

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
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## The Effect of Chelation by Nonbridging Ligands on the Rate of Reduction of Cobalt(III) Sulfato and Acetato Complexes<sup>1</sup>

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The chromium(II) and vanadium(II) reductions of some aminocobalt(III) sulfato and acetato complexes have been studied. The rate of reduction of the acetates is not affected when four ammonia groups (NH<sub>3</sub>) are replaced by two ethylenediamine molecules or when five ammonias are replaced by a single tetraethylenepentamine ligand. In all cases when Cr(II) is the reductant the rate constant for the second-order reaction is 0.18 l. mole<sup>-1</sup> sec.<sup>-1</sup>. In contrast, the rate of Cr(II) reduction of the sulfate complexes falls off with increasing chelation, from  $k = 23$  l. mole<sup>-1</sup> sec.<sup>-1</sup> for (NH<sub>3</sub>)<sub>5</sub>CoSO<sub>4</sub><sup>+</sup> to 1.6 l. mole<sup>-1</sup> sec.<sup>-1</sup> for one of the H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>(NHCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>CoSO<sub>4</sub><sup>+</sup> isomers, but the rate of reduction of a series (NH<sub>3</sub>)<sub>5</sub>CoO<sub>2</sub>CR<sup>2+</sup> (R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub>, *o*-IC<sub>6</sub>H<sub>4</sub>) is not greatly affected by the nature of the substituent R. All evidence suggests that the principal factor controlling simple electron transfer (transfer free from such effects as chelation of the reductant in the transition state) in a related series of complexes is not the inductive effect of the chelate amines but is a solvation requirement.

### Introduction

Since the discovery<sup>2</sup> of the bridged mechanism for oxidation-reduction reactions and its extension to include mediation by organic ligands,<sup>3</sup> much work has been done to investigate the factors controlling rates of electron-transfer processes. The effectiveness of conjugated ligands, especially those containing aromatic systems, has been demonstrated<sup>4,5</sup> and attack by the reductant at more than one site on the ligand has been shown to occur.<sup>6</sup> Although it has not been possible to relate the over-all rate of the electron-transfer reaction to any property such as the mobile bond order of the mediator,<sup>7,8</sup> electromeric effects of substituents have been shown<sup>9</sup> to control in part the rate of reaction. Reductions involving a double bridge in the transition state also occur, with complexes containing two potential mediators in the *cis* configuration<sup>10</sup> as well as with complexes containing a single mediator (such as oxalate) chelated to the oxidant.<sup>11</sup> This paper reports the kinetic consequences of chelation of the oxidant by the nonbridging ligands.

### Experimental

The ethylenediamine (Fisher Certified, anhydrous) and ammonia (reagent grade) were taken from freshly opened bottles. Technical grade tetraethylenepentamine (Distillation Products) was purified by the method of Jonassen.<sup>12</sup>

**Preparation of Complexes.**—Pentaamminesulfatocobalt(III) bisulfate was prepared from the pentaammineaquo sulfate<sup>13</sup>

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(3) H. Taube, *ibid.*, **77**, 4481 (1955).

(4) D. K. Sebera and H. Taube, *ibid.*, **83**, 1785 (1961).

(5) R. T. M. Fraser and H. Taube, *ibid.*, **83**, 2239 (1961).

(6) R. T. M. Fraser, *ibid.*, **83**, 564 (1961).

(7) J. Halpern and L. E. Orgel, *Discussions Faraday Soc.*, **29**, 32 (1960).

(8) R. T. M. Fraser, *J. Am. Chem. Soc.*, **83**, 4920 (1961).

(9) R. T. M. Fraser, *ibid.*, **84**, 3436 (1962).

(10) R. Snellgrove and E. L. King, *ibid.*, **84**, 4609 (1962).

(11) R. T. M. Fraser, *ibid.*, **85**, 1747 (1963).

(12) H. B. Jonassen, F. W. Frey, and A. Schaafsma, *J. Phys. Chem.*, **61**, 504 (1957).

