tron impact measurements[11] show that a chlorine atom is not as effective as a CF_3 group in increasing the IP. Thus CH_3SCl and CF_3SCl have IP's of 9.2 ± 0.1 and 10.7 ± 0.1 eV, respectively. The IP of CF_3SH by the same method is 11.35 ± 0.1 eV. The reverse trend has been reported for the first IP's of several derivatives of arsine, AsH_3.[12]

The first IP of H_2S_2 is estimated to be 10.2 eV,[13] so the series of compounds RS–SR (R = CF_3 or CH_3) shows a variation in IP similar to that of the RSR compounds. The increase in IP going from HS–SH to $CF_3S–SCF_3$ is less than that found for HSH and CF_3SCF_3. This is because each sulfur atom is bound to only one CF_3 group in the disulfides. The dramatic lowering of the first IP's of the compounds $(CF_3)_2S_x$ as x increases and the slow change in the series $(CH_3)_2S_x$ are noteworthy. It seems reasonable to expect that as x increases both series will converge near 9.5 eV, the value of the first IP of S_8.[14]

The inner IP's of these compounds (Table I) come from the first measurements of this kind to be made on divalent sulfur compounds.

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The Acid Dissociation of the Aquo(diethylenetriamine)(ethylenediamine)cobalt(III) Ion

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The acid dissociation constants for cobalt(III)–amine complex ions previously have been observed for only a limited number of ions. It is expected that a systematic comparison of a number of these cations will give additional insight in the nature of the cobalt(III)–amine complexes. In this study, the acidity of Co(dien)(en)H_2O^{3+} due to the reaction

$$\underset{\text{I}}{\mathrm{Co(dien)(en)H_2O^{3+}}} + \mathrm{H_2O} \rightleftharpoons \underset{\text{II}}{\mathrm{Co(dien)(en)OH^{2+}}} + \mathrm{H_3O^+}$$

is compared with the acidities of the cobalt(III)–amine complexes which have appeared in the literature. Diethylenetriamine is abbreviated to dien, while ethylenediamine is shortened to en.

The ion Co(dien)(en)H_2O^{3+} was first reported by Pearson, *et al.*,[1] in a study of the hydrolysis of Co(dien)(en)Cl^{2+}; House and Garner[2] obtained the same cation as an impurity in the synthesis of [Co(tetren)Cl]-[$ZnCl_4$].[3] The cation was found to be a product of the acid-induced decomposition of (en)(dien)CoO_2Co(dien)(en)$^{4+}$ by Beaumont.[4]

Experimental Section

Apparatus.—Potentiometric measurements were made with a Beckman Expandomatic pH meter equipped with glass and calomel electrodes. A three-necked, 250-ml, round-bottom flask was fitted with cork and rubber stoppers which held in place capillary-tipped glass tubing and the electrodes of the pH meter. One tube allowed addition of acid or base solution from a 10-ml buret; the others permitted the escape and addition of a stream of scrubbed nitrogen gas. The flask was mounted over a magnetic stirrer and was thermally shielded by asbestos pads.

Chemicals and Reagents.—Recrystallized [Co(dien)(en)Cl]Cl_2 was prepared by heating [(en)(dien)CoO_2Co(dien)(en)]$Cl_4 \cdot 6H_2O$ with 12 *M* hydrochloric acid and was used as the source of Co(dien)(en)H_2O^{2+}. Solutions of HCl and NaOH were prepared from Baker and Adamson CP reagent HCl and from carbonate-free saturated NaOH, respectively. For the latter solution, deionized, distilled, and freshly boiled water was used; the same water was used for the solution of [Co(dien)(en)Cl]Cl_2. The NaOH solution was standardized with primary standard potassium hydrogen phthalate; the HCl solution was standardized with the NaOH solution. For ionic strength variation, Fisher potassium chloride for pH determinations was used without further purification but was dried at 105° prior to being weighed. Nitrogen was obtained from a cylinder provided by Wolverine Gas Products, Inc.

