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Abstract

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ON THE STRONG TRANS-INFLUENCE OF THE HYDROXO GROUP IN DIOXIMINES OF TRIVALENT COBALT

(Presented by Academician I. I. Chernyaev, December 25, 1956)

In studying the acidic properties of nitro-bis-dimethylglyoxime aquocobalt $[CoH_2O(DH)_2NO_2]$, it was found that this compound dissolves completely in concentrated alkali, forming a dark-red solution. On gentle heating of this solution, an abundant reddish-brown crystalline precipitate of composition $K[Co(DH)_2(OH)_2] \cdot 3H_2O$* separates. The sodium salt was obtained in the same way.

Nitric acid, acting on these salts, forms the red-colored nitrate of bis-dimethylglyoxime diaquocobalt, with the formation of an intermediate product being clearly visible:

$$K[Co(DH)_2(OH)_2] + HNO_3 = [CoH_2O(DH)_2OH] + KNO_3;$$

$$[CoH_2O(DH)_2(OH)] + HNO_3 = [Co(H_2O)_2(DH)_2]NO_3.$$

The intermediate compound—hydroxo-bis-dimethylglyoxime aquocobalt—was obtained in pure form by cautiously treating chloro-bis-dimethylglyoxime aquocobalt with a solution of potassium carbonate. If the chloro aquo compound is treated with alkali, the dihydroxo compound is obtained. This method is more convenient for preparing the latter.

Below are given the electrical conductivity and pH values of solutions of the three compounds described above at a dilution of 1000 l/mol:

Compound	M_{100}^{25}, Ω^{-1} cm^2	pH
$K[Co(DH)_2(OH)_2] \cdot 3H_2O$	132.8	9.46
$[CoH_2O(DH)_2(OH)] \cdot H_2O$	9.7	7.02
$[Co(H_2O)_2(DH)_2]NO_3$	217.9	5.79

Potassium dihydroxo-bis-dimethylglyoxime cobaltate gives an alkaline reaction as a result of hydrolysis according to the equation:

$$[Co(DH)_2(OH)_2]^- + H_2O \rightleftarrows [CoH_2O(DH)_2(OH)] + OH^-.$$

The diaquo-bis-dimethylglyoxime cobalt ion dissociates according to the equation:

$$[Co(H_2O)_2(DH)_2]^+ \rightleftarrows [CoH_2O(DH)_2(OH)] + OH^+.$$

Hydroxo-bis-dimethylglyoxime aquocobalt is an ampholyte:

$$[CoH_2O(DH)_2(OH)] \rightleftarrows [Co(DH)_2(OH)_2]^- + H^+,$$

$$[CoH_2O(BH)_2(OH)] + H^+ \rightleftarrows [Co(H_2O)_2(DH)_2]^+.$$

On heating dihydroxo-bis-dimethylglyoxime cobaltate with concentrated hydrochloric acid, dichloro-bis-dimethylgly-

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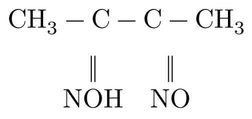
* DH denotes the residue of dimethylglyoxime



$$\begin{array}{c} CH_3 - \underset{\underset{NOH}{\|}}{C} - \underset{\underset{NO}{\|}}{C} - CH_3 \end{array}$$

oximocobaltic acid H[Co(DH)Cl], of a characteristic green color. This reaction forces one to assign one and the same configuration to all cobalt dioximes of the type $[Co(DH)_2X_2]$.

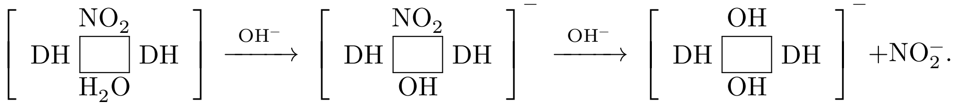
On the basis of the regularities of the trans effect, one of us expressed the assumption that in the compounds $[Co(DH)_2X_2]$ the two residues X are in the trans position to one another (1). Further study confirmed this spatial configuration of the dioximes of trivalent cobalt (2, 3). Recently, on the basis of a study of infrared spectra, Nakahara (4) also obtained evidence for the trans configuration

