The Electrolytic Conductances of Bis(halogenoacetato)bis(ethylenediamine)cobalt(III) Ions in Water

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The electrolytic conductances of bis(halogenoacetato)bis(ethylenediamine)cobalt(III) perchlorate, [Co(halac)$_2$(en)$_2$]ClO$_4$ where Hhalac=CH$_3$CO$_2$H, CH$_2$ClCO$_2$H, CHCl$_2$CO$_2$H, CCl$_3$CO$_2$H, and CF$_3$CO$_2$H were measured in water at 25°C. The equivalent conductances of the solutions ($c=10^{-3}$—10^{-4} mol/l) were obtained from the conductance kinetic runs by extrapolating conductances to time zero. The ionic equivalent conductances of the complex ions were 21.5—17.2 ohm^{-1}cm^{2}eq.$^{-1}$, and decreased with the increase of the chlorine content in the chloroacetato ligands. Little differences in the ionic equivalent conductances were observed between a pair of cis and trans isomers. The rate constants of the first order aquation of the complexes were estimated.

The electrolytic conductance of a complex ion has often been measured in order to determine (1) the electric charge of the ion, (2) the velocity of substitution reaction such as aquation, and (3) the equilibrium constant of the complex formation or the association constant with a counter ion.

Although many data are available in literature[1], we can hardly find any systematic research which directs out attention to the elucidation of the relation between the conductivity and the structure of complexes. In order to grasp the relation, this study deals with the conductance of bis(halogenoacetato)bis(ethylenediamine)cobalt(III) perchlorate, [Co(halac)$_2$(en)$_2$]ClO$_4$, in aqueous solution at 25°C, where Hhalac=CH$_3$CO$_2$H, CH$_2$ClCO$_2$H, CHCl$_2$CO$_2$H, CCl$_3$CO$_2$H, and CF$_3$CO$_2$H.[2] The group of complexes has the following benefits to elucidate the dependence of conductivity on the structure of complexes. They are uni-univalent electrolytes which are the easiest type of electrolyte for theoretical consideration. The *cis*- and *trans*-isomers for various halac have been identified.[3] The size of the complexes increases steadily with the increase of the number of halogene atom in the halac ligands. The counter ion - perchlorate - has little tendency to associate with the complex ions in the range of concentration which were measured ($c=10^{-3}\sim10^{-4}$ mol/l). Their aquation velocities are relatively slow, despite the fact that they belong to the diacido-complex which generally aquates quickly.[4] Thus it is possible to obtain reliable values for equivalent conductance at infinite dilution.

Experimental

Materials. The complexes were prepared by the procedures described previously.[3] They were recrystallized at least twice and washed with absolute ethanol many times in order to remove completely the perchloric acid or sodium perchlorate which were used to precipitate the complexes in recrystallization. They were then dried in a vacuum desiccator over silica gel until the weight of the materials did not change any more. The specific conductance of the water was in a range 6×10^{-7}—7×10^{-7} ohm^{-1} cm^{-1}.

Apparatus and Measurement. A Jones-type bridge was used for the measurements and an alternative current of 10 kc frequency was applied to the bridge. A weighed sample in a small polyethylene dish was dissolved by magnetic stirring in one of two flask-type conductivity cells which had been placed in an oil-thermostat and contained a definite amount of conductivity water (~400 g). The cell constants of the cells were 0.23308 and 0.05355. Immediately after the dissolution, the resistance was measured at definite time intervals. A few complexes were measured in both of the cells, and the agreement of the results was satisfactory. As an example of the measurements, Fig. 1 shows the time-dependence of the specific conductance L of *cis*-[Co(dclac)$_2$(en)$_2$]ClO$_4$. We see that the specific conduc-

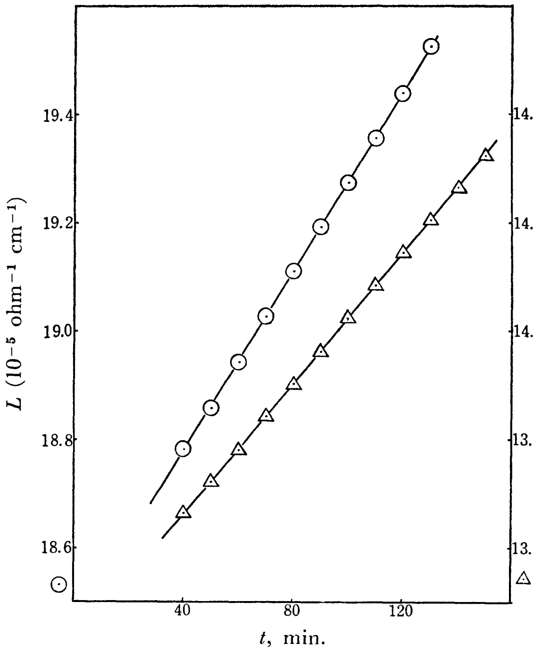

Fig. 1. Variation of specific conductance L of *cis*-[Co(dclac)$_2$(en)$_2$]ClO$_4$ solution with time.
⊙ $c=2.272\times10^{-3}$, △ $c=1.638\times10^{-3}$.

