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The Synthesis of Potassium Pentacyanohydroxochromate(III)

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Synopsis. The crystals of $K_3[Cr(CN)_5(OH)]\cdot H_2O$ have been obtained by making $[CrCl(NH_3)_5]Cl_2$ react with KCN, followed by purification on a Sephadex gel column.

On the cyano-hydroxo- and aqua-cyano- mixed-coordinated chromate(III) complexes, there have been only a few works reported.[1-4] All the experiments in those studies had been made on samples of the complexes formed in the aquation process of the $[Cr(CN)_6]^{3-}$ ion in an aqueous solution.

Accordingly, the works have more or less had difficulties in the isolation as well as in the identification of the complexes under consideration, which were yielded very scantly and had the property of continuing the sequential release of coordinating cyano ligands in an aqueous solution.

By the use of a new method quite different from the earlier processes, the present authors have obtained $K_3[Cr(CN)_5(OH)]\cdot H_2O$ in crystals. This product proved to be just the complex which had been presumed in one of the reports to have been formed in the reviewed aquation process;[3] this fact affords solid ground for the satisfactory settlement of an intriguing problem with regard to the spectrum-identification of the aqua-cyano-coordinated chromate(III) complexes.

The unit cell dimensions of the crystal were determined by means of X-ray diffraction.

Experimental

Potassium cyanide (25.5 g, 0.415 mol) and $[CrCl(NH_3)_5]Cl_2$ (15.0 g, 0.072 mol) were added to 170 cm^3 of water, after which the mixture was boiled while being stirred. A considerable amount of undissolved $[CrCl(NH_3)_5]Cl_2$ which was at first observed disappered qiuckly at the beginning of the boiling, and the solution's color changed from deep-red to orange-yellow. The temperature of the oil-bath was maintained at about 140 °C, and the boiling was continued for 2—3 min after the disappearance of the solid $[CrCl(NH_3)_5]Cl_2$. Attention must be paid to the reaction time, since if the boiling is prolonged, most of the products are decomposed rapidly to form a black precipitate, and the desired complex is not obtained. The reaction mixture was cooled and evaporated to about one-half volume by means of a rotary evaporator. The concentrate, after the removal of a small amount of the black substance, was passed through a Sephadex G-15 gel column (5.5×49 cm). The fractionation of the products on the Sephadex column is illustrated in Fig. 1. The separated orange-yellow fraction which contained the desired complex was refined twice more by means of the same Sephadex column. The purified $K_3[Cr(CN)_5(OH)]$ solution was then evaporated to dryness in a rotary evaporator (the temperature being kept below 35 °C); 7.6 g of orange-yellow crystals as small needles were thus obtained. The crude crystals (2 g) were recrystallized by dissolving them in 2 cm^3 of water and by slowly evaporating the solution thus formed in a KOH desiccator. About two days later, the deposited needle crystals were collected by filtration, washed with ethyl alcohol containing 20% water, and dried in a vaccum desiccator with sodium hydroxide: yield, 1.2 g. Analytical result, Found: Cr, 15.28; C, 17.72; H, 1.03; N, 21.05; K, 35.0; H_2O, 5.3%. Calcd for $K_3[Cr(CN)_5(OH)]\cdot H_2O$: Cr, 15.55; C, 17.96; H, 0.90; N, 20.94; K, 35.1; H_2O, 5.4%. The water of crystallization was determined by thermobalance analysis although the results varied to some extent corresponding to the conditions of drying applied to the crystals. The infrared spectrum is illustrated in Fig. 2.

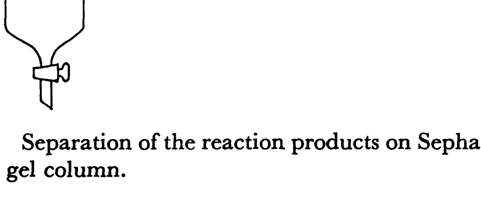

Fig. 1. Separation of the reaction products on Sephadex G-15 gel column.

