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A. V. ABLOV and N. M. SAMUS'

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Abstract

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CHEMISTRY

A. V. ABLOV and N. M. SAMUS'

COMPLEX COMPOUNDS OF TRIVALENT COBALT CONTAINING THIOUREA

(Presented by Academician I. I. Chernyaev, 26 VI 1958)

Thiourea (thio) gives addition products with the salts of numerous metals ([1–3]).

In the chemistry of divalent platinum, N. S. Kurnakov' s reaction with this reagent is widely known; it makes it possible to decide unambiguously whether a compound of composition (PtA_2X_2) has a cis or trans structure ([4]).

Only a few, comparatively unstable compounds of divalent cobalt salts with thiourea are known ([5]). Compounds of trivalent cobalt containing this addend in the inner coordination sphere have not hitherto been described.

Continuing our investigations of complex compounds of trivalent cobalt with dimethylglyoxime, we succeeded in introducing thiourea into the inner coordination sphere. Study of the reactions of these compounds showed that, in the dioximes of trivalent cobalt, thiourea possesses an enhanced trans effect.

When chloro-bis-dimethylglyoximoaquocobalt is allowed to interact with an aqueous or alcoholic solution of thiourea, taken in a 1 : 1 ratio, even at room temperature there is formed in good yield a yellow-brown, finely crystalline substance, namely chloro-bis-dimethylglyoximothiocarbamidocobalt. The reaction proceeds according to the following equation:

$$[CoH_2O(DH)_2Cl] + CS(NH_2)_2 = [CoCS(NH_2)_2(DH)_2Cl] + H_2O.$$

The same substance can be obtained by the general method described by L. A. Chugaev ([6]), namely by oxidation with air of an alcoholic solution of cobalt chloride (1 mole), dimethylglyoxime (2 moles), and thiourea (1 mole). The reaction follows the overall equation:

$$4CoCl_2 + 4thio + 8DH_2 + O_2 = 4[Co(thio)(DH_2)Cl] + 4HCl + 2H_2O.$$

On slight heating with an aqueous or alcoholic solution of thiourea, chloro-bis-dimethylglyoximothiocarbamidocobalt passes into solution, from which crystals of chlorobis-dimethylglyoximodithiocarbamidocobalt chloride, $[Co(thio)_2(DH)_2]Cl \cdot 5H_2O$, precipitate.

The latter compound can be obtained by oxidation with air of an alcoholic solution of cobalt chloride (1 mole), dimethylglyoxime (2 moles), and thiourea (more than 2 moles). By the latter route other salts of composition $[Co(thio)_2(DH)_2]X$ were also obtained, where $X = Br, NO_3$. When introduced into water, these salts readily lose one molecule of thiourea and pass into a sparingly soluble compound of composition $[Co(thio)(DH)_2X]$. This reaction is reversible, and the precipitated compounds readily dissolve again in water upon addition of thiourea. Using this circumstance, salts of the complex cation $[Co(thio)_2(DH)_2]^+$ can be obtained by a double-exchange reaction. At the same time, when a salt of an alkali metal MeX is added to a solution containing the cation $[Co(thio)_2(DH)_2]^+$, neutral salts of composition $[Co(thio)(DH)_2X]$ precipitate in the pure state.

Attention is drawn to the unequal bonding of the two thiourea molecules in the complex $[Co(thio)_2(DH)_2]^+$. One molecule of thiourea is split off and reattached exceptionally easily—it is very labile. Undoubtedly, this reaction proceeds through formation of the aquo cation $[Co(H_2O)thio(DH)_2]^+$ according to the equation

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

The second thiourea molecule cannot be removed in neutral medium either by treatment with a large excess of the salt MeX (where $X = Cl, Br, NO_2, J, CNS$) or at elevated temperature.

As was shown by one of us, on the basis of I. I. Chernyaev' s regularity of the trans effect ([7]), in the dioximes of trivalent cobalt the two dimethylglyoxime residues are located in one plane ([8]). Consequently, in the complex cation $[Co(thio)_2(DH)_2]^+$ the two thiourea molecules are arranged in the trans position to one another. The facts presented receive their natural explanation if thiourea in the cobalt dioximes is assigned, in reactions proceeding in neutral medium, a trans effect greater than that of the acid residues Cl, Br, NO_2, J, and CNS.

