregular and there is no apparent reason why the coordination number of Mo should be greater than 6 in this complex.

At the present time, it is not possible to say whether these complexes exist as the cis or trans isomers. Because of their paramagnetic nature nmr measurements are precluded and infrared data, although perhaps suggesting a cis configuration, are inconclusive.

The infrared spectrum of $Mo(acac)_2Cl_2$ together with tentative assignments is given in Table II. The identification of the acetylacetonate vibrations were made by comparison with the spectra of $Mo(acac)_3$,[15] $Mo_2O_3(acac)_4$,[21] $MoO_2(acac)_2$,[27] and several $Ti(acac)_2X_2$ complexes.[28] The assignments for the acetylacetonate ligands are based on the normal-coordinate analysis of metal acetylacetonates by Nakamoto[29] modified slightly by later work with the deuterated ligand.[30] The spectrum is consistent only with chelated acetylacetonate ligands and the absence of strong carbonyl bands at frequencies higher than 1600 cm^{-1} in the spectra of the other $M(diket)_2Cl_2$ complexes shows that the diketonate ligands in these complexes are also chelated in the normal fashion. The two fairly intense bands which are seen in the spectrum of $Mo(acac)_2Cl_2$ at 342 and 312 cm^{-1} have tentatively been assigned as Mo–Cl stretching vibrations. This assignment seems to be quite reasonable since bands are observed in this region for several other $Mo(diket)_2Cl_2$ complexes and Mo–Cl stretching vibrations are known to occur in the 300–400-cm^{-1} region.[31,32] Further, examination of a number of molybdenum acetylacetonate complexes reveals that no strong ligand vibrations are seen in this spectral region and that Mo–O stretching vibrations are usually seen at much higher frequencies. Only one Mo–Cl stretching band should be seen in the spectrum of the more symmetrical trans isomer; however, this evidence is much too speculative to rule out a trans structure.

TABLE II

INFRARED SPECTRA OF $Mo(acac)_2Cl_2$

ν,[a] cm^{-1}	Assignment	ν,[a] cm^{-1}	Assignment
1525 vs	$C\overset{\cdots}{-}O$ str + $C\overset{\cdots}{-}C$ str	818 s	C–H out-of-plane def
1410 m	CH_3 degen def	676 s	Ring def + Mo–O str
1362 m	CH_3 sym def	595 m	Mo–O str
1340 m	$C\overset{\cdots}{-}O$ str	542 vs	Out-of-plane def
1286 s	$C\overset{\cdots}{-}C$ str	469 s	$C-CH_3$ def + Mo–O str
1019 m	CH_3 rock	420 m	In-plane def
938 w	$C-CH_3$ str + $C\overset{\cdots}{-}O$ str	342 s	Mo–Cl str
927 m		312 m	Mo–Cl str

[a] Key: s, strong; m, medium; w, weak; v, very.

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Cobalt-59 Nuclear Magnetic Resonance Study of Acid Dissociation Equilibria in Aquopentaamminecobalt(III) Perchlorate and *cis-* and *trans-*Aquoamminebis(ethylenediamine)cobalt(III) Bromide

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Nuclear magnetic resonance (nmr) of metal ions such as Al(III),[1,2] Ga(III),[3] and Cu(I)[4] is quite useful in studying kinetics and equilibrium of metal complexes in solution. In the present study ^{59}Co line widths and chemical shifts are measured to investigate the acid dissociation equilibria and kinetics of proton exchange in concentrated (≥ 0.20 *M*) aqueous solutions of $[Co(NH_3)_5H_2O](ClO_4)_3$ and *cis-* and *trans-*$[Co(en)_2NH_3H_2O]Br_3$.

Experimental Section

$[Co(NH_3)_5H_2O](ClO_4)_3$ and *cis-* and *trans-*$[Co(en)_2NH_3H_2O]Br_3$ were prepared by the typical procedures given in the literature.[5,6]

Nmr measurements were made at 25.0° with the use of a JEOL LNM-WB-20 spectrometer operating at 13.557 MHz. Some measurements were carried out on a Varian VF-16 spectrometer at several frequencies. Chemical shifts were measured in aqueous solution containing a trace amount of $Co(en)_3^{3+}$ ion as an internal standard. Line widths were obtained as the

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peak-to-peak interval of the first derivative of absorption signals which were recorded with effectively small amplitude of modulation at a modulation frequency of 35 Hz.

All pH measurements were made with a TōA Model HM-5A pH meter equipped with a standard glass electrode and a saturated calomel reference electrode. The pH's of solutions were controlled by using sodium hydroxide, perchloric acid, and hydrobromic acid which are all reagent grade chemicals.

