CHEMISTRY

A. V. ABLOV, M. P. FILIPPOV, and N. M. SAMUS’

1960

SovietRxiv

Fig. 1. Absorption curves.

Figure 1: Fig. 1. Absorption curves.

Abstract

Full Text

CHEMISTRY

A. V. ABLOV, M. P. FILIPPOV, and N. M. SAMUS’

ON THE EXISTENCE OF CIS- AND TRANS-DIAQUO-BIS-DIMETHYLGLYOXIMATOCOBALTIC SALTS

(Presented by Academician I. I. Chernyaev, 29 II 1960)

Complex compounds of trivalent cobalt with dimethylglyoxime of the types $[COA_2(DH)_2]X$ (a), $[CoA(DH)_2X]$ (b), and $H[Co(DH)_2(NO_2)_2]$ (c) were discovered by L. A. Chugaev (1–3).

Proceeding from I. I. Chernyaev’ s trans-influence regularity, in 1954 one of us (4) presented evidence that in the last compound the two nitro groups are in trans position to one another and that, consequently, the two dioxime residues lie in one plane. Further study confirmed this spatial configuration for various diacido-bis-dimethylglyoximatocobaltate ions (5–7). In (4) it was shown that cobalt dioximes—dinitro acid, nitroaquo compound, and chloronitro acid—retain their spatial configuration during chemical transformations. In 1955, Nakahara (8,9), independently, on the basis of an investigation of the i.r. spectra, showed that the dioxime residues in $H[Co(DH)_2Cl_2]$, $H[Co(DH)_2(NO_2)_2]$, and certain other cobalt dioximes of types (a), (b), and (c) are arranged in one plane.

Spectrophotometric study of the removal of a proton from cobalt dioximes clearly showed that dioximes of all three types (a, b, c) behave very similarly. In all cases studied, there is an increase in intensity and a shift of the 245–250 mμ band into the 250–260 mμ region and of the 300 mμ band into the 280 mμ region.

Fig. 1. Absorption curves. 1 $-[CoH_2O(DH)_2 \cdot OH] \cdot H_2O$; 2 $-[CoH_2O(DH)_2OH]\cdot H_2O$; 3 $-K[Co(DH)_2(OH)_2]\cdot 3H_2O$; 4 $-K[Co(DH)_2(OH)_2]\cdot 3H_2O$; 5 $-[Co(DH)_3] \cdot 3H_2O$ in $0.01\,N$ $HClO_4$; 6 $-[Co(DH)_3] \cdot 3H_2O$ in $0.01\,N$ KOH

In 1957, A. V. Ablov and N. M. Samus’ (10), by treating chloro-bis-dimethylglyoximatoaquocobalt with a concentrated solution of potassium carbonate in the cold, obtained the hydroxoaquo compound $[CoH_2O \cdot (DH)_2OH] \cdot$

Fig. 2. Absorption curves of hydroxo-bis-dimethylglyoximatocobaltate.

Figure 2: Fig. 2. Absorption curves of hydroxo-bis-dimethylglyoximatocobaltate.

H_2O. On heating the chloroaquo compound, as well as other acidoaquo compounds, with concentrated (50%) potassium hydroxide solution, potassium dihydroxo-bis-dimethylglyoximatocobaltate $K[Co(DH)_2(OH)_2] \cdot 3H_2O$ was isolated. By treating the latter with HNO_3, diaquo-bis-dimethylglyoximatocobalt nitrate $[Co(H_2O)_2(DH)_2]NO_3$ was obtained.

In the spectrophotometric study of these compounds we found that, contrary to expectations, the light-absorption curves of hydroxo-bis-dimethylglyoximatoaquocobalt and potassium dihydroxo-bis-dimethylglyoximatocobaltate, recorded in a sufficiently acidic medium ensuring their complete conversion to diaquo compounds, do not coincide with one another (Fig. 1). Two different light-absorption curves are also obtained when the spectra of these two compounds are recorded in a sufficiently alkaline medium, ensuring in both cases the presence only of dihydroxo anions.

The spectra were recorded on a nonrecording quartz spectrophotometer SF-4 at 15–17°. In all cases, when recording the spectra, $10^{-3}M$ aqueous solutions of the substances were used. Curves for which the time of action of alkali or acid is not indicated were recorded immediately after dissolution of the substance. The recording time did not exceed 20–25 min.

Fig. 2. Absorption curves of hydroxo-bis-dimethylglyoximatocobaltate.
1 —in $2 \cdot 10^{-3}$ N KOH, 2 —3 hours after dissolution in 0.04 N KOH, 3 —3 hours after dissolution in 0.2 N KOH, 4 —1 hour after heating in 3.2 N KOH on a water bath

The supposition that the dihydroxo salt obtained under very severe conditions (^{10}) is contaminated with decomposition products has to be rejected, since the spectra of this substance obtained in different syntheses coincide completely. The facts cited force one to assume the existence of two forms of the dihydroxo-bis-dimethylglyoximatocobaltate ion and, correspondingly, of two forms of the bis-dimethylglyoximatodiaquocobalt ion.