Experimental Part

1. Chloro-bis-dimethylglyoximothiocarbamidecobalt $[Co(thio)(DH)_2Cl]$**. I.** To 3.4 g of chloro-bis-dimethylglyoximoaquocobalt $[CoH_2O(DH)_2Cl]$ ([9]) and 0.76 g of thiourea, approximately 100 ml of water are added. On stirring the mixture already at room temperature, and better with gentle heating, the brown-green chloroaquo compound changes into a yellow finely crystalline substance, which is filtered off and washed with water, alcohol, and ether. Yield 80% of theory. The compound obtained is very sparingly soluble in water, somewhat better in alcohol and ether. A solution of silver nitrate in the cold

does not cause precipitation of silver chloride; on heating, turbidity gradually appears. Under the microscope the crystals have the form of yellow prisms. An air-dried substance was taken for analysis.

Found, %: Co 14.52; 14.43; S 7.90

$[Co(CH_4N_2S)(C_4H_7N_2O_2)Cl]$. Calculated, %: Co 14.71; S 8.00

II. 11.7 g of dimethylglyoxime are dissolved with heating in 150 ml of alcohol. To the filtered hot solution are added 12.0 g of cobalt chloride, 3.8 g of thiourea, and a strong current of air is passed through for 3 hours. Yield 90% of theory.

Found, %: Co 14.41; Cl 8.87; 8.44; 8.60; S 8.28; 8.43; N 21.23; 20.91

$[Co(CH_4N_2S)(C_4H_7N_2O_2)_2Cl]$. Calculated, %: Co 14.71; Cl 8.85; S 8.00; N 20.98

2. Chloride of bis-dimethylglyoximodithiocarbamidecobalt $[Co(thio)_2(DH)_2]Cl \cdot 5H_2O$**. I.** 4.0 g of chloro-bis-dimethylglyoximothiocarbamidecobalt (1 mole) and 2.3 g (3 moles) of thiourea are heated on a water bath with 50 ml of water. In this process the sparingly soluble chloromonothiocarbamide compound readily passes into a dark-brown solution, from which, on cooling, cherry-brown long quadrangular prisms precipitate. The substance is filtered off, washed two or three times with an aqueous and then an alcoholic solution of thiourea. From the mother liquor, on evaporation in air, a new portion of the substance separates. In an aqueous solution of thiourea, $[Co(thio)_2(DH)_2]Cl \cdot 5H_2O$ dissolves readily. The water of crystallization is lost very easily, partly already on storage in air, completely—in a desiccator over phosphoric anhydride.

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* DH denotes the dimethylglyoxime residue

$$CH_3\text{-}C(=NOH)\text{-}C(=NO)\text{-}CH_3$$

II. Heating chloro-bis-dimethylglyoximoaquocobalt with an aqueous solution of thiourea, taken in an amount of 3–4 mol., can convert this substance first into the monothiocarbamide compound, which then passes into solution, from which well-formed long prisms gradually separate. An excess of thiourea does not hinder the reaction. The substance can be recrystallized from water to which a certain amount of thiourea has been added.

III. The substance can most conveniently, and in very good yield (up to 80% of theory), be obtained as follows: hot solutions of 12.0 g of cobalt chloride in 30 ml of ethyl alcohol and 11.7 g of dimethylglyoxime in 150 ml of alcohol are mixed. To the filtered mixture 8–9 g, i.e., slightly more than 2 mol., of thiourea are added, and air is passed through for 4 hours. Crystals of the dithiocarbamide complex gradually separate. To obtain larger crystals,

the mixture is heated on a water bath and slowly cooled. For analysis a freshly prepared substance, dried between sheets of filter paper, was taken.

