

The *m*-carborane¹ isomer gave a spectrum (Figure 3) that could be completely evaluated with the aid of heteronuclear decoupling in a manner similar to that described for *o*-carborane. The evaluation is in good agreement with the corresponding 64.2-Mc/sec spectrum (Figure 3f).

The critical lines in the decoupled spectra are singlets at 502 cps in Figure 3b, 598 cps in Figure 3c, and 660 cps in Figure 3d.

A potential pitfall of this technique is shown in the singlet at 634 cps in Figure 3e. This spectrum was obtained at a relative decoupling frequency of $-12,448$ cps. Since the spectra shown in Figures 3b, 3c, and 3d were obtained at relative decoupling frequencies of $-13,139$, $-12,880$, and $-12,632$ cps, respectively, and since Figures 3b and 3d show the extreme low-field and the extreme high-field peaks, respectively, decoupled, this merging of peaks at 634 cps is most reasonably interpreted as a superimposition of two lines, each of a different peak.

The *p*-carborane isomer was used to test the compatibility of techniques. Since the 19.3-Mc/sec spectrum consisted of two lines of equal intensity which fall at 556 and 722 cps (Figure 4a), the decoupled spectrum should have only one peak at 639 cps. The decoupled singlet was found at 640 cps. The coupling constants and chemical shifts measured from the 19.3-Mc/sec spectrum and the 64.2-Mc/sec spectrum are in good agreement.

Conclusions

These studies indicate that heteronuclear spin decoupling does aid the evaluation of ¹¹B spectra in that the information obtained is compatible with the information obtained from the 64.2-Mc/sec spectra.

Further, we note that these spectral evaluations might suggest an unexpected consideration pertaining to spectral assignments. Both the *ortho* and *meta* isomers have one pair of equivalent boron nuclei more intimately neighbored to carbon than the four equivalent boron nuclei and two pairs of equivalent boron nuclei further removed from carbon than the four equivalent boron nuclei. This suggests that the spectra should have one doublet on one side of the resonance of the four equivalent boron nuclei and two doublets on the other side. In both cases, the doublet is at higher field than the resonance of the four equivalent boron nuclei, and the pair of doublets is at lower field. This seems to suggest that carbon could be imparting a diamagnetic shift to its neighboring boron nuclei. A paramagnetic shift would be expected if only relative electronegativities were considered.

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Basicity of Coordinated Oxalate in Ammine Oxalatocobalt(III) Complexes

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It is well-known that coordination of a compound to a metallic ion considerably alters its acid-base properties. Water, for example, becomes appreciably acidic in ligand form, as exemplified by the pK_1 values for the species² $\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$ and $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$ (6.55 and 5.95, respectively, at 25°, compared to the nominal pK of water of about 16). In the present work, a study has been made of the proton affinity of the typical mono- and bidentate oxalato complexes, $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$ and $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$.

Experimental Section

$[\text{Co}(\text{NH}_3)_6\text{CO}_3]\text{NO}_3$ was obtained by standard procedure³ and converted to the aquoperchlorate by treatment with excess of concentrated HClO_4 . The crystals of $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ were filtered off, washed with ice water, and redissolved to form a saturated aqueous solution at 50°. This solution was treated with the stoichiometric amount of boiling saturated solution of NaHC_2O_4 . The red crystalline salt obtained on cooling was purified by recrystallization and subjected to chemical analysis. *Anal.* Calcd for $[\text{Co}(\text{NH}_3)_5\text{HC}_2\text{O}_4](\text{ClO}_4)_2$: Co, 13.85; C_2O_4 , 20.40; ClO_4 , 46.05. Found: Co, 14.04; C_2O_4 , 20.45; ClO_4 , 46.42. The deprotonated form of this complex was obtained by neutralization of a saturated solution to pH ~ 8 with dilute alkali and recrystallization of the $[\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4]\text{ClO}_4$ product from the cooled solution. The tetraammine analog was obtained by a very similar procedure, using $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$, prepared by standard methods,⁴ as the starting material. The deep red crystals of $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]\text{ClO}_4 \cdot \text{H}_2\text{O}$ on chemical analysis yielded data in good agreement with that calculated from the formula given.

pH measurements were made on a Beckman Research Model pH meter, and conductance data were obtained by use of a General Radio Type 1650-A impedance bridge with a suitable conductance cell. A Varian A60 instrument was used to provide the nmr spectra. All chemicals used were of AR or CP grade.

