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Abstract

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Chemistry

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Synthesis of Potassium Disulfotricyanoaquo-cobaltate

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Cyanometallates of the mixed, prusside type have been investigated to a considerably lesser extent than the corresponding homogeneous compounds. This observation applies fully to sulfur-containing cyano complexes of metals, among which only a few representatives are known, described in the works of E. Peshard (^{1}), K. Heide, K. Hofmann (^{2}), and E. Krepach (^{3}). In the most recent literature (^{4}), sulfur-containing complex iron cyanides of composition $Na_{6n}[Fe_2(CN)_8S_2]_n$ are mentioned, whose formation makes it possible to detect sulfur ions in an alkaline medium.

Our previous works ($^{5-7}$), devoted to hydroxosulfotetracyanomolybdates, showed the possibility of successful replacement of hydroxyl groups by the sulfur ion.

It was desirable to test this reaction for other metals forming hydroxycyano compounds. Such a possibility presented itself for cobalt, which forms the compound $K_3[Co(OH)(CN)_5] \cdot H_2O$, obtained by L. Smith, J. Kleinberg, and E. Griswold (^{8}). The initial compound of trivalent cobalt was obtained by the method of the above-mentioned authors through the action of a calculated amount of potassium cyanide on nitrosylcobalt and further oxidation of potassium pentacyanoaquo-cobaltate with atmospheric oxygen.

We studied the reaction of this compound with potassium sulfide, which proceeds according to the equation:

$$K_3[Co^{3+}(OH)(CN)_5] + 2K_2S + H_2O = K_4[Co^{3+}(CN)_3S_2(H_2O)] + 2KCN + KOH.$$

Potassium sulfide was added to a 30% solution of the starting compound in molar ratios of 1 : 1 and 1 : 2.

In both cases a gradual change in the color of the solution from dark brown to yellow-orange was observed. The reaction proceeded at room temperature over several hours; the product was precipitated the next day with ethyl alcohol. The compound forms large rhombic crystals of dark amber color. Irrespective of the amount of potassium sulfide introduced, a substance of one and the same composition was obtained.

Chemical analysis gave the following results:

Found %: K 35.21; 34.82; Co 12.82; 12.63;
N 9.03; 9.11; S 13.91; 13.74;
H_2O 19.93; 19.87

$K_4[Co(CN)_3S_2(H_2O)] \cdot 4H_2O$. Calculated %: K 34.94; Co 13.17;
N 9.38; S 14.33;
H_2O 20.13

To establish the coordination formula of the compound, the electrical conductivity of its solution was measured. The value of the molecular conductivity at a dilution of 1000 l per 1 gram-mole of salt, $\mu^{25^\circ}_{1000\ \mathrm{l}} = 580.5\ \mathrm{ohm}^{-1} \cdot \mathrm{cm}^2$, corresponds to a five-ion electrolyte. The composition

the synthesized complex compound can be expressed by the formula $K_4[Co(CN)_3S_2(H_2O)] \cdot 4H_2O$.

The four water molecules removed at a temperature of 110° are waters of crystallization. One H_2O molecule is bound more strongly; we regard it as coordination-bound and place it in the inner sphere of the complex.

If the complex salt is precipitated from aqueous solution with solid alkali, another compound with a lower sulfur content is obtained.

Nitric acid, 10% hydrogen peroxide, and other oxidizing agents destroy the complex with simultaneous oxidation of the sulfur.

Cations of heavy and cyanophilic metals form colored precipitates of sparingly soluble compounds with the sulfur-containing complex cyanide of trivalent cobalt. Mn^{2+}, Zn^{2+}, and Cd^{2+} give white precipitates; Fe^{2+}, Cu^{2+}, and Ni^{2+} give light-green precipitates; Co^{2+}, a yellow-orange one; Ag^{+}, a light-brown one; and Fe^{3+}, a green precipitate. In the case of Hg^{2+} and Pb^{2+}, yellow precipitates were formed, which indicates the absence of free sulfur ions and confirms the high stability of the complex. The reaction for obtaining potassium disulfotricyanoaquo-cobaltate confirms the possibility of successful replacement of water molecules, hydroxyl groups, and cyano groups by sulfur ions not only for molybdenum but also for cobalt.

It should be assumed that reactions of this kind are also possible for other cyanometallates.

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Note: Figure translations are in progress. See original paper for figures.