$$H[Co(DH)_2Cl_2].$$

The conversion of nitro-bis-dimethylglyoximoaquocobalt into potassium dihydroxo-bis-dimethylglyoximocobaltiate can be explained as follows, proceeding from the regularity of the trans effect of I. I. Chernyaev (5). Under the action of alkali, the nitroaquo compound first changes into nitrohydroxo-bis-dimethylglyoximocobaltiate

$$K[Co(DH)_2(OH)NO_2] \cdot H_2O.$$

The hydroxo group, to which a stronger trans effect must be attributed than to the nitro group, weakens the bond of the NO_2 group with the cobalt atom, and the latter is replaced by a hydroxo group:



$$\left[\begin{array}{c} NO_2 \\ DH\ \boxed{}\ DH \\ H_2O \end{array}\right] \xrightarrow{OH^-} \left[\begin{array}{c} NO_2 \\ DH\ \boxed{}\ DH \\ OH \end{array}\right]^- \xrightarrow{OH^-} \left[\begin{array}{c} OH \\ DH\ \boxed{}\ DH \\ OH \end{array}\right]^- + NO_2^-.$$

The intermediate product $K[Co(DH)_2(OH)NO_2] \cdot H_2O$ was obtained by the action of potassium carbonate on the nitroaquo compound.

The supposition that in dioximes of trivalent cobalt the hydroxo group possesses a strong trans effect was put forward to explain the action of alkali on the anion of di-isothiocyanato-bis-dimethylglyoximocobaltic acid (^{2}), but at that time it was not sufficiently substantiated. Acting with alkali on isothiocyanato-bis-dimethylglyoximoaquocobalt, we have now been able to isolate dihydroxo-bis-dimethylglyoximocobaltiate in crystalline form.

Thus, the hydroxo group possesses a greater trans activity than the rhodano and nitro groups. Taking into account that the rhodano group possesses greater trans activity than the nitro group (^{3}), these three groups must be arranged in the following order of increasing trans activity in dioximes of trivalent cobalt:

$$OH > NCS > NO_2$$

Experimental part

Action of alkalis on nitro-bis-dimethylglyoximoaquocobalt

a) 2.0 g of nitro-bis-dimethylglyoximoaquocobalt (^{6}) are treated with 10 ml of a 50% solution of caustic potassium. On mixing, a dark-red solution is formed. On heating the latter, an abundant crystalline precipitate separates. The salt obtained is transferred to a glass filter, washed with absolute ethyl alcohol or butanol, and finally with ether. From the filtrate, on standing for some time, a new portion of product separates. The total yield is 75% of theory. Under the microscope the substance appears as dark-red, long quadrangular prisms. It dissolves very well in water, and is insoluble in absolute alcohol and ether.

A solution of the potassium salt of dihydroxo acid forms precipitates with $Rb^{\bullet}$, Cs, $Hg^{\bullet}$, $Hg^{\bullet\bullet}$, $Pb^{\bullet\bullet}$. For analysis the substance was dried between sheets of filter paper. Loss in weight at 105°: 13.80%.

Found %: Co 14.06; 14.07; N 13.64; 13.31

$K[Co(C_4H_7N_2O_2)_2(OH)_2] \cdot 3H_2O$. Calculated %: Co 14.17; N 13.46;

The potassium salt of dihydroxo-bis-dimethylglyoximocobaltic acid was first obtained by Cambi (7) by the action of 3 moles of potassium alcoholate on a suspension of $[CoDH_2(DH)Br_2]$ in absolute alcohol.

b) On the action of caustic soda on the nitroaquo compound, sodium dihydroxo-bis-dimethylglyoximocobaltiate, $Na[Co(DH)_2(OH)_2] \cdot 5H_2O$, is obtained; it is a brownish-red crystalline precipitate. Under the microscope it has the appearance of long quadrangular plates. Yield 65% of theory. Loss in weight at 105°: 20.02%.

Found %: Co 13.39; 13.21; N 12.82

$Na[Co(DH)_2(OH)_2] \cdot 5H_2O$. Calculated %: Co 13.51; N 12.84; H_2O 20.65

The substance dried at 105° avidly absorbs water from the air.

Diaquo-bis-dimethylglyoximocobalt nitrate $[Co(H_2O)_2(DH)_2]NO_3$. The salt of the dihydroxo acid is dissolved in a minimal quantity of cold water. To the resulting solution, concentrated nitric acid is added dropwise with stirring until precipitation begins. On cooling, the amount of the latter increases. The substance is transferred to a glass filter and washed with absolute alcohol and ether. It dissolves very well in water. Yield 50% of theory.