Results and Discussion

The ^{59}Co nmr line widths for $[Co(NH_3)_5H_2O](ClO_4)_3$ and *cis*- and *trans*-$[Co(en)_2NH_3H_2O]Br_3$ are strongly dependent upon the pH of the solutions. At pH 2 these complexes give broad ^{59}Co nmr spectra, whereas the line widths become sharper with an increase in pH. The pH dependence of the line widths for $[Co(NH_3)_5H_2O](ClO_4)_3$ is given in Figure 1. The pH dependence of the line width may be interpreted in terms of the protolytic reaction

$$Co(NH_3)_5H_2O^{3+} \rightleftharpoons Co(NH_3)_5OH^{2+} + H^+ \qquad (1)$$

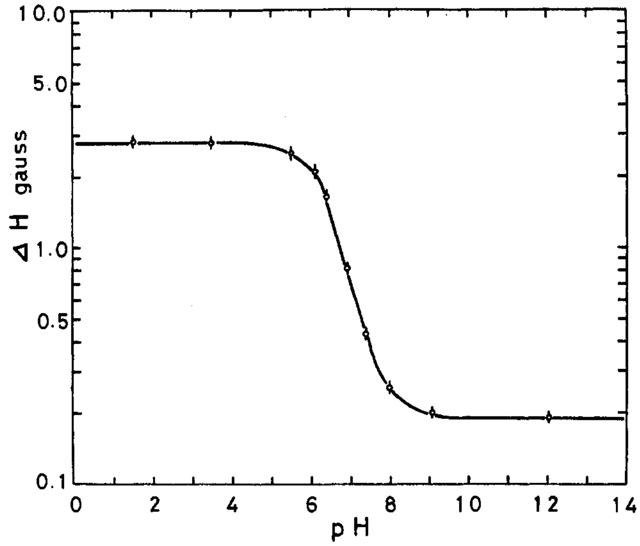

Figure 1.—The pH dependence of the ^{59}Co nmr line widths (♁) for $[Co(NH_3)_5H_2O](ClO_4)_3$ in aqueous solution (0.20 *M*). Solid curve is calculated from eq 3 with $pK_A = 6.36$.

The line widths observed at pH ≤ 5 should be equal to that of $Co(NH_3)_5H_2O^{3+}$, whereas at high pH values (pH ≥ 10) the observed line widths should represent that of $Co(NH_3)_5OH^{2+}$. In the intermediate pH range (pH $\sim$5–10), both hydroxo and aquo complexes exist to an appreciable amount. That a sharp single line is observed in this region shows that there is rapid proton exchange between these two complexes. The observed line width, ΔH_o, may be written as

$$\Delta H_o = P_a \Delta H_a + P_b \Delta H_b \qquad (2)$$

where P and ΔH are the fractional population and the line width for each species, respectively, and subscripts a and b correspond to $Co(NH_3)_5H_2O^{3+}$ and $Co(NH_3)_5OH^{2+}$, respectively. The relation between the line widths and pH is given by

$$pH = pK_A - \log \frac{\Delta H_o - \Delta H_b}{\Delta H_a - \Delta H_o} \qquad (3)$$

where K_A is the acid dissociation constant in eq 1. Line width data in the intermediate pH region where $[Co(NH_3)_5H_2O^{3+}] \simeq [Co(NH_3)_5OH^{2+}]$ are used to determine the equilibrium constant. The pK_A value is estimated at 6.36 ± 0.05 from the experimental point at pH 6.41 where the ionic strength $\mu = 1.0$. This value is in good agreement with 6.40 which was obtained by Bjerrum[7] using a glass electrode at relatively high ionic strength, $\mu = 1.04$. In the present experiments where the concentration of the complex is quite high (0.20 *M*), it is impossible to adjust the ionic strength by merely adding an inert electrolyte. However, the pK_A values which are obtained near the half-equivalent point (pH from 6 to 7) are constant within experimental error regardless of a change in ionic strengths (μ from 0.9 to 1.1).

Similar pH dependence of the line widths is observed for *cis*- and *trans*-$[Co(en)_2NH_3H_2O]Br_3$ in aqueous solution. It has been reported that in the case of $Co(en)_2NH_3H_2O^{3+}$ cis–trans isomerization takes place with increasing pH.[8] Therefore, pK_A values determined by using a glass electrode possibly have an uncertainty due to the isomerization reaction

$$\begin{array}{ccc} cis\text{-}Co(en)_2NH_3H_2O^{3+} & \rightleftharpoons & cis\text{-}Co(en)_2NH_3OH^{2+} + H^+ \\ \upharpoonleft\downharpoonright \text{ slow} & & \upharpoonleft\downharpoonright \text{ fast} \\ trans\text{-}Co(en)_2NH_3H_2O^{3+} & \rightleftharpoons & trans\text{-}Co(en)_2NH_3OH^{2+} + H^+ \end{array} \qquad (4)$$

Since the difference in chemical shift between *cis*- and *trans*-$Co(en)_2NH_3OH^{2+}$ ions is large (110 ppm), the pK_A values for the cis and trans isomers can be determined accurately from the line broadening of each spectrum, regardless of the cis–trans isomerization.