(13) Ya. A. Fialov and V. D. Panasyuk, *Zh. Neorgan. Khim.*, **2**, 1007 (1957).

and then converted to the perchlorate by treatment with barium perchlorate. Bisethylenediaminesulfatocobalt(III) bromide was

TABLE I  
RATES OF REACTION AS FUNCTIONS OF TEMPERATURE  
( $\mu = 1.0$ )

Complex <sup>a</sup>	Reductant		Temp., °C.	$k_{\text{obsd}}$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>	
	[Cr(II)], M	[V(II)], M			
(NH <sub>3</sub> ) <sub>5</sub> CoSO <sub>4</sub> <sup>+</sup> <sup>b</sup>	0.0029		30.0	31.6	
	.0029		19.0	17.0	
	.0029		9.0	10.7	
	.0014		9.0	10.9	
		0.02	19.5	6.25	
		.04	19.5	6.3	
		.02	10.0	4.4	
		.04	10.0	4.3	
	(en) <sub>2</sub> NH <sub>3</sub> CoSO <sub>4</sub> <sup>+</sup> <sup>c</sup>	.02		29.0	4.5
		.02		19.0	2.5
.04			19.0	2.48	
.02			8.0	0.93	
		.02	24.0	5.7	
		.02	19.0	4.5	
		.02	10.0	2.6	
		.04	10.0	2.7	
(tetren)CoSO <sub>4</sub> <sup>+</sup> (fast) <sup>d</sup>	.02		28.0	8.7	
	.04		28.0	8.6	
	.02		21.0	6.7	
	.02		8.0	2.2	
		.02	19.5	5.8	
		.04	19.5	5.6	
		.02	10.0	3.5	
		.04	10.0	3.4	
(tetren)CoSO <sub>4</sub> <sup>+</sup> (slow)	.02		28.0	1.95	
	.04		28.0	2.0	
	.02		21.0	1.2	
	.04		21.0	1.3	
(en) <sub>2</sub> NH <sub>3</sub> CoO <sub>2</sub> CCH <sub>3</sub> <sup>2+</sup>	.02		25.0	0.186	
	.04		25.0	.182	
	.02		12.3	.087	
(tetren)CoO <sub>2</sub> CCH <sub>3</sub> <sup>2+</sup>	.02		25.0	.179	
	.04		25.0	.175	
	.02		12.3	.083	
	.04	12.3	.082		

<sup>a</sup> [Co(III)L] = 6.0 × 10<sup>-4</sup> M unless otherwise noted. <sup>b</sup> [Co(III)] = 4.0 × 10<sup>-3</sup> M. <sup>c</sup> en = ethylenediamine. <sup>d</sup> tetren = tetraethylenepentamine.

TABLE II  
 RATES AS FUNCTIONS OF TEMPERATURE AND ACIDITY ( $\mu = 1.0$ )

Complex	Reductant		Temp., °C.	$k_{\text{obsd.}}, \text{l. mole}^{-1} \text{sec.}^{-1}$		
	[Cr(II)], M	[V(II)], M		[H <sup>+</sup> ], M		
				0.2	0.4	0.6
<i>trans</i> -(en) <sub>2</sub> Co(O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> <sup>+</sup> <sup>a</sup>	0.0029		34.2	9.0	12.1	14.5
	.0029		20.5	5.1	7.3	9.3
	.0029		14.0	4.1	5.9	7.6
	.02		9.0	1.3	1.7	2.2
<i>cis</i> -(en) <sub>2</sub> Co(O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> <sup>+</sup> <sup>b</sup>	.02		29.5	1.0	1.95	3.1
	.04		12.0	0.55	1.23	1.83
(en) <sub>2</sub> Co(O <sub>2</sub> CCH=) <sub>2</sub> <sup>+</sup> <sup>a</sup>	.0006		20.0	142	158	175
(en) <sub>2</sub> CoSO <sub>4</sub> <sup>+</sup> <sup>a</sup>	.0014		22.0	47	60	70
		0.02	30.0	12.7	14.3	16.5
		.04	30.0	12.5	14.5	16.8
		.02	19.0	6.5	8.0	9.4
		.04	19.0	6.6	7.9	9.4
(tetren)CoH <sub>2</sub> O <sup>3+bb</sup>	.02		25.0	11.8	9.4	8.7
	.04		25.0	11.7	9.4	8.6

<sup>a</sup> [Co(III)L] =  $4 \times 10^{-3}$  M. <sup>b</sup> [Co(III)L] =  $6 \times 10^{-4}$  M.

prepared by the method of Tobe<sup>14</sup> and converted to the perchlorate using Dowex 1 anion-exchange resin in the perchlorate form. The other sulfato complexes were obtained from the corresponding chloro compounds by heating with concentrated sulfuric acid, dissolving the product in the least volume of water, and precipitating with ethanol and ether. Bisethylenediamine-dicarboxylato complexes were prepared by methods similar to those used for the analogous tetraammines.<sup>11</sup> The purity of the cobalt(III) complexes was established by titration with base, determination of the perchlorate content by precipitation with tetraphenylarsonium chloride, and nitrogen analysis by a modified Kjeldahl method.<sup>9</sup>