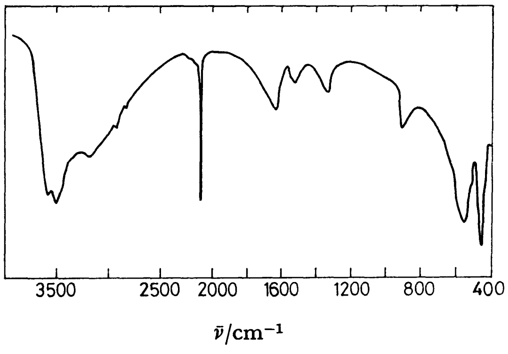

Fig. 2. Infrared spectrum of $K_3[Cr(CN)_5(OH)]\cdot H_2O$ in the 4000—400 cm^{-1} region.

Results and Discussion

The complex, $[CrCl(NH_3)_5]Cl_2$, was first made to react with KCN on the presumption that $K_3[CrCl(CN)_5]$ might be obtained, because an analogous cobaltate(III) complex, $K_3[CoCl(CN)_5]$, had been prepared[5] by making $[CoCl(NH_3)_5]Cl_2$ react with 5 mol of KCN. The complex isolated from the reaction products, however, was found to be not a chloro, but a hydroxo, complex, $K_3[Cr(CN)_5(OH)]$. In the past, the isolation of the pure substance of this complex was difficult, as has previously been explained, and the crystal could not be obtained. Accordingly, the properties of the complexes have been solely investigated on their aqueous solutions, the identification of the complexes being made mainly by means of the electronic spectra and the molar ratio, CN$^-$/Cr, of the solution.

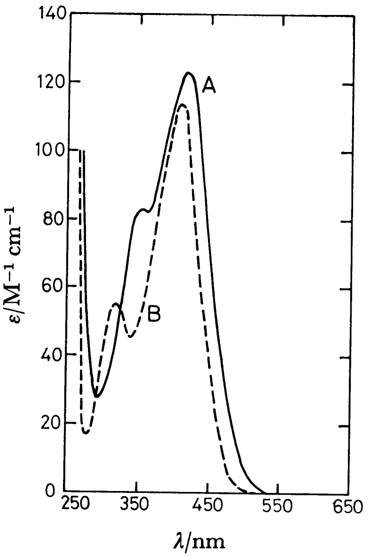

Fig. 3. Absorption spectra of $K_3[Cr(CN)_5(OH)]\cdot H_2O$ at pH 10.3 (——), and at pH 4.2 (– – –) in an aqueous solution.

Now, by virtue of the markedly increased yield by the new reaction process and the excellent ability of Sephadex gel to act as a molecular sieve, the complex has been obtained in crystals.

As a proof of the presence of a OH^- ligand in this complex, a 0.04 mol dm^{-3} (as $K_3[Cr(CN)_5(OH)]$) solution (pH=10.3) was titrated with 0.05 mol dm^{-3} amidosulfuric acid. A single break with a pK value of 8.8 was observed on the titration curve, indicating that the complex was a base with 1 g equivalent/mol. When the solution was made acidic, the complex varied to $K_2[Cr(CN)_5(H_2O)]$, and at pH 4.2 the electronic spectrum of the solution was observed to have been shifted in the direction of the shorter wave length from its initial position at pH 10.3, reinforcing our account of the OH^- ligand, as is illustrated in Fig. 3.

With respect to the spectrum of the cyano-aqua-mixedly coordinated complex of chromium(III), two arguments have been advanced by pioneers. The spectrum, which is identical to the B curve in Fig. 3, has been taken by Schaap *et al.*[1-2] as the spectrum of $[Cr(CN)_4(H_2O)_2]^-$, while the same spectrum was concluded to be that of $[Cr(CN)_5(H_2O)]^{2-}$ by Jeftić and Feldberg.[3] To the investigating made by the foregoing investigators, however elaborate, the result of our work can add adequate evidence which they wanted. The presented method would be of great value in preparing the authentic sample in crystals in quantity. On the three dimensional X-ray diffraction data collected by counter methods, the crystal was found to be monoclinic, with a unit cell of the dimensions: $a=4.45$, $b=8.29$, $c=20.23$ Å, $\beta=105.52°$, $Z=2$. Details of the crystal structure will be presented in another paper.

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