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[1] For example, W. A. Millen, and D. W. Watts, *J. Amer. Chem. Soc.*, **89**, 6858 (1967); S. Katayama and R. Tamamushi, This Bulletin, **41**, 606 (1968), **43**, 2354 (1970).

[2] The following abbreviation is used for the halogenoacetato ligands: CH$_3$CO$_2$H=Hac, CH$_2$ClCO$_2$H=Hmclac, CHCl$_2$CO$_2$H=Hdclac, CCl$_3$CO$_2$H=Htclac, CF$_3$CO$_2$H=Htfac.

[3] K. Kuroda and P. S. Gentile, This Bulletin **38**, 1362, 1368, 2159 (1965).

[4] D. R. Stranks, "Modern Coordination Chemistry," ed. by J. Lewis and R. G. Wilkins, Interscience Publishers Inc., New York, N. Y. (1960), p. 129.

Table 1. Equivalent conductances of the aqueous solutions of $[Co(halac)_2(en)_2]ClO_4$ and related complexes at 25°C

10^4c (mol/l)	Λ (ohm^{-1} cm^2/eq.)	10^4c (mol/l)	Λ (ohm^{-1} cm^2/eq.)
cis-$[Co(ac)_2(en)_2]ClO$		*cis*-$[Co(mclac)_2(en)_2]ClO_4$	
4.648	87.17	2.903	87.14
8.130	86.67	9.310	85.23
14.58	85.63	18.12	84.22
24.98	84.86	30.64	82.71
cis-$[Co(dclac)_2(en)_2]ClO_4$		*cis*-$[Co(tclac)_2(en)_2]ClO_4$	
6.501	83.47	6.660	82.59
10.37	82.66	9.844	82.02
16.38	81.98	23.84	80.70
22.72	81.25		
trans-$[Co(mclac)_2(en)_2]ClO_4$		*trans*-$[Co(dclac)_2(en)_2]ClO_4$	
9.520	84.98	3.645	85.93
13.96	84.46	7.091	85.08
18.33	84.05	8.701	84.90
		13.39	84.36
trans-$[Co(tclac)_2(en)_2]ClO_4$			
3.810	83.32		
9.118	82.21		
12.60	81.80		
cis-$[Co(tfac)_2(en)_2]$acetate		*trans*-$[Co(tfac)_2(en)_2]ClO_4$	
4.868	59.55	4.257	86.27
12.25	58.67	6.832	85.90
22.22	57.76	10.57	85.29
		16.22	84.62
cis-$[Co(mclac)_2(NH_3)_4]ClO_4$		*trans*-$[Co(mclac)_2(NH)_3)_4]ClO_4$	
7.687	89.57	3.183	90.85
8.588	89.43	4.972	90.54
18.76	88.56	12.45	89.80
24.15	88.15	22.97	88.56

tance of all the complexes increased linearly with time in the region 40—100 min. The values obtained within 20 min sometime deviated slightly from the straight line. This can be attributed to the non-homogeneity of the solution, even though all the solid sample dissolved completely in a few minutes. The specific conductance at time zero was extrapolated from the straight line, and the equivalent conductance was calculated.

For each of the complex salts, the measurement was carried out with at least three different concentrations. The equivalent conductances thus obtained are given in Table 1.

Discussion

Dependence on Concentration. The concentration dependence of the equivalent conductance Λ of all the complex salts agreed with the Onsager limiting conductance equation for the uni-univalent salts