The purification of the water used for the kinetic measurements, the preparation of the solutions of chromium(II) and vanadium(II) perchlorates, and the syringe method used for following the rates of reaction have all been discussed previously.<sup>11</sup> The ionic strength of the reaction mixtures was adjusted to 1 by the addition of sodium perchlorate and perchloric acid.<sup>9</sup> The temperature of the system during the rate study was controlled to  $\pm 0.05^\circ$  by circulating water from a constant temperature bath through the double-walled optical cell.

## Results

All the reactions examined were found to be first order in reductant and cobalt(III) complex. Rate studies were carried out both with an excess of reductant (as pseudo-first-order reactions) and with a slight excess of cobalt complex (as second-order reactions). The reduction involving the chelated sulfate and maleate and the diacetate complexes proceeded by two paths, the second of which is first order in reductant, oxidant, and hydrogen ion. The rate constants were evaluated by standard methods<sup>4</sup> and some of the values observed are listed in Tables I and II. Table III summarizes the rate constants for the reactions at 25°. Table IV lists the activation parameters. Duplicate determinations of the rate constants agreed within  $\pm 2\%$ ; this gives rise to an uncertainty of  $\pm 0.2$  kcal./mole in the evaluation of  $\Delta H^*$  and  $\pm 0.6$  e.u. in  $\Delta S^*$ . The uncertainty in the  $\Delta F^*$  value is therefore  $\pm 0.4$  kcal. mole. The rates of hydrolysis of the cobalt(III) complexes were studied in solutions of ionic strength 1 and at the acidities used in the rate measurements: in all cases the rate of aquation was at least one thousandth that of the oxidation-reduction process,

(14) C. G. Barraclough and M. L. Tobe, *J. Chem. Soc.*, 3091 (1961).

 TABLE III  
 SUMMARY OF RATE CONSTANTS AT 25° (L. MOLE<sup>-1</sup> SEC.<sup>-1</sup>)

Complex	Cr(II)	V(II)
(NH <sub>3</sub> ) <sub>5</sub> CoSO <sub>4</sub> <sup>+</sup>	23	7.8
(en) <sub>2</sub> NH <sub>3</sub> CoSO <sub>4</sub> <sup>+</sup>	3.5	6.2
(tetren)CoSO <sub>4</sub> <sup>+</sup> (fast)	7.5	6.5
(tetren)CoSO <sub>4</sub> <sup>+</sup> (slow)	1.6	...
(en) <sub>2</sub> CoSO <sub>4</sub> <sup>+</sup>	35 + 56[H <sup>+</sup> ] (22°)	6.6 + 9.3[H <sup>+</sup> ]
<i>trans</i> -(NH <sub>3</sub> ) <sub>4</sub> Co(O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	15 + 50[H <sup>+</sup> ] <sup>a</sup>	...
<i>trans</i> -(en) <sub>2</sub> Co(O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	4 + 13.5[H <sup>+</sup> ]	...
<i>cis</i> -(en) <sub>2</sub> Co(O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	5[H <sup>+</sup> ]	...
(NH <sub>3</sub> ) <sub>4</sub> Co(O <sub>2</sub> CCH=) <sub>2</sub> <sup>+</sup>	125 + 50[H <sup>+</sup> ] <sup>b</sup>	...
(en) <sub>2</sub> Co(O <sub>2</sub> CCH=) <sub>2</sub> <sup>+</sup>	126 + 82[H <sup>+</sup> ] (20°)	...
(tetren)CoOH <sub>2</sub> <sup>3+</sup>	7.1 + 0.93/ [H <sup>+</sup> ]	...

<sup>a</sup> Reference 15. <sup>b</sup> Reference 11.

