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THERMAL ANALYSIS OF COORDINATION COMPOUNDS OF COBALT(III) WITH α-DIOXIME AND GUANIDINE DERIVATIVES

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ABSTRACT

We studied the trans-dioximines of cobalt(III) of general formula $[CoX(Dioxim)_2GuR] \cdot nH_2O$, where Dioxim-are dimethylglioxime or α-benzyldioxime ions; X - Cl, Br, I, NCO, NCS, NCSe, NO_2; GuR - Guanidine (Gu), tetramethylguanidine (Tmgu), diphenylguanidine (Dfgu), cyanoguanidine (NC-Gu), phenylcyanoguanidine (PhNC-Gu). The thermal analysis of these compounds shows that first of all crystalizated water is eliminated. The thermolysis of complexes begins at 130-250° and proceeds stepwise.

INTRODUCTION

It is known that cobalt dioximines are analogies of vitamin B_{12}. Some dioximines are used as catalysts. The systematic thermic analysis of cobalt dioximines provides the information about the heat stability of complexes, the thermolysis mechanism, as well as about the influence of other ligands nature and method of coordination on the durability of complexes /1/.

MEASURING METHODS

The measurements were carried out with an OD-102 derivatograph system F. Paulik, J. Paulik, L. Erdey /2/ (Hungarian Optical Works, Budapest). 100 mg of powdered (diameter = 9 mm) over the temperature range 20 to 500° at a constant heating rate of 5 deg/min and the atmosphere was air or helium. Inert substance: Al_2O_3 (ignited).

Infrared spectra were recorded on an UR-20 instrument (Carl Zeiss, Jena, GDR) in the region 400-4000cm^{-1}. For recording we took a thint grinted paste of powder in vaseline oils as well as pellets in KBr.

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RESULTS AND DISCUSSION

The complexes of general formula $[CoX(DH)_2Gu] \cdot nH_2O$, where DH are dimethylglioxime ions, decompose mainly at the temperatures exceeding 200° (table 1)

Table 1. Characteristics of the thermic decomposition of complexes $[CoX(DH)_2Gu] \cdot nH_2O$

X	Dehydration			Decomposition of the dehydrated complexes			
	T°, C	mass loss,%		T°, C		mass loss,%	
		obtained	calculated	begining of the exoeffect	maximum of the exoeffect	obtained	calculated
Cl	-	-	-	200	260	45,0	45,39
Br	-	-	-	200	260	40,0	40,68
I	-	-	-	240	280	37,0	36,66
NCO	50-150	8,0	8,44	190	230	14,0	13,85
NCS	50-120	4,5	4,24	190	210	14,0	13,92
NCSe	30-100	7,5	7,35	170	250	12,0	12,07
NO_2	-	-	-	220	240	15,0	14,98

when X= Cl, Br, I the calculations were performed for Gu+DH and when X= NCO, NCS, NCSe, NO_2 the calculations were performed for Gu. The n values are respectively equal: 0, 0, 0, 2, 1, 2, 0.

The data obtained show that the nature of axial ligands has a sufficient influence on the complexes stability /3/. The thermic analysis of the complexes $[CoX(DH)_2Tmgu] \cdot nH_2O$ showed that for Cl-Br-I-line the temperature of the begining of decomposition increases by 60°. Such a strengthening of complexes is due to apparently increasing contribution of π-dative bond Co-halogen /4/. It was observed, that NCO and NO_2 groups also influence the thermic decomposition of the complexes. For $[CoX(DH)_2Dfgu] \cdot nH_2O$ it was determined that coordination effect and the nature of dioxime, influence on the stability of complex in general, an diphenylguanidine in particular /5/.

The temperature values of decomposition begining of the complexes $[CoX(DifH)_2Dfgu] \cdot nH_2O$ in helium atmosphere are close to those in aerial sorroundings. The difference is than in air at temperatures higher than 200°, thermolysis products interacts with oxygen while in helium, practically, only the destruction of complex takes place /6/.

On the whole it can be said that the temperature of decomposition begining of complexes depends on equatorial and axial organic ligands nature as well as on the nature of acid rests. For Cl-Br-I-line it was found a natural temperature change for begining of complexes decomposition, and in the case of other structural peculiarities it is observed a drop or increasing of the begining of complexes decomposition.

Cyanoguanidine $N{\equiv}C{-}NH{-}C({=}NH)NH_2$ has four nitrogen atoms with different electron surroundings. We obtained dimethylglioxime cobalt(III) complexes with cyanoguanidine in which NC-Gu carries out two ways of coordination: through nitrogen atom of $N{\equiv}C$ or $NH{=}C{=}$ radicals. The different ways of coordination of cyanoguanidine affect on the temperature value of the begining of complexes decomposition (Fig 1)

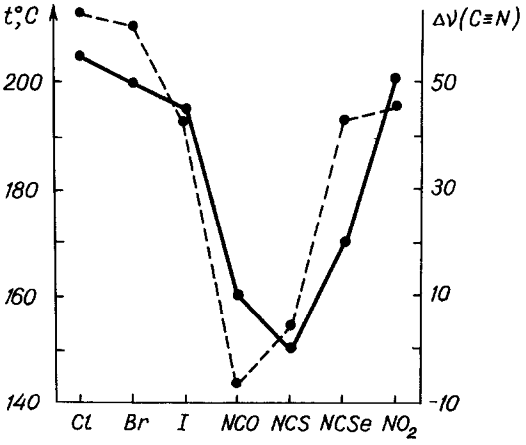

Figure 1. Correlation between the complexes $[CoX(DH)_2NC{-}Gu]$ thermic stability and the $\Delta\nu(C{\equiv}N)$ in the IR spectra of cyanoguanidine

For example, in case the NC-Gu bond with cobalt is carried out through $N{\equiv}C$-group (the complexes with Cl, Br, I, NO_2) the complexes stability is the highest (above 200°) (Fig. 1). In the case of coordination by means of $NH{=}C{=}$ group (complexes with groups NCO and NCS) the temperature of the begining of complexes decomposition is no more than $150\text{-}160^{\circ}$. The increasing of complexes stability of $Co \leftarrow N{\equiv}C$ bond if comparised with the complexes stability of $Co \leftarrow NH{=}C$ bond may be attributed to the contribution of back π -dative bond d-cobalt electrons π -orbitals cyanoguanidine and interaction of ligands on the X-Co-NC-Gu coordinate /7/.

The method of thermal analysis was used for identification of $[CoCl(DH)_2NC\text{-}Gu]$ bond isomers. The composition being identical with bond through $N{\equiv}C$-group decomposes at 205° , and isomer having cyanoguanidine bonded with central ion through $NH{=}C$ group nitrogen, decomposes at 170°.

CONCLUSIONS

It was established that the temperature of the begining of decomposition of complexes depends on the nature of equatorial and axial organic ligands as well as on the nature of acid rests.

It was found that the $\Delta\nu(C{\equiv}N)$ value is the qualitative characteristic of thermal stability of complexes.

The temperature of the begining of decomposition of bond isomers may be used for their identification.

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