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{c}. \qquad (1)$$

Table 2. Limiting conductance of $[Co(halac)_2(en)_2]^+$ and related complexes

	Λ_0	$\lambda_0{}^+$	R^+(Å)	Λ_0	$\lambda_0{}^+$	R^+(Å)
	$[Co(halac)_2(en)_2]ClO_4$					
	cis			*trans*		
ac	88.9	21.5	4.3	—	—	—
mclac	87.7	20.3	4.5	87.4	20.0	4.6
dclac	85.4	18.0	5.1	87.3	19.9	4.6
tclac	84.6	17·2	5.3	84.6	17.2	5.3
tfac	61.2[a]	20.3	4.5	88.0	20.6	4.4
	$[Co(halac)_2(NH_3)_4]ClO_4$					
	cis			*trans*		
mclac	91.7	24.3	3·8	92.4	25.0	3.7

a) acetate

Thus, from this equation, it is possible to estimate the equivalent conductance at infinite dilution Λ and the ionic equivalent conductance $\lambda_0{}^+$ by subtracting $\lambda_0{}^-$(67.4 for perchlorate and 40.9 for acetate[5]) from Λ_0. These values are summarized in Table 2. The effective ionic radii R^+ are also indicated which are calculated from the following equation,[6] assuming the Stokes law holds in the ionic transportation:

$$R^+ = Fe/1800\pi\eta\lambda_0{}^+ \qquad (2)$$

where F is the Faraday charge, e the electronic charge, and η the viscosity coefficient of water.

We see that the ionic equivalent conductance decreases and the effective ionic radii increases with increase of the chlorine content in the halac ligand, and that there hardly exists a difference in conductivity between a pair of *cis*- and *trans*-isomers. These results are worthy of discussing.

In a dilute solution, the equivalent conductance of ions depends on the volume or the ionic radii and not on the mass, when the charge of the ions are identical. If actual conductivity of a group of ions is not parallel to the radii of the ions, as in the case of the alkali ions, the cause is attributed to the different degree of the solvent association of ions. Thus, the effective volume of an ion in a solution can be estimated from the conductivity measurement. In the present *cis*- and *trans*-series of the complexes, the association of water molecule (if any) is considered to be identical except at the site of the methyl and the chloromethyl radicals. As the radicals are not hydrophilic, the association at this site would be negligible. Thus, in each series of the complexes, it can be reasonably accepted that the effect of the solvent association does not affect the order of the conductivity of the complexes. Actually, the experimental results showed the normal order expected from the size of the complexes. In the tables, the values of *cis*- and *trans*-$[Co(mclac)_2(NH_3)_4]ClO_4$ are shown for comparison. It is seen that the tetraammine-complexes have a higher conductivity than the corresponding bis(ethylenediamine)-complexes.

Rate of Aquation. The conductivity of the complexes increases with time. This can be undoubtedly attributed to the aquation

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5) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed. Butterworths, London (1959), p. 463.

6) R. M. Fuoss and F. Accascina, "Electrolyte Conductance," Interscience Publishers Inc., New York, N. Y. (1959), p. 60.

$$[\mathrm{Co(halac)_2(en)_2}]^+ + \mathrm{H_2O} \rightarrow [\mathrm{Co(halac)(H_2O)(en)_2}]^{2+} + \mathrm{halac}^-.$$

If the conductivity of the resulting halogenoacetatoaquo complexes were known, it would be possible to evaluate accurately the rate of aquation from the time dependence of conductivity. However, the halogenoacetatoaquobis(ethylenediamine)cobalt(III) salts have not been isolated, and the conductivity of the ions are unknown. Thus, an assumption is necessary for the calculation of the rate constant.

The size of the ions which determines the conductivity of this group of complexes can be approximately equal in a reactant bis(halogenoacetato)-complex and the resulting halogenoacetatoaquo-complex, because the replacement of a halogenoacetato ligand by a water molecule does not considerably change the total size of the ion. The resultant ions are divalent. Therefore, it is reasonable to assume that the conductivity of the resultant complex ion is twice as large as that of the corresponding reactant complex ion. The variation of the conductivity with time was examined on this assumption and with λ_0^-'s of the halogenoacetate ions.[7] The plots of log ($L_\infty-L$) of *cis*-$[\mathrm{Co(ac)_2(en)_2}]\mathrm{ClO_4}$ *versus* time are shown in Fig. 2 as an illustration. The plots are linear. This means that the aquation is a first order reaction similar to the acid-hydrolyses of many analogous complex ions. The first order rate constants obtained by the above procedure are summarized in Table 3. It is interesting to note that the rate constants do not differ considerably among the complexes under the present conditions, *viz.* in the severe neutral solution, although a deviation is observable in *trans*-$[\mathrm{Co(dclac)_2(en)_2}]^+$. On the other hand, it has been observed quantitatively in $[\mathrm{Co(halac)(NH_3)_5}]^{2+}$[8] or in the related complexes such as $[\mathrm{Co(aminoacid)(NH_3)_5}]^{2+}$[9] that aquation is accelerated with hydrogen ion depending on the basicity of the halac ligands. A similar behavior was noted qualitatively with this series of complexes (the acidic solution of a complex of the series changes its absorption spectrum faster than the neutral solution). Thus, the aquation (acid hydrolysis) is an acid-catalyzed reaction and the reaction has been supposed to proceed *via* the following path,[8] the larger the basicity of the ligand, the greater being the acceleration of the reaction rate by hydrogen ion.

