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Preparation of Hydroxoaquo- and Diol-Type Cobalt(III) Complexes with Analogues of Nitrilotriacetic Acid1)

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The following hydroxoaquo- and diol-type cobalt(III) complexes were prepared: K[Co(OH)(α-abda)(H_2O)]·$2H_2O$ (I), K[Co(OH)(vda)(H_2O)]·1.5 H_2O (II), K[Co(OH)pgda(H_2O)] (III), K_2[nipda Co$(OH)_2$-Co nipda]·$2H_2O$ (IV), K_2[(α-abda) Co$(OH)_2$Co (α-abda)]·$3H_2O$ (V), K_2[vda Co$(OH)_2$Co vda]·$3H_2O$ (VI), K_2[*l*da Co$(OH)_2$Co *l*da]·$2H_2O$ (VII) and K_2[pgda Co$(OH)_2$Co pgda]·$2H_2O$ (VIII), where α-abda, vda, pgda, nipda and *l*da are the abbreviations of *d*,*l*-α-amino-*n*-butyric-*N*,*N*-diacetate, *l*-valine-*N*,*N*-diacetate, *d*-α-phenylglycine-*N*,*N*-diacetate, nitriloisopropionicdiacetate and *l*-leucine-*N*,*N*-diacetate ions, respectively. From the measurements of electronic spectra, conductivities and coagulation values and the results of derivatography, it was found that the diol complexes IV—VIII were also formed from the correspoindng hydroxoaquo complexes in the thermal reaction process.

Studies on the preparation and the properties of chromium(III) and cobalt(III) complexes with some analogues of nitrilotriacetic acid (NTA) have been reported.2–4) When these chelating agents coordinate to metals in the hydroxoaquo-type complexes, $[M(OH)L(H_2O)]^-$, where M is cobalt (III) or chromium(III) and L is a quadridentate analogue of NTA, the ligands, OH^- and H_2O, should inevitably be situated in *cis*-positions. It is well known that a hydroxoaquo complex may liberate the coordinating water, resulting in the formation of the corresponding diol complexes under certain conditions. Such examples were found in the complexes $[Co(OH)(NH_3)_4(H_2O)]X_2$5,6) and $[Cr(OH)en_2(H_2O)]Cl_2$7) for the first time. Studies2,3) concerning diol-formation from K[Co(OH)nipda(H_2O)]·$2H_2O$ and K[Co(OH)*l*da(H_2O)]·H_2O were recently carried out in our laboratory.

In order to extend the study on diol-formation, the present work was undertaken (1) to prepare several hydroxoaquo complexes as the starting material and their corresponding diol complexes, and (2) to find the consistency between the diol complexes thermally obtained and those directly prepared.

For the sake of convenience, the general, rational formula and the abbreviations of chelating agents used in the present work are given in Table 1.

Experimental

Preparation of Hydroxoaquo Complexes. The general paths for the preparation of the hydroxoaquo and the diol complexes are given in Table 2, where L denotes one of the analogues of nitrilotriacetate ion.

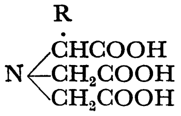
*1) Potassium Hydroxo-*d,l*-α-amino-*n*-butyric-*N,N*-diacetatoaquocobaltate(III) Dihydrate, K[Co(OH)(α-abda)(H_2O)]·$2H_2O$ (I):* Ten grams of *d*,*l*-α-amino-*n*-butyric acid was dissolved in 30 m*l* of water containing 6 g of potassium hydroxide. 19 g of monochloroacetic acid was dissolved in 200 m*l* of water, and then gradually neutralized with 20 g of potassium hydrogen carbonate. The two solutions were mixed together and heated on a water bath. After the temperature of the solution reached 70—80°C, 12 g of potassium hydroxide was added. An exothermic reaction took place. Heating was continued for about one hour in order to complete the reaction. When the resulting solution was cooled in a refrigerator, potassium chloride was precipitated. After the precipitate was removed by filtration, the filtrate was used as the starting material.

To the filtrate, 300 m*l* of water containing 20 g of cobalt(II) chloride hexahydrate was gradually added under magnetic stirring, since rapid addition often produced undesirable sediments such as cobalt hydroxide. The pH of the solution was adjusted to 6—7 by means of potassium hydrogen carbonate or acetic acid, and then 5 m*l* of hydrogen peroxide solution was dropped in order to oxidize cobalt(II) salt. Bluish violet crystals were obtained from the cooled solution. The crude products were recrystallized from aqueous solution. Yield about 5 g.

