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Hydration of the Cobalt(III) Complexes. II

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In our previous papers,[1-4] we reported the determination of hydration number of complexes by measurement of ultrasonic velocity. The complexes were those of cobalt and hexacyanoferate, and the effect of such lignads as en, pn, dien, and edta on the degree of hydration was also studied.

The present study deals with the determination of the degree of hydration of such complexes as $NH_4[Co(NO_2)_4(NH_3)_2]$, $NH_4[Co(C_2O_4)_2(NH_3)_2]\cdot H_2O$, $K[Co(NO_2)_4(NH_3)_2]$, $K[Co(NO_2)_2C_2O_4(NH_3)_2]\cdot H_2O$, $[Co(NO_2)(H_2O)_3(NH_3)_2]\cdot H_2O$, $[Co(H_2O)_3(NH_3)_3](NO_3)_3$, $[CoH_2O(NH_3)_5]Cl_3$, KNO_2, $KHC_2O_4\cdot H_2O$, and $K_2C_2O_4\cdot \frac{1}{2}H_2O$

The hydrated water around an ion can be conventionally divided into two layers,[5] a primary hydration layer in an extreme vicinity of the ion and a secondary outer layer. The water molecules in the former have no freedom of translational motion, and they move with the movement of the ion itself. The hydrated water molecules in the latter have some freedom of motion but they are also subjected to the electrostatic force of the ion. These hydrated water molecules play an important role in phenomena such as salt-in and salt-out effects.

The amount of hydrated water in the incompressible region around the ion is determined by the compressibility method. In order to obtain the relationship between the hydration numbers in the incompressible and primary layers, the complexes having H_2O in the inner sphere such as $[Co(H_2O)_3(NH_3)_3](NO_3)_3$ and $[CoH_2O(NH_3)_5]Cl_3$ were chosen. The salts such as $KHC_2O_4\cdot H_2O$ and $K_2C_2O_4\cdot \frac{1}{2}H_2O$ were taken to examine the effect of COO^- radical on the hydration.

The degree of hydration was determined from the adiabatic compressibilities of aqueous solutions obtained by the measurements of ultrasonic velocity by an ultrasonic interferometer. Measurements were carried out at 25°C. Details of experimental procedures and methods of determining the hydration number are the same as before.[1] The complexes were prepared by the methods in literature, and purified by recrystallization from their aqueous solutions. Since it is highly probable that in aqueous solutions the ligands NO_3 in $[Co(NO_3)_3(NH_3)_3]$ are completely relpaced by H_2O as

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1) F. Kawaizumi, H, Nomura, and Y. Miyahara, *Nippon Kagaku Zashi*, **87**, 939 (1966).

2) F. Kawaizumi and Y. Miyahara, *ibid*, **88**, 937 (1967).

3) F. Kawaizumi and Y. Miyahara, *ibid.*, **89**, 655 (1968).

4) F. Kawaizymi and Y. Miyahara, *ibid*, **91**, 333 (1970).

5) J. O'M. Bockris, *Quart. Rev.*, **3**, 173 (1949).

Table 1. Results for the complexes

Sample	κ_1	K_{mo} (ml/mol)	h (mol/mol)
$NH_4[Co(NO_2)_4(NH_3)_2]$	44.74	64.9	3.6
$NH_4[Co(C_2O_4)_2(NH_3)_2]$	44.79	116	6.4
$K[Co(NO_2)_4(NH_3)_2]$	44.76	90.9	5.1
$K[Co(NO_2)_2C_2O_4(NH_3)_2]$	44.75	158	8.8
$[Co(H_2O)_3(NH_3)_3](NO_3)_3$	44.74	126	7.0
$[CoH_2O(NH_3)_5]Cl_3$	44.74	198	11.0
$[Co(NH_3)_6](NO_3)_3$	—	135[1]	7.5[1]
KNO_2	44.72	67.7	3.8

Table 2. Results for the oxalates

	κ_1	K_{mo}(ml/mol)	h(mol/mol)
$H_2C_2O_4$	—	8[6]	0.4[6]
KHC_2O_4	44.72	120	6.6
$K_2C_2O_4$	44.77	250	13.9

$$[Co(NO_3)_3(NH_3)_3] \xrightarrow{\text{in water}} [Co(H_2O)_3(NH_3)](NO_3)_3$$

we used an aqueous solution of $[Co(NO_3)_3\ (NH_3)_3]$ for the sample of $[Co(H_2O)_3(NH_3)_3](NO_3)_3$.

For all solutions, the ultrasonic velocity changed linearly with concentration.

The results are summarized in Tables 1 and 2, where κ_1 is the compressibility of solvent, K_{mo} the molar hydration volume, and h the hydration numbdr (mol/mol).

A hydration number was assigned for each single ion. The results are given in Tables 3 and 4. We see from Table 2 that the hydration number of oxalate increases linearly with the number of potassium atoms in a molecule, and the hydration number of potassium ion can be estimated from the slope. The hydration number 7 obtained is, however, much larger than that in Table 3.

The hydration number of $[Co(NO_2)_4(NH_3)_2]^-$ calculated from its ammonium salt and potassium salts are 1.6 and 1.9 respectively, confirming the additivity rule of hydration number.

Table 3. Hydration numbers of ionic species

Ionic species	h(mol/mol)
NH_4^+	2[2]
K^+	3.2[7]
NO_3^-	1.1[7]
NO_2^-	0.6
$[Co(NO_2)_4(NH_3)_2]^-$	1.6[a]—1.9[b]
$[Co(NO_2)_2C_2O_4(NH_3)_2]^-$	5.6
$[Co(C_2O_4)_2(NH_3)_2]^-$	4.4

a) from ammonium salt
b) from potassium salt

Table 4. Hydration numbers of cobalt complexes

Ionic species	h(mol/mol)
$[Co(H_2O)_3(NH_3)]^{3+}$	3.7
$[Co\ H_2O(NH_3)_5]^{3+}$	5.3
$[Co(NH_3)_6]^{3+}$	3.7—4.4[1]

It is interesting to note that by the replacement of one of NO_2 in $[Co(NO_2)_4(NH_3)_2]^-$ with C_2O_4 the hydration number increased remarkably. This suggests that C_2O_4 shows hydration when it is contained in the complex as a ligand, while –COOH as the single species shows hardly any hydration effect (Table 2). A similar effect of COO^- in $[Co\ edta]^-$ has been reported.[3,4]

Table 4 shows the change of hydration with the increase of the number of H_2O contained as a ligand. Here, water molecules contained as ligand are not counted as hydration water. Since the change is not so remarkable, it can be concluded that the water molecules contained as ligand correspond to the primary hyration layer, Frank and Wen's region A and those hydrated outside the ligand to the secondary layer, their region B.

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