Results and Discussion

Titrimetric experiments in which 0.01 *M* $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]\text{ClO}_4$ solution was titrated with 0.1 *M* HCl solution showed that no acid-base equilibrium was detectable in this system. The pH vs. titer of HCl curve was identical within experimental error with that obtained in a blank experiment with complex salt absent. It was further found that the pH of 0.01 *M* HCl solution remains essentially unchanged for as long as 30 min on addition of sufficient solid complex tetraammine salt to

(1) NSF Summer Research Participant, 1963 and 1965.

(2) L. G. Sillén, "Stability Constants of Metal-Ion Complexes, Section I: Inorganic Ligands," Special Publication No. 17. The Chemical Society, London, 1964.

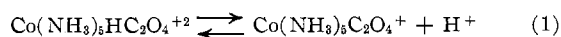
(3) F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 172 (1953).

(4) G. Schlessinger, *ibid.*, **6**, 173 (1960).

make the solution 0.01 *M* in the latter. This inertness of the chelated oxalate in the $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$ ion is in keeping with expectation based on the known stability of $\text{Co}(\text{en})_2\text{C}_2\text{O}_4^+$ ion in strong acid solution.⁵ Ions of this type must be regarded as very weak bases, with proton-acceptor properties comparable to a large alkali metal ion.

The pentaammine complex ion acid-base properties were examined in a number of ways. In preliminary experiments it was found by titration of an aqueous solution of $[\text{Co}(\text{NH}_3)_5\text{HC}_2\text{O}_4](\text{ClO}_4)_2$ with alkali that it is a moderately strong acid, having a *pK* between 2 and 3. Back titration of the deprotonated form with acid, in which the forward curve was retraced without hysteresis, proved the complete reversibility of the proton transfer.

The acid dissociation constant of the protonated pentaammineoxalato complex ion was determined from conductivity data obtained at 25°. The value of the molar conductance at infinite dilution, $\Lambda_0 = 572$, was obtained in the usual way by extrapolation of the linear plot of Λ_c vs. \sqrt{c} , where *c* is the molar concentration. Since the ionic conductances at infinite dilution have the known values $\lambda_{\text{H}^+}^0 = 350$ and $\lambda_{\text{ClO}_4^-}^0 = 68$, it follows that $\lambda_{\text{B}^+}^0 = 86 \text{ ohm}^{-1} \text{ cm}^2$, where $\text{B}^+ \equiv [\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4]^+$. Then, for the equilibrium



it is readily derived that, to a first approximation, the degree of dissociation α is given by

$$\alpha = (\Lambda_c - \lambda_{\text{BH}^{+2}}^0 - 2\lambda_{\text{ClO}_4^-}^0) / (\Lambda_0 - \lambda_{\text{BH}^{+2}}^0 - 2\lambda_{\text{ClO}_4^-}^0) \quad (2)$$

In this, $\text{BH}^{+2} \equiv \text{Co}(\text{NH}_3)_5\text{HC}_2\text{O}_4^{+2}$ and can reasonably be assumed to have twice the conductance of B^+ . Using the approximate α values derived from eq 1 and the fact that the ionic strength of the solution is given by $(3 - \alpha)c$, one can apply the Debye-Hückel-Onsager theory⁶ to estimate corrected values for the various ionic conductances at concentration *c*. Thus, a better value for α is obtainable from the more exact expression

$$\alpha = (\Lambda_c - \lambda_{\text{BH}^{+2}} - 2\lambda_{\text{ClO}_4^-}) / (\lambda_{\text{B}^+} + \lambda_{\text{H}^+} - \lambda_{\text{BH}^{+2}}) \quad (3)$$

(again making the assumption that $\lambda_{\text{BH}^{+2}} = 2\lambda_{\text{B}^+}$). These corrected α values are then employed to calculate *K* according to the conventional Ostwald expression, $K = \alpha^2 c / (1 - \alpha)$, with the results as indicated in Table I.