Found: N, 3.55; C, 25.07; H, 4.31%. Calcd for K[Co(OH)(α-abda)(H_2O)]·$2H_2O$: N, 3.63; C, 24.96; H, 4.45%.

*2) Potassium Hydroxo-*l*-valine-*N,N*-diacetatoaquocobaltate(III) Sesquihydrate, K[Co(OH)vda(H_2O)]·1.5H_2O (II):* This

TABLE 1. RATIONAL FORMULA AND ABBREVIATION OF CHELATING AGENTS

Rational formula	R	Full name	Abbreviation
	$-CH_3$	Nitriloisopropionicdiacetic acid	NIPDA
	$-CH_2\cdot CH_3$	*d*,*l*-α-Amino-*n*-butyric-*N*,*N*-diacetic acid	α-ABDA
	$-CH(CH_3)_2$	*l*-Valine-*N*,*N*-diacetic acid	VDA
	$-CH_2CH(CH_3)_2$	*l*-Leucine-*N*,*N*-diacetic acid	LDA
	$-C_6H_5$	*d*-α-Phenylglycine-*N*,*N*-diacetic acid	PGDA

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1) Presented at the 23rd Annual Meeting of Chemical Society of Japan, Tokyo, April, 1970.

2) A. Uehara, E. Kyuno, and R. Tsuchiya, This Bulletin, **43**, 414 (1970).

3) M. Tachibana, A. Uehara, E. Kyuno, and R. Tsuchiya, *ibid.*, **43**, 1061 (1970).

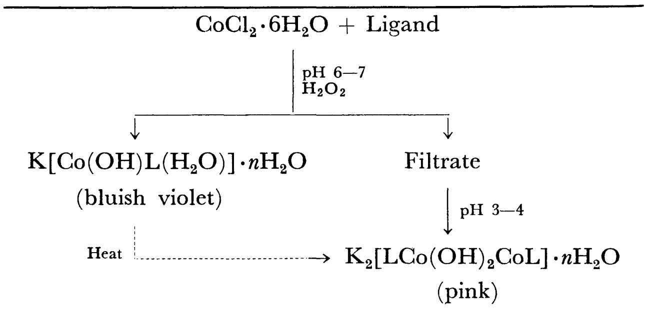
4) A. Uehara, E. Kyuno, and R. Tsuchiya, *ibid.*, **44**, 1548 (1971).

5) A. Werner, *Ber.*, **40**, 4434 (1907).

6) W. W. Wendlandt and J. K. Fisher, *J. Inorg. Nucl. Chem.*, **24**, 1685 (1962).

7) H. Pfeiffer, *Z. Anorg. Allg. Chem.*, **56**, 261 (1907).

Table 2. A general path for preparation of complexes



complex was prepared by a similar procedure to that for α-ABDA except that 12 g of *l*-valine was used as the starting material in stead of *d,l*-α-amino-*n*-butyric acid. The crystals were also bluish violet. Recrystallization was carried out from water. Yield 7 g.

Found: N, 3.46; C, 27.81; H, 4.40%. Calcd for K-[Co(OH)vda(H_2O)]·1.5H_2O: N, 3.59; C, 27.72; H, 4.65%.

*3) Potassium Hydroxo-*d-α-*phenylglycine-*N,N-*diacetatoaquocobaltate(III), K[Co(OH)pgda(H₂O)] (III)*: Five grams of d-α-phenylglycine was dissolved in 10 m*l* of water containing 2 g of potassium hydroxide. Nine grams of monochloroacetic acid was dissolved in 30 m*l* of water and gradually neutralized with 20 g of potassium hydrogen carbonate. Further procedure for obtaining the solution containing the desired ligand material was the same as that for α-ABDA except that 4 g of potassium hydroxide was added to the warmed solution on a water bath.

6.5 g of cobalt(II) chloride hexahydrate was dissolved under magnetic stirring in the solution obtained after the above procedure. After the pH of the solution was adjusted to 7—7.5, a few milliliters of hydrogen peroxide solution was added. The solution turned violet. In this case, the violet solution often turns pink as a result of the partial formation of the diol complex, and it is important to take care to keep the pH value of the solution in the desired range as exact as possible. From the rapidly cooled solution, bluish violet crystals were obtained. Recrystallization was carried out from water. Yield about 0.5 g.