Found %: Co 14.94; 15.06; N 18.06

$[Co(H_2O)_2(DH)_2]NO_3$. Calculated %: Co 15.23; N 18.08

On gentle heating of the diaquo nitrate with an excess of potassium rhodanide and acidification of the solution, diisothiocyanato-bis-dimethylglyoximocobaltic acid precipitates almost quantitatively. Heating with hydrohalic acids leads to green dihalogeno acids, for example $H[Co(DH)_2Cl_2]$.

Hydroxo-bis-dimethylglyoximoaquocobalt $[CoH_2O \cdot (DH)_2OH] \cdot H_2O$. Chloro-bis-dimethylglyoximoaquocobalt (8) is treated with a cold concentrated solution of potash or soda and stirred until it has completely changed from gray-green to light yellow. The substance is filtered through a glass filter and washed with a small amount of cold water, with alcohol, and finally with ether. Yield 55% of theory. Under the microscope the hydroxoaquo compound has the appearance of short quadrangular prisms. Readily soluble in water and alcohol.

Found %: Co 17.19; 17.28; N 16.58

$[CoH_2O(DH)_2(OH)] \cdot H_2O$. Calculated %: Co 17.22; N 16.36

Hydroxo-bis-dimethylglyoximoaquocobalt, on interaction with one equivalent of alkali, is converted into the dihydroxo compound, and on interaction with concentrated hydrochloric acid the dichloro acid is formed.

When chloro-bis-dimethylglyoximoaquocobalt is treated in the cold with alkali, the dihydroxo compound is formed, which after standing for some time precipitates in the crystalline state. This is a very convenient way of obtaining this compound.

Potassium nitrohydroxo-bis-dimethylglyoximocobaltiate $K[Co(DH)_2(OH)\cdot NO_2]\cdot H_2O$. Powdered nitro-bis-dimethylglyoximoaquocobalt is added to a concentrated solution of potassium carbonate and stirred until the brownish-red color of the solid phase has completely turned yellow. The substance is transferred to a filter and washed quickly with cold water, then with alcohol and ether. Yield 70% of theory. Under the microscope, potassium nitrohydroxo-bis-dimethylglyoximocobaltiate is a finely crystalline yellow powder.

On treatment with water, the nitroaquo compound is converted into nitro-bis-dimethylglyoximoaquocobalt, and on interaction with alkali the dihydroxo compound is formed.

For analysis, an air-dry substance was taken. Loss in weight at 105°: 4.88%.

$$\mathrm{K[Co(DH)_2(OH)NO_2]\cdot H_2O.}$$

Found, %: Co 14.37; 14.46; 14.33; N 17.46
Calculated, %: Co 14.40; N 17.11; H_2O 4.39

Sodium isorhodanohydroxo-bis-dimethylglyoximatocobaltate $Na[Co(DH)_2NCS(OH)]\cdot 3H_2O$. Isorhodano-bis-dimethylglyoximoaquocobalt is treated at room temperature with a 50% solution of caustic soda. On stirring, the isorhodanoaquo compound is completely converted into a chestnut-red crystalline substance, which is rapidly suction-filtered on a glass filter and washed with absolute alcohol and ether. Under the microscope it has the appearance of short quadrangular prisms. Yield: 60% of theory.

When treated with water, the isorhodanohydroxo compound is converted into yellow, finely crystalline isorhodano-bis-dimethylglyoximoaquocobalt.

On prolonged storage in air, isorhodanohydroxo-bis-dimethylglyoximocobalt, under the action of moisture and carbon dioxide, is likewise converted into the isorhodanoaquo compound.

For analysis, a substance dried between sheets of filter paper was taken.

$$\mathrm{Na[Co(C_4H_7N_2O_2)_2(OH)NCS]\cdot 3H_2O.}$$

Found, %: Co 13.20; 13.30; CNS 12.90; 12.85
Calculated, %: Co 13.35; CNS 13.16

On heating sodium isorhodanohydroxo-bis-dimethylglyoximocobaltate with a concentrated solution of caustic soda, sodium dihydroxo-bis-dimethylglyoximocobaltate is formed.

$$Na[Co(C_4H_7N_2O_2)_2(OH)_2] \cdot 5H_2O.$$

Found, %: Co 13.40; N 12.90
Calculated, %: Co 13.51; N 12.84

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

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