 TABLE IV  
 ACTIVATION PARAMETERS FOR ACID-INDEPENDENT PATH  
 ( $\mu = 1.0$ )

Complex	Reductant	$\Delta H^*$ , kcal. mole <sup>-1</sup>	$\Delta S^*$ , e.u.
(NH <sub>3</sub> ) <sub>5</sub> CoSO <sub>4</sub> <sup>+</sup>	Cr(II)	8.3	-25
	V(II)	6.1	-34
(en) <sub>2</sub> NH <sub>3</sub> CoSO <sub>4</sub> <sup>+</sup>	Cr(II)	10.4	-21
	V(II)	9.1	-25
(tetren)CoSO <sub>4</sub> <sup>+</sup> (fast)	Cr(II)	9.7	-22
	V(II)	8.1	-27
(tetren)CoSO <sub>4</sub> <sup>+</sup> (slow)	Cr(II)	11.7	-19
	V(II)	10.2	-21
(en) <sub>2</sub> CoSO <sub>4</sub> <sup>+</sup>	V(II)	10.2	-21
<i>trans</i> -(NH <sub>3</sub> ) <sub>4</sub> Co(O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	Cr(II)	7.9 <sup>a</sup>	-26 <sup>a</sup>
<i>trans</i> -(en) <sub>2</sub> Co(O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	Cr(II)	8.9	-26

<sup>a</sup> Reference 15.

 TABLE V  
 $\Delta F^*$  VALUES FOR THE CHROMOUS ION REDUCTION OF THE  
 COBALT(III) SULFATO COMPLEXES AT 25°

Complex	$\Delta F^*$ , kcal. mole <sup>-1</sup>
(NH <sub>3</sub> ) <sub>5</sub> CoSO <sub>4</sub> <sup>+</sup>	15.8
(en) <sub>2</sub> NH <sub>3</sub> CoSO <sub>4</sub> <sup>+</sup>	16.8
(tetren)CoSO <sub>4</sub> <sup>+</sup> (fast)	16.4
(tetren)CoSO <sub>4</sub> <sup>+</sup> (slow)	17.4

(15) K. D. Kopple and R. R. Miller, *Proc. Chem. Soc.*, 306 (1962).

so that changes observed in the absorption spectra of the compounds resulted only from the reductions.

### Discussion

Chelation has previously been used<sup>16</sup> to show that the hydrolysis of aminocobalt(III) chloro complexes does not proceed by a *trans* SN2 mechanism, for the values of the rate constants for aquation in acid solution decrease steadily but only slowly with increasing number of chelate rings. As the chloride is replaced by a water molecule the charge on the metal increases, and so additional solvation by the water molecules of the second coordination sphere is necessary, but the larger the ion (the more chelate rings) the less its solvation energy and the more difficult it becomes to form. This is shown by an increase in the  $\Delta F^*$  values. A similar situation occurs in the electron-transfer reactions studied here: an electron is transferred and a sulfate group replaced by a water molecule. The net result is the formation of an ammineaquocobalt(II) ion, that is, an increase of charge from +1 to +2 occurs. In accordance with this,  $\Delta F^*$  is found to increase as the number of chelate rings increases, as shown in Table V. (Only two of the four possible geometric isomers of the tetraethylenepentamminecobalt(III) complex can be distinguished here kinetically.) In contrast to the  $\Delta F^*$  values, the entropies of activation become more favorable along the series  $(\text{NH}_3)_5\text{CoSO}_4^+ < (\text{en})_2\text{NH}_3\text{CoSO}_4^+ \sim (\text{tetren})\text{CoSO}_4^+ (\text{fast}) < (\text{tetren})\text{CoSO}_4^+ (\text{slow})$ , suggesting that the more bulky the nonbridging ligands the less reorganization is required (or indeed is possible) for the formation of the activated complex.

If the sulfate ligand is now replaced by a group such as chloride or acetate so that the resulting cobalt(III) and chromium(III) complexes have over-all charges of +2, there should be no change in  $\Delta F^*$  as the chelation is increased. This is just what is observed, although not with halide complexes, because the rate constants are too large to be measured ( $k > 10^6$  l. mole<sup>-1</sup> sec.<sup>-1</sup>). Table VI lists some parameters for the chromium(II) reduction of the pentaamine-, bisethylenediamineammine-, and tetraethylenepentamminecobalt(III) acetato complexes.

In the ammine aquo complexes, the charge change during reaction is from +3 to +2, that is, a change opposite in direction to that of the sulfato complexes.

TABLE VI

ACTIVATION PARAMETERS FOR THE CHROMOUS ION REDUCTION OF THE COBALT(III) ACETATO COMPLEXES AT 25°

Complex	$k$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>	$\Delta F^*$ , kcal. mole <sup>-1</sup>	$\Delta H^*$ , kcal. mole <sup>-1</sup>	$\Delta S^*$ , e.u.
$(\text{NH}_3)_5\text{CoO}_2\text{CCH}_3^{2+}$	0.18 <sup>a</sup>	18.5	3.5 <sup>a</sup>	-50 <sup>a</sup>
$(\text{en})_2\text{NH}_3\text{CoO}_2\text{CCH}_3^{2+}$	.19	18.5	14.3	-14
$(\text{tetren})\text{CoO}_2\text{CCH}_3^{2+}$	.18	18.4	10.3	-27

<sup>a</sup> Reference 4.