Found: N, 3.31; C, 34.31; H, 3.80%. Calcd for K-[Co(OH)pgda(H_2O)]: N, 3.37; C, 34.73; H, 3.64%.

Preparation of Diol Complexes. *4) Potassium μ-Dihydroxobis(nitriloisopropionicdiacetato)dicobaltate(III) Dihydrate,* K_2*[nipda Co(OH)₂Co nipda]·2H₂O (IV)*: Five grams of NIPDA[8] was dissolved in 100 m*l* of aqueous solution containing 6 g of cobalt(II) chloride hexahydrate. The solution was heated on a water bath and neutralized with 5 g of potassium hydrogen carbonate. After the pH of the solution was adjusted to 6—7, a few milliliters of hydrogen peroxide was dropped into the solution in order to oxidize cobalt(II) salt, when bluish violet crystals of K[Co(OH)nipda-(H_2O)]·H_2O[3] were obtained. After the crystals were separated, the pH of the filtrate was adjusted to 3—4 with acetic acid. The solution was warmed gently until the color turned from violet to pink. Pink crystals were obtained from the cooled solution after several days. They were recrystallized from water. Yield 0.5 g.

Found: N, 4.14; C, 25.64; H, 3.45%. Calcd for K_2-[nipda $Co(OH)_2Co$ nipda]·2H_2O: N, 4.18; C, 25.10; H, 3.31%.

*5) Potassium μ-Dihydroxobis(*d,l-α-*amino-*n-*butyric-*N,N-*diacetato)dicobaltate(III) Trihydrate.* K_2*[(α-abda) Co(OH)₂Co (α-abda)]·3H₂O*: This was crystallized from the filtrate after the removal of complex I in its preparation. After the pH of the filtrate was adjusted to 3—4 with acetic acid, the solution was warmed gently on a water bath until it turned pink. On cooling for several days, pink crystals were obtained which were recrystallized from water. Yield about 0.6 g.

Found: N, 3.92; C, 26.80; H, 3.77%. Calcd for K_2-[(α-abda) $Co(OH)_2Co$ (α-abda)]·3H_2O: N, 3.91; C, 26.84; H, 3.94%.

*6) Potassium μ-Dihydroxobis(*l-*valine-*N,N-*diacetato)dicobaltate(III) Trihydrate,* K_2*[vda Co(OH)₂Co vda]·3H₂O (VI)*: This was crystallized from the filtrate in the preparation of complex II by a procedure similar to that for complex V. Pink crystals were recrystallized from water. Yield about 1 g.

Found: N, 3.71; C, 29.04; H, 4.61%. Calcd for K_2-[vda $Co(OH)_2Co$ vda]·3H_2O: N, 3.76; C, 29.06; H, 4.33%.

*7) Potassium μ-Dihydroxobis(*l-*leucine-*N,N-*diacetato)dicobaltate(III) Dihydrate,* K_2*[*lda *Co(OH)₂Co* lda*]·2H₂O (VII)*: This complex was prepared by a similar procedure to that for complex IV except that six grams of *l*-leucine-*N,N*-diacetic acid (LDA)[2] was used as a starting ligand in place of NIPDA. The complex was pink as in the case of complex IV. Recrystallization was carried out from water. Yield 0.5 g.

Found: N, 3.65; C, 31.48; H, 4.31%. Calcd for K_2-[*l*da $Co(OH)_2Co$ *l*da]·2H_2O; N, 3.71; C, 31.86; H, 4.54%.

*8) Potassium μ-Dihydroxobis(d-α-phenylglycine-*N,N-*diacetato)-dicobaltate(III) Dihydrate,* K_2*[pgda Co(OH)₂Co pgda]·2H₂O (VIII)*: This was prepared in a procedure similar to that for complex V except that the filtrate in the preparation of complex III was used. It was also recrystallized from water. In the preparation of the pgda-complex, the diol salt was more easily formed as compared with the corresponding hydroxoaquo salt, whereas in the case of the other complexes, hydroxoaquo salts were more readily produced than the corresponding diol salts. Yield 0.5 g.