The pH meter was standardized with a thymol-stabilized saturated solution of potassium hydrogen tartrate which had previously been recrystallized from deionized and distilled water (pH 3.56 at 25°).[5]

Procedure.—A 0.3–0.4-mmol sample of [Co(dien)(en)Cl]Cl_2 (0.10–0.13 g) was dissolved in a slight excess of the standard NaOH solution (0.5 mmol) and diluted to 50 ml in a volumetric flask. After a few hours, aliquots of this solution were added to 50-ml volumetric flasks containing preweighed quantities of potassium chloride. After addition of water, the contents of the latter flasks were then emptied into the titration flask which had been previously purged for several hours with a slow stream of nitrogen. For each titration, the total volume was brought to 100 ml by washing the emptied volumetric flask with water from another 50-ml volumetric flask.

Two titrations were made of each sample solution. Dilute HCl was added in the first titration until it was in excess and then dilute NaOH was added in the second until excess base was present. Plots of pH *vs.* volume of titrant gave the apparent equilibrium constants at the half-equivalence points of the titration.

Results and Discussion

The titrations yielded curves typical of those observed in the titrations of weak acids and bases. End points were determined graphically and by use of the obtained $\Delta pH/\Delta V$ data. The half-equivalence points in the titrations of Co(dien)(en)H_2O^{3+} were then calculated and the pH values were found at these points. These values are summarized in Table I.

In Figure 1, the extrapolation of half-equivalence pH values *vs.* the square root of the ionic strength gives the value of the equilibrium constant at zero ionic strength. The best line by least-squares treatment is that which

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TABLE I

SOLUTIONS AT HALF-EQUIVALENCE POINTS

Solution[a]	Total molarity of Co(dien)(en)H_2O^{3+} and Co(dien)(en)OH^{2+}	$\sqrt{\mu}$	Obsd pK
1 (a)	0.000154	0.0423	5.30
(b)	0.000153	0.0449	5.21
2 (a)	0.000573	0.0795	5.32
(b)	0.000560	0.0834	5.38
3 (a)	0.00189	0.149	5.51
(b)	0.00169	0.157	5.53
4 (a)	0.00164	0.243	5.72
(b)	0.00156	0.242	5.77
5 (a)	0.00154	0.312	5.83
(b)	0.00147	0.309	5.90

[a] (a) indicates addition of acid; (b) indicates addition of base.

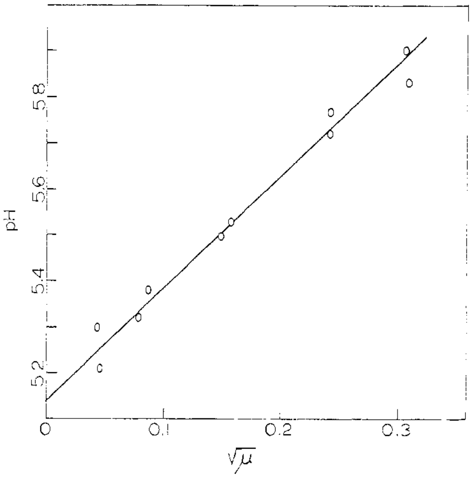

Figure 1.—Extrapolation to zero ionic strength of pH values observed at half-equivalence points (see Table I).

crosses the axis at pH 5.14. Justification for this method is given by the equation

$$-\log K^* = -\log \frac{f_{II}}{f_I} - \log a_{H_3O^+} \qquad (1)$$

The letters a and f symbolize activity and activity coefficients, respectively; K^* denotes the thermodynamic equilibrium constant. It is assumed that f obeys the Debye–Hückel relationship. As the ionic strength approaches zero, the activity coefficients of both cobalt species should approach 1 and the penultimate term in eq 1 should approach zero. Hence, $-\log K^*$ = pH at an ionic strength of zero.