Absorption spectra at different pH values were recorded for the dihydroxo-bis-dimethylglyoximatocobaltate ion described in (^{10}) and for tris-dimethylglyoximatocobalt described by Nakahara (^{11}) (Fig. 1). The similarity of the curves of these two compounds is immediately striking, which leads to the conclusion that the three oxime residues in tris-dimethylglyoximatocobalt and the two oxime residues in the dihydroxo compound are arranged in a similar manner. This means that in the dihydroxo compound the two hydroxyl groups are in the *cis* position to one another. This, in turn, forces one to assume that under the working conditions described in paper (^{10}), i.e., on heating in a strongly alkaline medium, the trans-dioximines $[Co(DH)_2AB]^-$ pass into cis-dioximines $[Co(DH)_2(OH)_2]^-$. This conclusion was confirmed in a spectrophotometric study of the changes undergone by hydroxo-bis-dimethylglyoximatoaquocobalt in alkaline solution. To two portions of 0.05 mmol each of $[CoH_2O(DH)_2OH] \cdot H_2O$ in the solid state were added, respectively, 2 and 10 equiv. of potassium hydroxide dissolved in 5.5 ml of water. These concentrated solutions were diluted before recording the spectrum to 50 ml.

As is seen from the curves (Fig. 2), gradually at ordinary temperature, and rapidly on heating, the trans form passes into the cis form. However, on heating, partial decomposition of the product also occurs, as is evident from the rise of the long-wavelength branch of curve 4.

The results of the spectrophotometric study were confirmed by synthesis of salts of the cis and trans series. Earlier in (^{10}), bis-dimethylglyoximatodiaquocobalt nitrate $[Co(H_2O)_2(DH)_2]NO_3$, of red-brown color, was described; according to what has been set forth above, it must have a cis configuration.

The nitrate of the trans series, $[Co(H_2O)_2(DH)_2]NO_3 \cdot H_2O$, was obtained from hydroxo-bis-dimethylglyoximatoaquocobalt by dissolving it in the necessary amount of $2N$ HNO_3 and adding conc. HNO_3 dropwise to the resulting solution while cooling. The precipitate that separated, yellow-brown in color, was filtered off on a glass filter and washed several times with cold water, alcohol, and ether. Under the microscope the nitrate has the appearance of quadrangular prisms.

$$[Co(C_4H_7O_2N_2)_2(H_2O)_2]NO_3{\cdot}H_2O.$$

Found %: Co 14.31; 14.60; 14.48; N 17.19; 17.32
Calculated %: Co 14.54; N 17.28

In an analogous manner, the perchlorate of trans-bis-dimethylglyoximatodiaquocobalt, $[Co(H_2O)_2(DH)_2]ClO_4 \cdot 5H_2O$, was obtained; under the microscope it has the appearance of yellow, long, quadrangular plates.

$$[Co(C_4H_7O_2N_2)_2(H_2O)_2]ClO_4 \cdot 5H_2O.$$

Found %: Co 11.20; 11.46
Calculated %: Co 11.45

The absorption curves of the last two salts in an acid medium completely

Fig. 3. Diagrams of reflection angles and line intensities on Debyegrams of trivalent cobalt dioximes: 1 —cis-$[Co(H_2O)_2(DH)_2]NO_3$, 2 — trans-$[Co(H_2O)_2(DH)_2]NO_3 \cdot H_2O$

coincide with curve 1 (Fig. 1). Figure 3 gives Debyegrams of the nitrates of cis- and trans-bis-dimethylglyoximatodiaquocobalt.

Fig. 3. Diagrams of reflection angles and line intensities on Debyegrams of trivalent cobalt dioximes: 1 —cis-$[Co(H_2O)_2(DH)_2]NO_3$, 2 —trans-$[Co(H_2O)_2(DH)_2]NO_3 \cdot H_2O$

Figure 3: Fig. 3. Diagrams of reflection angles and line intensities on Debyegrams of trivalent cobalt dioximes: 1 —cis-$[Co(H_2O)_2(DH)_2]NO_3$, 2 —trans-$[Co(H_2O)_2(DH)_2]NO_3 \cdot H_2O$

Moldavian Branch of the Academy of Sciences of the USSR
Kishinev State University

Received
25 II 1960

CITED LITERATURE

1. L. A. Chugaev, ZhRKhO, **37**, 610 (1905); *Zs. anorg. Chem.*, **46**, 144 (1905).
2. L. A. Chugaev, *Studies in the Field of Complex Compounds*, Moscow, 1906.
3. L. A. Chugaev, *Ber.*, **41**, 2226 (1908); ZhRKhO, **41**, 1355 (1909).
4. A. V. Ablov, DAN, **97**, 1019 (1954).
5. A. V. Ablov, G. P. Syrtsova, ZhOKh, **25**, 1304 (1955).
6. A. V. Ablov, N. M. Samus' , M. S. Popov, DAN, **106**, 665 (1956).
7. A. V. Ablov, N. M. Samus' , ZhNKh, **4**, 1753 (1959).
8. A. Nakahara, *Bull. Chem. Soc. Japan*, **28**, 473 (1955).
9. A. Nakahara, J. Fujita, R. Tsuchida, *Bull. Chem. Soc. Japan*, **29**, 296 (1956).
10. A. V. Ablov, N. M. Samus' , DAN, **113**, 1265 (1957).
11. A. Nakahara, R. Tsuchida, *J. Am. Chem. Soc.*, **76**, 3103 (1954).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.