Found: N, 3.61; C, 35.97; H, 3.19%. Calcd for K_2-[pgda $Co(OH)_2Co$ pgda]·2H_2O: N, 3.53; C, 36.30; H, 3.30%.

Apparatus. The apparatus used in the present study is the same as reported previously.[9]

Results and Discussion

Electronic Spectra. A striking difference in features between the hydroxoaquo and the diol complexes is that the former is bluish violet, whereas the latter is pink. Spectra for all the complexes were obtained but only representative examples in a pair of VDA complexes, II and VI, are shown in Fig. 1. Complex II gives the first and the second bands at 53.57 and 76.53×10^{13} sec^{-1} respectively. Complex VI does not show the second band distinctly, but a new band at $\sim 100 \times 10^{13}$ sec^{-1}. All the complexes, IV, V, VII, and VIII exhibit the same features in their spectra as those of complex VI.

It is known[10] that the ol-ammine complexes show the specific band due to the bridged OH group at

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[8] A. Uehara, E. Kyuno, and R. Tsuchiya, This Bulletin, **41**, 2393 (1968).

[9] A. Uehara, E. Kyuno, and R. Tsuchiya, This Bulletin, **41**, 2385 (1968).

[10] Y. Inamura and Y. Kondo, *Nippon Kagaku Zasshi*, **74**, 627 (1953).

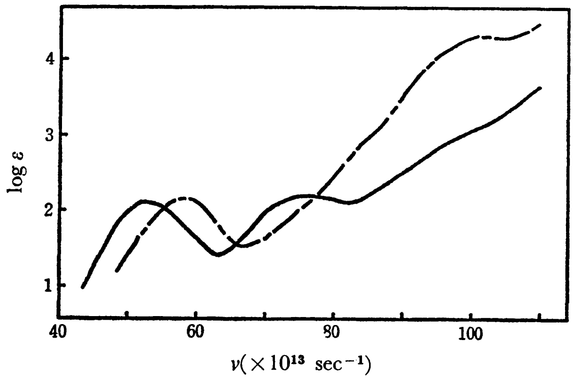

Fig. 1. Electronic spectra for complexes II (——) and VI (----).

TABLE 3. ABSORPTION MAXIMA

Complex	ν_1 (log ε_1)	ν_2 (log ε_2)[a]	Complement[b]
I	53.10 (2.15)	75.38 (2.35)	
II	53.38 (2.09)	76.34 (2.26)	
III	53.10 (2.13)	76.73 (2.29)	
IV	59.76 (2.11)		~100 (~4.2)
V	59.64 (2.13)		~100 (~4.3)
VI	59.06 (2.16)		~100 (~4.2)
VII	59.76 (2.18)		~100 (~4.3)
VIII	59.29 (2.18)		~105 (~4.6)

a) The second bands of complexes IV to VIII can not be clearly detected because of the overlap with the specific band due to the bridging OH groups.
b) These values show the specific bands due to the bridging OH groups. The band can not be clearly detected because of its broadening.

about 100×10^{13} sec^{-1}. In some cases the second band does not appear due to being concealed by the strong specific band. Such a difference[11] may propose one evidence that VI is a diol and II a hydroxoaquo complex. The numerical values of absorption maxima for all the complexes prepared in the present work are summarized in Table 3.

Conductivity and Coagulation Value. To determine the type of electrolytes for the complexes, the molar conductivities and coagulation values were measured in an aqueous solution at 25°C. The numerical data are shown in Table 4. All the complexes show a molar conductivity of the same order. Accordingly, no distinction could be detected between the hydroxoaquo and the diol complexes by this method. However, it is known that the average coagulation values for uni- and bivalent complex anions are 6.6 mF and 0.48 mF, respectively.[12] The values measured with an iron(III) hydroxide sol for the complexes I to III was 5—6 mF, while for complexes IV to VIII, 0.6—0.8 mF, indicating that the former three are 1 : 1 type (hydroxoaquo complex anion) and the latter four 1 : 2 type electrolytes (diol complex anion).

TABLE 4. MOLAR CONDUCTIVITY (λ) AND COAGULATION VALUE (mF)

Complex	λ[a] mho cm^{-1}	mF
I	113.1	6
II	117.6	6
III	123.1	5
IV	121.2	0.6
V	145.6	0.8
VI	162.3	0.7
VII	153.2	0.6
VIII	132.5	0.7

a) 10^{-3} mol/l aqueous solution was used.