The data may be treated in a different manner which leads to the same value for the acid dissociation constant. One may use the observed hydronium ion activities at the half-equivalence points in conjunction with the activity coefficients of I and II. Since values for these are not known, the activity coefficients for the ions $Co(en)_3^{3+}$ and $Co(H_2O)_6^{2+}$, respectively, might be employed because they are very similar in size and charge. The values for these coefficients at various ionic strengths have been determined by Kielland.[6]

By substitution of the activity coefficients and the hydronium ion activity into eq 1, one may calculate the thermodynamic equilibrium constant. Since the hydronium ion activity was not found experimentally at the same ionic strengths as the activity coefficients of the complex ions as obtained by Kielland, values for the activity were obtained from the line in Figure 1. Table II summarized the data employed and Figure 2 shows that 5.14 is the limiting value for pK^* as the ionic strength approaches zero.

TABLE II

CALCULATION OF pK^* WITH ACTIVITY COEFFICIENTS

μ	f[a] [Co(dien)(en)H_2O^{3+}]	f[b] [Co(dien)(en)OH^{2+}]	$10^6 a_{H_3O^+}$	pK^*
0.005	0.52	0.749	4.85	5.1 (56)[c]
0.010	0.415	0.675	4.12	5.17 (4)
0.050	0.195	0.485	2.05	5.29 (0)
0.100	0.13	0.405	1.22	5.4 (19)

[a] Activity coefficient actually for $Co(en)_3^{3+}$; see ref 6. [b] Activity coefficient actually for $Co(H_2O)_6^{2+}$; see ref 6. [c] Parentheses indicate uncertain figures due to only two and three significant figures in columns 2 and 3.

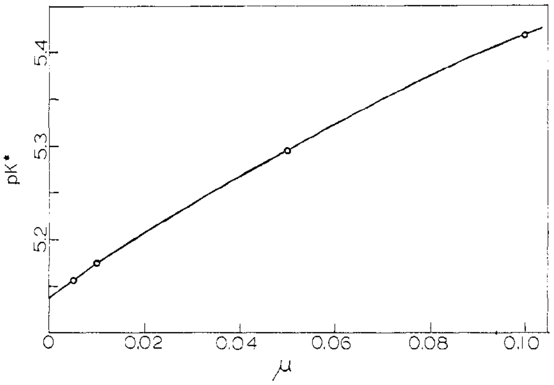

Figure 2.—Extrapolation of calculated values of pK^* to zero ionic strength (see Table II).

The facts that the calculated values of pK^* (Table II) give a smooth curve which is very nearly a straight line, that the curve has only a small slope, and that 5.14 is approached by pK^* at zero ionic strength probably indicate that the ratio of activity coefficients for $Co(en)_3^{3+}$ and $Co(H_2O)_6^{2+}$ varies only slightly differently with ionic strength than does the ratio for Co(dien)(en)H_2O^{3+} and Co(dien)(en)OH^{2+}. If the ratios were identical, a horizontal straight line should be observed.

From the pK_1^* values of the various complex ions in Table III,[7–10] it may be deduced that the trends in acidities do not follow the accepted order in *trans*-effect strength of the ligand lying *trans* to an acidic water molecule. If the accepted order of decreasing strength is secondary amine, primary amine, ammonia, hydroxide ion, and water, one would expect, if the acidities were dependent only on a simple *trans* effect, that the pK^* values would vary inversely; that is, that a water molecule *trans* to another water molecule would be the most acidic of the

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TABLE III

THERMODYNAMIC CONSTANTS FOR THE ACID DISSOCIATION OF COBALT(III)–AMINE COMPLEX IONS

Complex ion	Ref	Temp, °C	pK_1^{*a}
$Co(NH_3)_5H_2O^{3+}$	7	25°C	6.55
$Co(dien)(en)H_2O^{3+}$	This work	24	5.14
$Co(NH_3)_4(H_2O)^{3+}$	8	25	5.32
cis-$Co(NH_3)_4(H_2O)_2^{3+}$	7	25	5.95
cis-$Co(en)_2(H_2O)_2^{3+}$	9	25	6.06
trans-$Co(en)_2(H_2O)_2^{3+}$	9	25	4.45
$Co(NH_3)_3(H_2O)_3^{3+}$	10	15	4.73
$Co(NH_3)_2(H_2O)_4^{3+}$	10	15	3.40

[a] pK_1^* is for the first acid dissociation of each ion.