The rate law for the chromium(II) reduction of pentaammineaquocobalt(III) perchlorate at 25° is<sup>17</sup>

$$R = \{0.55 + (2/[\text{H}^+])[\text{Co(III)L}]\} [\text{Cr(II)}]$$

the acid inverse path signifying reaction of the hydroxy complex,  $(\text{NH}_3)_5\text{CoOH}^{2+}$ . Using a value of  $1.8 \times 10^{-6}$  for the dissociation constant of the aquo complex, the rate law becomes

$$R = \{0.55[(\text{NH}_3)_5\text{CoOH}_2^{3+}] + 10^6[(\text{NH}_3)_5\text{CoOH}^{2+}]\} [\text{Cr(II)}]$$

The rate of reduction of  $(\text{tetren})\text{CoOH}_2^{3+}$  is also acid inverse, and the dissociation constant for the complex is  $2.2 \times 10^{-6}$ , so that the rate law (from the values in Table II) becomes

$$R = \{7.1[(\text{tetren})\text{CoOH}_2^{3+}] + (4.2 \times 10^6)[(\text{tetren})\text{CoOH}^{2+}]\} [\text{Cr(II)}]$$

that is, the rate of reduction of the aquo species increases as chelation is increased ( $\Delta F^*$  is 17.7 kcal./mole for  $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ , but 16.2 kcal./mole for  $(\text{tetren})\text{CoOH}_2^{3+}$ ), whereas there is a slight *decrease* for reduction of the hydroxy complex ( $\Delta F^*$  changes from 9.3 to 9.8 kcal./mole for the tetren), a reaction where there is no charge change.

Other experiments<sup>18</sup> have shown that  $\Delta F^*$  for the chromium(II) reduction processes is not affected when the nonbridging ligands are kept constant but the size of the bridging ligand is increased, as long as the path for electron transfer is the same. When the size of the R group in  $(\text{NH}_3)_5\text{CoO}_2\text{CR}^{2+}$  is increased from methyl ( $\text{CH}_3$ ) to *o*-iodophenyl ( $\text{IC}_6\text{H}_4$ ),  $\Delta F^*_{25^\circ}$  increases only 0.5 kcal. mole<sup>-1</sup> (18.5 to 19.0). Attack by the reductant takes place in each case at the  $-\text{COO}-$  group. The result of the electron transfer is again the replacement of a water molecule in  $(\text{H}_2\text{O})_6\text{Cr}^{2+}$  by a carboxylato ligand, simultaneously with electron loss, to give  $(\text{H}_2\text{O})_5\text{CrO}_2\text{CR}^{2+}$ , and there is no charge increase on the ion. In the same way, although the cobalt is reduced from an oxidation state of +3 to +2, there is no charge change on the ion because the carboxylato group is replaced by a water molecule. No increased solvation is required and  $\Delta F$  should not show any great change.

The chelated sulfato complex,  $(\text{en})_2\text{CoSO}_4^+$ , reacts much more rapidly with Cr(II) than does the monodentate  $(\text{en})_2\text{NH}_3\text{CoSO}_4^+$ . Increases in rate such as this have been found previously<sup>11</sup> only when chelation of the reductant by the mediator can occur in the activated complex: it is not found, for example, with the tetraamminesuccinatocobalt(III) chelate, which is reduced at the same rate as *trans*-tetraamminediacetatocobalt(III), because in both reactions the chromium must attack the ligand at a  $-\text{COO}-$  group adjacent to the cobalt. The corresponding oxalato complex reacts at least ten times faster and  $(\text{H}_2\text{O})_4\text{Cr}(\text{O}_2\text{C}-)_2^+$  is formed. Experiments to show the presence of a chelated Cr(III) sulfato complex after reaction were not successful; instead, by the time the product could be examined, both infrared spectra and elution from

(17) A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **81**, 1288 (1959).

(18) R. T. M. Fraser, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Company, New York, N. Y., 1961, p. 287.

(16) R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

a Dowex-50 column showed the chromium was present as  $(\text{H}_2\text{O})_5\text{CrSO}_4^+$ .