Found, %:
I. Co 10.29; S 11.40
II. Co 10.40; S 11.25
III. Co 10.44; 10.30; Cl 6.38; S 11.65; N 19.66; loss over P_2O_5 16.16
$[Co(CH_4N_2S)_2(C_4H_7N_2O_2)_2]Cl \cdot 5H_2O$. Calculated, %: Co 10.39; Cl 6.25; S 11.30; N 19.76; H_2O 15.87

3. Bromide bis-dimethylglyoximodithiocarbamidecobalt $[Co(thio)_2(DH)_2]Br \cdot 2H_2O$**.**

The substance is obtained in the form of dark-brown prisms by method III, described for the preceding compound, with a yield of 75% of theory. The substance does not lose its water of crystallization over phosphorus anhydride. The latter can be removed only on heating to 105°.

Found, %: Co 10.47; 10.45; S 11.01; loss in weight at 105° 6.54
$[Co(CH_4N_2S)_2(C_4H_7N_2O_2)_2]Br \cdot 2H_2O$. Calculated, %: Co 10.57; S 10.96; H_2O 6.46

4. Nitrate bis-dimethylglyoximodithiocarbamidecobalt $[Co(thio)_2(DH)_2]NO_3 \cdot 2H_2O$**.**

Preparation analogous to the preceding. Yield 70% of theory.

Found, %: Co 10.71; 10.74; 10.81; S 14.51
$[Co(CH_4N_2S)(C_4H_7N_2O_2)_2]NO_3 \cdot 2H_2O$. Calculated, %: Co 10.93; S 14.93

5. Iodide bis-dimethylglyoximodithiocarbamidecobalt $[Co(thio)_2(DH)_2]J \cdot 2H_2O$**.**

This compound was obtained by a double-exchange reaction in the presence of an excess of thiourea.

3.0 g of nitrate bis-dimethylglyoximodithiocarbamidecobalt and 1.0 g of thiourea are dissolved with gentle heating in approximately 75 ml of water. To the still-warm solution 1 g of potassium iodide is added. Long prisms gradually separate; these are filtered off and washed with an aqueous and then with an alcoholic solution of thiourea.

Found, %: Co 9.64; 9.82; S 5.50
$[Co(CH_4N_2S)(C_4H_7N_2O_2)_2]J \cdot H_2O$. Calculated, %: Co 9.76; S 5.29

6. Bromo-bis-dimethylglyoximothiocarbamidecobalt $[Co(thio)(DH)_2Br]$**.**

3.0 g of nitrate bis-dimethylglyoximothiocarbamidecobalt and 1–2 g of potassium bromide are poured over with water. Gradually the nitrate passes into

a sparingly soluble dark-brown substance, which is transferred to a filter and washed repeatedly with water, alcohol, and ether. Under the microscope the substance has the appearance of dark-yellow elongated prisms.

Found, %: Co 13.14; Br 18.08; S 7.58
$Co(CH_4N_2S)(C_4H_7N_2O_2)_2Br$. Calculated, %: Co 13.24; Br 17.96; S 7.20

Analogously, other compounds of the type $[Co(thio)(DH)_2X]$ were also obtained.

7. **Nitro-bis-dimethylglyoximecarbamidocobalt** $[Co(thio)(DH)_2NO_2]$. A brick-yellow, finely crystalline precipitate, sparingly soluble in water and in organic solvents.

$$[Co(CH_4N_2S)(C_4H_7N_2O_2)_2NO_2].$$

Found, %: Co 14.29; 14.00; 14.08; S 8.13
Calculated, %: Co 14.33; S 7.79

8. **Thiocyanato-bis-dimethylglyoximothiocarbamidocobalt** $[Co(thio)(DH)_2NCS]$. Sparingly soluble in water, more readily in organic solvents. Under the microscope it has the appearance of light-brown prisms.

$$[Co(CH_4N_2S)(C_4H_7N_2O_2)_2NCS].$$

Found, %: Co 13.60; 13.74; S 15.73
Calculated, %: Co 13.92; S 15.14

9. **Iodo-bis-dimethylglyoximothiocarbamidocobalt** $[Co(thio)(DH)_2J]$. It is a dark-brown, finely crystalline substance. Practically insoluble in water. The action of an excess of potassium iodide on this substance, even on heating, causes no changes.

$$[Co(CH_4N_2S)(C_4H_7N_2O_2)_2J].$$

Found, %: Co 12.21; 11.98; J 25.93; 26.05; S 6.74
Calculated, %: Co 11.97; J 25.78; S 6.52.

Kishinev State University

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