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Preparation of Fluoroamminecobalt(III) Complexes

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Synopsis. New preparation methods are reported for some fluoroamminecobalt(III) complexes. The polarized spectra were measured by microspectrophotometry for some complexes. Coordination geometries of the complexes were predicted from the spectral data.

In order to compare Yamatera's rule1) with experimental result, a number of empirical splitting parameters are required. The spectra of aqua- and/or chloro-amminecobalt(III) series have been analyzed as reported in the previous paper.2) The results of the careful survey of the literatures3,4) yielded few reports concerning the preparation methods of fluoroamminecobalt(III) complexes. Linhard and Weigel5) have reported a spectrum of *cis*-difluorotetraamminecobalt(III) ion in aqueous solution, but they did not describe the preparation method of the complex. Siebert and Breitenstein6) have attempted to synthesize trifluorotriamminecobalt(III) by thermal decomposition of $[Co(NH_3)_6]F_3$, but the product was not the intended complex.

In this paper, new preparation methods are described for the complexes, $[CoF(NH_3)_4(H_2O)]X$, (sulfate, and perchlorate), *cis*-$[CoF_2(NH_3)_4]ClO_4$, and $[CoF_3(NH_3)_3]$.

Experimental

Preparations of Complexes. $[CoF(NH_3)_5](NO_3)_2$: Fluoropentaamminecobalt(III) nitrate was prepared as described7) previously. Found: Co, 20.06; F, 6.20%. Calcd for $[CoF(NH_3)_5](NO_3)_2$: Co, 20.54; F, 6.62%.

$[CoF(NH_3)_4(H_2O)]SO_4$: Potassium fluoride (1 g) and *cis*-$[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3\cdot 3H_2O$ (3 g) prepared according to the procedure in reference8) were dissolved in 10 cm^3 of water in a Teflon evaporating dish. The solution was then dried over P_2O_5 in a desiccator for several days. The product was powdered in an alumina mortar, added to 25 cm^3 of cold water and stirred. The violet residue was filtered off, and washed with cold water and ethanol. The product was dried over P_2O_5. Yield: 1.5 g. Found: Co, 22.49; NH_3, 25.28; F, 6.83%. Calcd for $[CoF(NH_3)_4(H_2O)]SO_4$: Co, 22.67; NH_3, 26.16; F, 7.30%.

$[CoF(NH_3)_4(H_2O)](ClO_4)_2$: $[CoF(NH_3)_4(H_2O)]SO_4$ (1 g) was dissolved in cold water (10 cm^3) which involves 60% perchloric acid (2 cm^3). To the solution, 60% perchloric acid (5 cm^3) was added with stirring. The purple crystals were then precipitated. The product was washed with ethanol, and air-dried. Yield: 0.6 g. Found: Co, 16.80; NH_3, 18.76; F, 5.28%. Calcd for $[CoF(NH_3)_4(H_2O)](ClO_4)_2$: Co, 16.24; NH_3, 18.74; F, 5.23%.

***cis*-$[CoF_2(NH_3)_4]ClO_4$:** *cis*-$[Co(NH_3)_4(H_2O)_2](ClO_4)_3$ was deposited by adding 60% perchloric acid to a concentrated aqueous solution of *cis*-$[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3\cdot 3H_2O$. The *cis*-diaqua complex perchlorate (3.2 g) dissolved in water (3.5 cm^3) was mixed with NH_4F (0.8 g) dissolved in water (2 cm^3). The slurry was stirred and cooled in an ice-salt bath. The precipitate (NH_4ClO_4) was removed with a Teflon funnel. The filtrate was concentrated to half volume in a Teflon evaporating dish on a steam bath. The solution was then cooled to room temperature. The violet crystals were collected, washed with ethanol, and dried at room temperature. Found: Co, 21.73; NH_3, 25.59; F, 14.80%. Calcd for *cis*-$[CoF_2(NH_3)_4]ClO_4$: Co, 22.29; NH_3, 25.72; F, 14.37%.

$[CoF_3(NH_3)_3]$: *fac*-$[Co(NH_3)_3(H_2O)_3](ClO_4)_3$ (6.7 g) synthesized by the method in reference9) was dissolved in 3.5 cm^3 of water in a Teflon evaporating dish. Potassium fluoride (2.5 g) dissolved in water (3.0 cm^3) was added to the solution with continuous stirring. The slurry was cooled with an ice-salt bath for 30 min. The precipitate ($KClO_4$) was removed with a Teflon funnel. The filtrate was then dried over P_2O_5 in a desiccator for about a week. The solid was powdered in an alumina mortar and dried at 120 °C. The powder was washed with cold water. The residue was dried at 120 °C for 2 h. Found: Co, 34.40; NH_3, 29.27; F, 33.82%. Calcd for $[CoF_3(NH_3)_3]$: Co, 35.30; NH_3, 30.55; F, 34.15%.