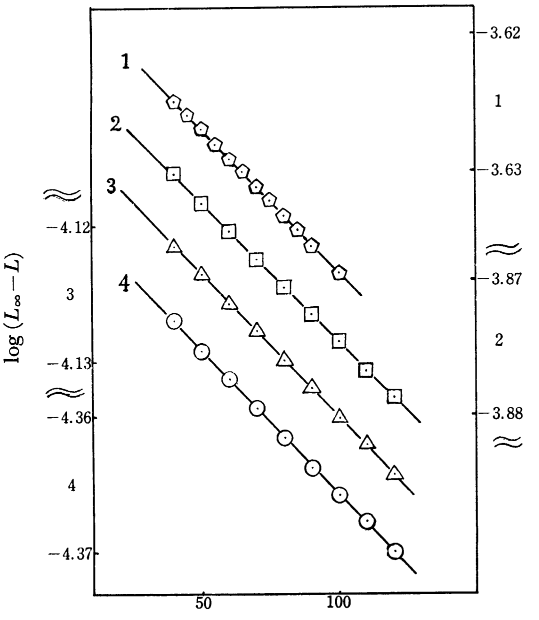
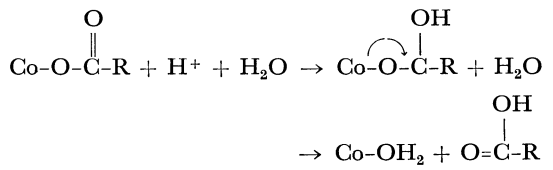


Fig. 2. The plots of $\log(L_\infty - L)$ *vs.* time of *cis*-$[\mathrm{Co(ac)_2(en)_2}]\mathrm{ClO_4}$.
1, $c=2.498\times10^{-3}$, 2, $c=1.458\times10^{-3}$, 3, $c=8.130\times10^{-4}$, 4, $c=4.648\times10^{-4}$.

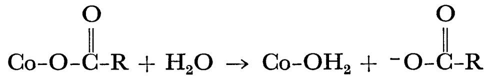
TABLE 3. FIRST ORDER RATE CONSTANTS OF AQUATION $[\mathrm{Co(halac)_2(en)_2}]^+$

	k_1 min^{-1}	k_1 min^{-1}
	$[\mathrm{Co(halac)_2(en)_2}]\mathrm{ClO_4}$	
	cis	*trans*
ac	4.8×10^{-4}	—
mclac	5.5×10^{-4}	1.2×10^{-4}
dclac	4.9×10^{-4}	$1\ \times10^{-5}$
tclac	5.2×10^{-4}	1.7×10^{-4}
tfac	5.6×10^{-4}	1.7×10^{-4}
	$[\mathrm{Co(halac)_2(NH_3)_4}]\mathrm{ClO_4}$	
	cis	*trans*
mclac	4.9×10^{-3}	0.9×10^{-4}



$$\mathrm{Co{-}O{-}\overset{\overset{O}{\|}}{C}{-}R} + \mathrm{H^+} + \mathrm{H_2O} \rightarrow \mathrm{Co{-}O{-}\overset{\overset{OH}{|}}{C}{-}R} + \mathrm{H_2O} \rightarrow \mathrm{Co{-}OH_2} + \mathrm{O{=}\overset{\overset{OH}{|}}{C}{-}R}$$

In neutral solution or at a negligible hydrogen ion concentration, the reaction takes place as



$$\mathrm{Co{-}O{-}\overset{\overset{O}{\|}}{C}{-}R} + \mathrm{H_2O} \rightarrow \mathrm{Co{-}OH_2} + \mathrm{{}^-O{-}\overset{\overset{O}{\|}}{C}{-}R}$$

and the rate of the reaction is almost independent of R.

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[7] The values of λ_0^- of dichloroacetate and trichloroacetate ions used in the calculation were 37.4 and 35.2, respectively. These values were obtained by the extrapolation of the conductivity data of potassium dichloroacetate and sodium trichloroacetate in aqueous solution at 25°C obtained by one of the authors (M.Y.).

[8] K. Kuroda, *Nippon Kagaku Zasshi*, **82**, 572 (1961).

[9] K. Ogino, T. Murakami, and K.Saito, This Bulletin, **41**, 1615 (1968)