possible combinations of the above ligands. This is in agreement with the acidity of *cis*-$Co(NH_3)_4(H_2O)_2^{3+}$ compared with those of *cis*-$Co(en)_2(H_2O)_2^{3+}$, of $Co(NH_3)_5H_2O^{3+}$, and of presumably mixed *cis*- and *trans*-$Co(NH_3)_4(H_2O)_2^{3+}$. Also in agreement is the acidity of *trans*-$Co(en)_2(H_2O)_2^{3+}$ relative to those of $Co(NH_3)_5H_2O^{3+}$, of *cis*-$Co(en)_2(H_2O)_2^{3+}$, and of $Co(dien)(en)H_2O^{3+}$; $Co(NH_3)_3(H_2O)_3^{3+}$ and $Co(NH_3)_2(H_2O)_4^{3+}$ appear to obey the predicted trend. In addition, Grinberg and Ryabchikov[11] observed a *trans*-effect influence on the acidities of square-planar *cis*- and *trans*-$Pt(NH_3)_2(H_2O)_2^{3+}$; the *trans* isomer was more acidic than the *cis* by a factor of 40.

There is a significant number of comparable pK^* values in Table III which leads one to conclude that the acidities do not obey a simple *trans* effect. These anomalous comparisons are of $Co(NH_3)_5H_2O^{3+}$ with *cis*-$Co(en)_2(H_2O)_2^{3+}$ and of $Co(dien)(en)H_2O^{3+}$ with $Co(NH_3)_5H_2O^{3+}$, with *cis*-$Co(en)_2(H_2O)_2^{3+}$, and with *cis*-$Co(NH_3)_4(H_2O)_2^{3+}$. Although the steric configuration of $Co(dien)(en)H_2O^{3+}$ as prepared is not known, the ligand *trans* to the water molecule must be a primary or secondary amine. That it may be a primary amine might be inferred from the inability of Crayton and Mattern[12] to isolate the *cis* isomers of several Co(dien)-X_3 compounds. Analogy with compounds containing triethylenetetramine (trien) is difficult because Sargeson and Searle[13] observed that the *cis*-α isomer was predominant while Goto, *et al.*,[14] observed that C-substituted trien–cobalt complexes preferentially formed in the *cis*-β configuration.

While there are insufficient data to make definite explanations for the variances from expected relative acidities due to *trans* effects, possibilities may be suggested. It is logical to assume that the *trans* effect of the σ-bonding ligands does influence the acidity of the water molecule *trans* to them. If this be true, then the acidities should vary inversely with the *trans*-effect strengths of the ligands. However, the latter is shown to be not true for a significant number of cases if only *trans* effects are considered; therefore, if the *trans* effect is present, there must be additional influence on the acidities of these complex ions.

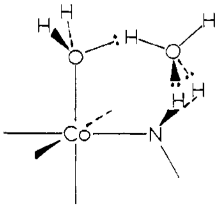

Figure 3.—Possible *cis* effect of coordinated amines through a water molecule in the outer coordination sphere (scale approximate).

One possible influence could be the nature of the ligands lying *cis* to the water molecule. Increased steric repulsion could cause an increase in acidity. Another *cis* effect might be due to the acidic character of the ligands *cis* to the water molecule. The various acidities of protons in water, ammonia, and primary and secondary amines could be transmitted to a *cis* water molecule *via* a water molecule in the outer coordination sphere which is hydrogen bonded to both ligands (see Figure 3). The magnitude or existence of such effects only can be revealed by careful study of a significant number of complex ions of known steric configuration.

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Rare Earth Plumbates with the Pyrochlore Structure

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Compounds with the pyrochlore structure and the formula $A^{III}_2B^{IV}_2O_7$, where A is a rare earth cation, have been reported[1–13] where B is Ti, Zr, Hf, Tc, Ru, Ir, Pd, Pt, Ge, or Sn. Brisse[13] has attempted to prepare rare earth pyrochlores of the type $A_2Pb^{IV}_2O_7$ but with only partial success. Concurrent work here revealed that pyrochlores of this type are readily prepared if the oxygen pressure is sufficiently high to prevent the re-

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