The pH dependence of the line widths for *cis*- and *trans*-$[Co(en)_2NH_3H_2O]Br_3$ in aqueous solution is shown in Figure 2; the pK_A values are estimated at 6.30 ± 0.05 (from the experimental point, pH 6.32, $\mu = 2.0$) and 6.06 ± 0.05 (from the experimental point, pH 6.12, $\mu = 2.0$) for *cis*- and *trans*-$Co(en)_2NH_3H_2O^{3+}$, respectively.

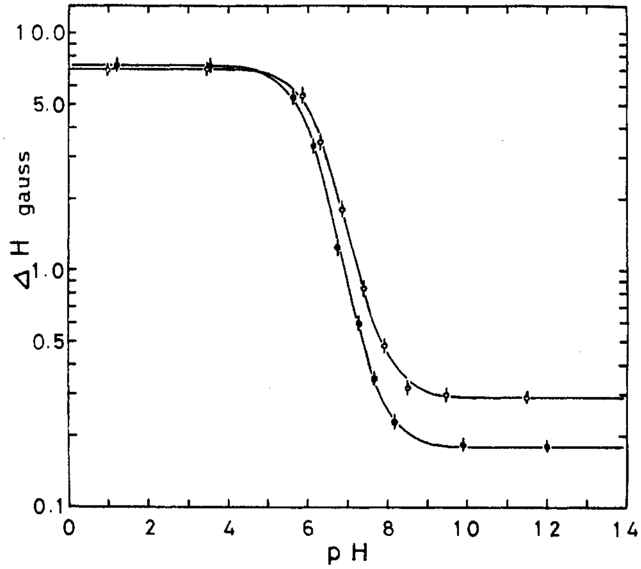

Figure 2.—The pH dependence of the ^{59}Co nmr line widths: ♁, 0.40 *M* *cis*-$[Co(en)_2NH_3H_2O]Br_3$; ♦, 0.40 *M* *trans*-$[Co(en)_2NH_3H_2O]Br_3$. Solid curves are calculated from eq 3 with $pK_A = 6.30$ for the cis isomer and $pK_A = 6.06$ for the trans isomer.

The above results show that ^{59}Co line width measurements give useful information about acid dissociation equilibria, especially in highly concentrated solutions. It is well known that *olation* takes place with an increase

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in concentration of complexes. Since polymerization and depolymerization occur very slowly in Co(III) complexes, the ^{59}Co line widths will not be affected even if a small amount of polymeric species is produced by *olation*. In the present experiments any signals which correspond to polymeric species were not detected, suggesting that in the present Co(III) system *olation* does not occur even in highly concentrated region.

It should be noted that the ^{59}Co line width for $Co(NH_3)_5OH^{2+}$ is one order of magnitude smaller than that for $Co(NH_3)_5H_2O^{3+}$. Hartmann and Sillescu[9] reported a nuclear quadrupole coupling constant of $[Co(NH_3)_5H_2O](ClO_4)_3$ (e^2qQ/h = 54.8 MHz at 298 K), while no data have been obtained for $[Co(NH_3)_5OH](ClO_4)_2$. According to the method of Hartmann and Sillescu,[9] the nuclear quadrupole coupling constant for $[Co(NH_3)_5OH]X_2$ is estimated at 16 MHz from the ^{59}Co line width in solution. This large difference in e^2qQ/h seems to be closely related to a difference in nature between the Co–OH and Co–OH_2 bonds. Hartmann and Sillescu[9] reported a ^{59}Co line width of 1.15 G for $[Co(NH_3)_5OH](NO_3)_2$ in aqueous solution. In the case of $Co(NH_3)_5OH^{2+}$ and $Co(NH_3)_5OH_2^{3+}$, the change in the line width with the counter anions (Cl^-, ClO_4^-, and NO_3^-) and the concentration of the complex (from 0.1 to 0.4 *M*) is small ($\leq$0.5 G for the aquo complex and $\leq$0.05 G for the hydroxo complex).[10] In view of these results this large line width, 1.15 G, seems to suggest that in aqueous solution $[Co(NH_3)_5OH](NO_3)_2$ is protonated to yield a considerable amount of $Co(NH_3)_5OH_2^{3+}$ ion.