The average value of *K*, excluding the last three sets of data (which involve very dilute solutions and are thus subject to considerable experimental unreliability), is $K = (6.3 \pm 0.3) \times 10^{-3}$ or *pK* = 2.2. It is of interest that this value lies somewhat to the acid side of the half-way point between the *pK* values of oxalic acid

TABLE I
CALCULATION OF DISSOCIATION CONSTANT OF
 $\text{Co}(\text{NH}_3)_5\text{HC}_2\text{O}_4^{+2}$ ION FROM CONDUCTANCE DATA AT 25°

Concn of $[\text{Co}(\text{NH}_3)_5\text{HC}_2\text{O}_4](\text{ClO}_4)_2$, <i>M</i>	Λ_c , $\text{ohm}^{-1} \text{ cm}^2$	α (First approx)	<i>I</i> , 10^2 M	α (cor)	$10^3 K$, <i>M</i>
0.010	411	0.39	2.61	0.54	6.3
0.005	457	0.56	1.22	0.66	6.4
0.004	470	0.61	0.96	0.70	6.5
0.003	483	0.66	0.70	0.74	6.3
0.002	500	0.73	0.46	0.79	5.9
0.001	522	0.81	0.22	0.86	5.3
0.0006	534	0.86	0.13	0.89	4.3
0.0004	540	0.88	0.09	0.91	3.7
(0.0000)	572 ^a				

^a Extrapolated value.

(*pK*₁ = 1.2 and *pK*₂ = 4.2). This is the same pattern as observed previously concerning the *pK* of the ion $\text{Co}(\text{NH}_3)_5\text{HCO}_3^{+2}$. Its *pK*⁷ is about 8 and thus is similarly bracketed by the *pK* values of carbonic acid (*pK*₁ = 6.4 and *pK*₂ = 10.3).

A rough confirmation of the magnitude of *K* for the pentaammineoxalato species is provided by experiments in which the measured pH values of solutions of various molar concentrations of the salt $[\text{Co}(\text{NH}_3)_5\text{HC}_2\text{O}_4](\text{ClO}_4)_2$ were compared with the calculated pH values using $K = 6.3 \times 10^{-3}$. The following data were obtained.

(Complex), <i>M</i>	0.04	0.03	0.02	0.01	0.005	0.001
pH (calcd)	1.88	1.95	2.07	2.27	2.48	3.05
pH (obsd)	1.86	1.91	2.02	2.21	2.55	3.05

It is apparent that only in solutions of pH well below 2 will the protonated form of the pentaammineoxalato complex be the major constituent. Tsuchiya's conclusion on the basis of conductivity data⁸ that the product he obtained by reaction of $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ with KHC_2O_4 was $[\text{Co}(\text{NH}_3)_5\text{HC}_2\text{O}_4]\text{C}_2\text{O}_4$ (I) and not the deprotonated analog $[\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4]_2\text{C}_2\text{O}_4$ (II) is probably incorrect. His preparation was made at pH ~2.7, which should yield a product about 75% in the deprotonated form. The molar conductances in dilute solution are much too low when calculated on the basis of his formula I, since they should be approaching values in excess of 500 ($\lambda_{\text{H}^+}^0 + \lambda_{\text{B}^+}^0 + \lambda_{\text{C}_2\text{O}_4^{2-}}^0 \sim 580$). Calculated on the basis of II, his values are indeed too high [$2\lambda_{\text{B}^+}^0 + \lambda_{\text{C}_2\text{O}_4^{2-}}^0 \cong 320$], as he points out. His figures can undoubtedly be reconciled on the basis of a mixture of compounds I and II, though the published data are inadequate for this purpose.

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