*trans*-Bisethylenediaminediacetatocobalt(III) is reduced more slowly than the tetraammine (increase in  $\Delta F^*$ ), and reduction of the *cis* isomer cannot be observed by the acid-independent path, although this may be due to crowding of the acetate groups together by the bulky ligands, preventing a close approach of the reductant. Bisethylenediaminemaleatocobalt(III), on the other hand, is reduced more rapidly than the corresponding tetraammine, but here a different mechanism has already been proposed.<sup>11</sup> The suggested mechanism involves chromium attack above the chelate ring rather than from the side, so that two of the ligand oxygens can become associated with the reductant.

Variations in rate constant are generally much smaller when V(II) is the reductant: this has been observed for cobalt(III) complexes containing ligands such

as nitrate, thiocyanate, and azide<sup>19</sup> and chloride and water.<sup>20</sup> In the past this has led to the suggestion<sup>20</sup> that V(II) reacts by an outer-sphere mechanism in some reductions. On the other hand, the similarities of the  $\Delta S^* - \Delta H^*$  relationships for V(II) and Cr(II) reductions of carboxylate complexes<sup>9</sup> suggest that there V(II) can act through a bridged mechanism. This is further supported by the observation that V(II) can induce the same *cis-trans* isomerism of the pentaamminemaleatocobalt(III) ion as Cr(II).<sup>21</sup> Direct evidence for bridging cannot be obtained because of the substitution-lability of V(III).

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(19) J. Halpern, unpublished results.

(20) A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961).

(21) R. T. M. Fraser and H. Taube, *ibid.*, **81**, 5514 (1959).

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## Carbonate Complexes of the Lighter Lanthanides

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The distribution of the lighter lanthanides between Dowex I-X8 (carbonate form) and  $\text{K}_2\text{CO}_3$  solutions has been studied as a function of carbonate concentration in order to elucidate their complexing behavior in the presence of an inorganic ligand. Elution chromatography was employed using radioactive isotopes of Ce, Pr, Nd, Pm, Sm, and Eu to facilitate the investigation. The distribution of tracer <sup>35</sup>S in the form of <sup>35</sup>SO<sub>4</sub><sup>-2</sup> between Dowex I-X8 and  $\text{K}_2\text{CO}_3$  solutions was studied to determine the effect on the system of imbibed electrolyte and changing internal and external activity coefficients. Analysis of the data indicates that imbibement and activity coefficient corrections are negligible over the concentration range covered, thus giving an experimental basis for the theoretical treatment of the data. Distribution coefficients were measured over the concentration range of 0.37 to 2.60 *m*  $\text{K}_2\text{CO}_3$ . Over this region a logarithmic plot of the distribution coefficient vs.  $\text{K}_2\text{CO}_3$  molality results in straight lines for all the lanthanides that were studied, indicating the presence of stable complex anions in solution. Analysis of these results indicates that the complexes are of the form  $[\text{M}(\text{CO}_3)_4]^{-6}$ .

Ion-exchange, potentiometric, and electrophoretic studies of  $\alpha$ -hydroxycarboxylate interaction with the lanthanides<sup>3</sup> (and actinides) have shown the presence of negatively charged complexes in solution with four ligands coordinated to the central ion at concentrations greater than 0.1 *M*. This result also has been obtained with acetate systems.<sup>4</sup> The occurrence of anionic complexes of the rare earths in carbonate solutions also has been demonstrated recently in a qualitative anion-exchange study.<sup>5</sup>

It is felt that the coordination properties of the rare earths in carbonate solutions are of interest for correlation with the acetate and  $\alpha$ -hydroxycarboxylate systems. The rare earth-carbonate system is also of interest from a separations point of view. The separation

of rare earths into two groups, La, Pr, Nd, Pm and Sm, Eu, Y, has been achieved in practice by digestion with 20%  $\text{K}_2\text{CO}_3$ , the last group being solubilized.<sup>6</sup>

For these reasons it was decided to study the behavior of rare earths in carbonate systems. The choice of technique for study of the system lanthanide-carbonate-water was severely limited by the insolubility of the rare earth carbonates, however, making necessary the use of radioactive isotopes of the rare earths in tracer concentrations of about  $10^{-10}$  *M*. The affinity of the metal ion for an anion-exchange resin as a function of ligand concentration was used to measure the degree of complexing, ion-exchange column chromatography being selected to facilitate the investigation.<sup>7</sup>

### Experimental

**Materials.**—The resin Dowex I-X8, 200–400 mesh, in the chloride form (lot Number 20283), potassium chloride, and potas-

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