The ^{59}Co chemical shifts can be used to estimate the rate of proton exchange between the aquo and hydroxo complexes. A sharp single line is observed for a solution containing $Co(NH_3)_5H_2O^{3+}$ and $Co(NH_3)_5OH^{2+}$ ions. With the use of the chemical shift difference, 1080 Hz, between these ions, the lower limit of the rate constant for the acid dissociation, k_a, and that for the reverse reaction, k_{-a}, are estimated at 10^3 sec^{-1} and 10^9 M^{-1} sec^{-1}, respectively. These results are to be compared with $k_a = 1.1 \times 10^5$ sec^{-1} and $k_{-a} = 9.6 \times 10^9$ M^{-1} sec^{-1} which have been obtained for the $Al(H_2O)_6^{3+}$ ion by means of the spin-echo technique.[11]

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The Structure of Crystalline Potassium Dioxotetracyanorhenium(V), $K_3ReO_2(CN)_4$

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Compared to the large number of tetraoxo ions (MO_4^{n-}) which are known, the number of dioxo ions which have been characterized is small. It can also be stated that few studies on the latter type ion have been made, and thus our chemical and physical knowledge is slim. A chemical study on the ^{18}O-exchange kinetics and some reactions of $K_3ReO_2(CN)_4$ has just been concluded[1] which brought to light the facile conversion of $ReO_2(CN)_4^{3-}$ into a dimer thought to be $ORe(CN)_4ORe(CN)_4O^{4-}$. A single-crystal X-ray structure determination was begun on a salt of the latter ion. This determination is now complete and will be communicated in the near future. For comparison, the molecular parameters were needed for $ReO_2(CN)_4^{3-}$. Such a structure determination was reported in 1961,[2] and our original intent was to improve upon the precision of the molecular parameters using more modern methods of data collection and computation. The results of this study revealed differences in the unit cell and much improved the precision in bond distances and angles in the ion. The improvement in the precision allows direct comparison with the dimeric complex ion whose structure will be presented later.

Experimental Section

Crystal Preparation.—$K_3ReO_2(CN)_4$ was prepared from $Re(en)_2O_2^+$ by the method previously described.[3] After purification[1] a final slow crystallization from water gave well-formed anhydrous crystals.

X-Ray Data.—Potassium dioxotetracyanorhenium(V), $K_3ReO_2(CN)_4$, crystallizes in the triclinic system with cell dimensions, as determined by careful centering of 23 reflections on a Picker diffractometer using Mo Kα radiation and a narrow vertical slit at the counter, of $a = 7.470 \pm 0.002$ Å, $b = 7.597 \pm 0.002$ Å, $c = 6.329 \pm 0.002$ Å, $\alpha = 105.37 \pm 0.02°$, $\beta = 110.20 \pm 0.02°$, $\gamma = 114.63 \pm 0.02°$, and $V = 268.9 \pm 0.1$ Å^3. These are the reduced cell dimensions from a Delauney reduction[4] of an unconventional cell. The density calculated on the basis of one formula per unit cell, 2.715 g/cm^3, is in good agreement with the reported density[5] of 2.704 g/cm^3.

These cell dimensions are not the same as those reported by earlier workers,[2] possibly due to a different choice of axes. The dimensions reported were $a = 7.35 \pm 0.02$ Å, $b = 7.73 \pm 0.02$ Å, $c = 6.32 \pm 0.02$ Å, $\alpha = 108.3 \pm 0.2°$, $\beta = 107.5 \pm 0.2°$, $\gamma = 114.3 \pm 0.2°$, and $V = 269.5$ Å^3; a and b as well as α and β have been interchanged from the original paper for comparison. The cell volumes are nearly identical, but the a and b dimensions are significantly different. We have applied the Delauney method to both cells giving the reduced cells above. Yet the observed differences in angles and distances give different axis systems, as suggested by K1 being at 0, $^1/_2$, $^1/_2$ in our cell and 0, $^1/_2$, 0 in the previous determination.

Intensities of some 4700 reflections, a complete sphere out to $2\theta = 65°$, were measured using Mo Kα radiation with a niobium β filter on a Picker four-angle programmer system. The intensity data were collected at a 2° takeoff angle using a θ–2θ scan at scan rate of 1.0°/min. The scan length ranged from 1.00 to 1.35° in 2θ to account for the increasing width due to α_1–α_2 splitting. Stationary counter backgrounds were taken for 20 sec on each side of the scan. Automatic attenuation was employed to prevent exceeding about 8000 cps during the scan. One-mil brass foils were used as attenuators to give attenuator factors of about 3. The pulse height selector was set for about a 95% window, centered on the Mo Kα peaks. The receiving aper-

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