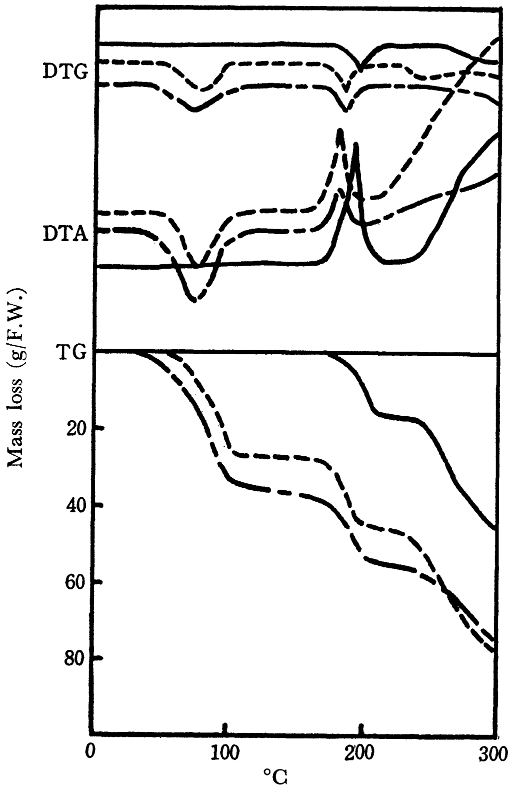

Fig. 2. Derivatograms for complexes I(—·—), II(----), and III (——).

Change from Hydroxoaquo- to Diol-Complex in the Thermal Reaction Process. The hydroxoaquo complexes in the solid phase are expected to liberate the coordinating water upon heating, forming the corresponding diol complexes as suggested by a broken arrow in Table 2. The thermal reaction for the complexes was measured with a derivatograph.[13] Figure 2 shows the derivatograms for complexes I, II, and III. Five hundred milligrams of the samples was used in each run in a constant nitrogen stream with a heating rate of 1°C/min. As seen from TG and DTA curves, complexes I and II are observed to liberate two moles of water at 50—110 and one and a half moles of water at 80—130°C, respectively, with endothermic

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[11] M. Mori, M. Shibata, E. Kyuno, and Y. Okubo, This Bulletin, **31**, 940 (1958).

[12] A. Nakahara, K. Nakamoto, and R. Tsuchida, *Nippon Kagaku Zasshi*, **74**, 488 (1953).

[13] R. Tsuchiya, Y. Kaji, A. Uehara, and E. Kyuno, This Bulletin, **42**, 1881 (1969).

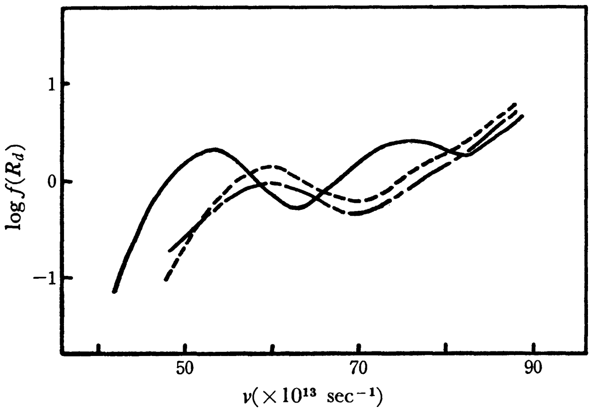

Fig. 3. Electronic spectra for complexes II (——), VI (----) and the sample II picked up at 190°C (—-—).

reactions. It is further found that one mole of coordinated water is liberated from the complexes I, II, and III at 185—200, 175—190, and 190—215°C, respectively, with exothermic reactions. At these steps, the color of the samples changed from bluish violet to pink as in the case of the corresponding NIPDA,$^{3)}$ LDA,$^{2)}$ and PADA (*d*,*l*-Phenylalanine-*N*,*N*-diacetic Acid)$^{4)}$ complexes.

Figure 3 gives the electronic spectra measured by the diffuse reflectance method for complexes II, VI and for the sample of complex II picked up at this heating step (190°C). The spectrum for the last sample resembles that for complex VI, suggesting that the structure of the sample picked up at this step is similar to that of complex VI. Accordingly, the fact that the diol complex is formed by heating the corresponding hydroxoaquo complex may be successfully verified by the above experimental results.

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