Chemical Analyses. Cobalt was determined colorimetrically by the nitroso R salt (1-nitroso-2-naphthol-3,6-disulfonic acid, disodium salt) method.10) The analysis of ammonia was carried out by the Kjeldahl method.11) Fluorine was separated by pyrolysis12,13) and determined14) spectrophotometrically with Dotite Alfusone (a mixture of 9,10-dihydro-3,4-dihydroxy-9,10-dioxo-2-anthrylmethylamine-*N*,*N*-diacetic acid and buffer reagent), Wako Pure Chem. Indust. Ltd.

Electrical Conductivity. Conductivities were measured with a Toa Denpa Model CM-1DB. The cell constant was determined using 0.1 mol dm^{-3} KCl. The molar conductivities, measured for aqueous solutions of aquafluorotetraamminecobalt(III) perchlorate (0.0027 mol dm^{-3}) and *cis*-difluorotetraamminecobalt(III) perchlorate (0.0015 mol dm^{-3}), were 104.9 and 274.5 Ω^{-1} cm^2 mol^{-1} at 25 °C, respectively.

Spectral Measurements. The solution spectra were recorded on a Jasco Uvidec 1 double beam spectrophotometer. The diffuse reflectance spectrum was measured with a Hitachi 3400 spectrophotometer. The infrared spectrum was determined with a Shimadzu IR 450S spectrophotometer. The sample for IR measurement was a fine powder of the complex suspended in a solid paraffin (softening point: 60 to 62 °C) plate.

Polarized Spectra. The polarized spectra of single crystal were measured with a microspectrophotometer system for fluoropentaammine, difluorotetraammine, and fluoroaquatetraammine complexes. Measurements and curve analysis are essentially the same as described in the previous paper.2)

Results and Discussion

The UV spectra of fluoropentaamminecobalt(III) nitrate and difluorotetraamminecobalt(III) perchlorate in aqueous solution were in good agreement with the data of Linhard and Weigel.5) The IR spectrum of the fluoropentaammine complex in the range of 200 to 600 cm^{-1} is similar to that of the analogous bromide reported by Shimanouchi and Nakagawa.15)

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Table 1. Positions of the Absorption Bands of Fluoroamminecobalt(III) Complexes

Complex	Average position of the second band/×10³ cm⁻¹	Analyzed positions of the first band/×10³ cm⁻¹	Predicted positions for the first band component/ ×10³ cm⁻¹
$[CoF(NH_3)_5](NO_3)_2$	28.49	18.99	
		21.59	
cis-$[CoF_2(NH_3)_4]ClO_4$	27.31	17.13	
		19.84	
$[CoF(NH_3)_4(H_2O)](ClO_4)_2$	28.12	17.48	17.44
		19.76	18.90, 19.83
$[CoF_3(NH_3)_3]$	26.3[a)]	17.7[a)]	

a) These are the peak values read directly from diffuse reflectance spectral data.

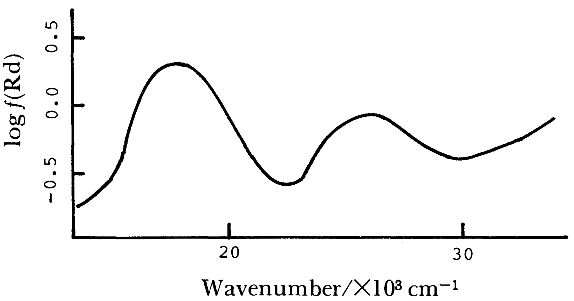

Fig. 1. Diffuse reflectance spectrum of trifluorotriamminecobalt(III).

The analyzed peak positions of the polarized spectra are summarized in the Table 1. An X-ray diffraction analysis[16)] for a crystal of difluorotetraamminecobalt(III) perchlorate suggested that the two fluoro ligands in the complex are in cis form. On the basis of spectral data of *cis*-difluorotetraammine and *cis*-diaquatetraammine complexes, the predicted band positions were calculated for the coordination structure of *cis*-fluoroaquatetraammine by the manner described in the previous report.[2)] The predicted values are in good agreement with the observed positions as shown in the table. The coordination geometry of the fluoroaquatetraammine complex may therefore be cis form.

Because trifluorotriamminecobalt(III) was in fine crystals and insoluble in water and in the ordinary solvents, the diffuse reflectance spectrum was measured. The spectrum obtained was corrected by the Kubelka-Munk function as shown in the Fig. 1. The first band (at 17.7×10³ cm⁻¹) of trifluoro complex shows no splitting. Comparison with the spectral patterns of *fac*- and *mer*-trichlorotriamminecobalt(III) complexes[17)] suggests that the coordination structure in the complex is in facial form.

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