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Abstract

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Dioximes of Trivalent Cobalt Containing a Selenocyanato Group

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A large number of complex compounds of trivalent cobalt with dimethylglyoxime, containing a thiocyanato group, are known, for example, $(\mathrm{CoPy(DH)_2(NCS)})^*$ (^{1}), $\mathrm{H(Co(DH)_2(NCS)_2)}$ (^{2}). Cobalt dioximes with thiourea have also been synthesized (^{3}).

X-ray structural studies have shown that thiourea and ethylenethiourea in addition products with salts of nickel (^{4}), cadmium (^{5,6}), and others are bonded to the metal atom through sulfur. There is no doubt that in cobalt dioximes containing thiourea, the bond is effected in the same way. In view of the considerable similarity in the behavior of cobalt dioximes that include thiourea in the inner sphere to dioximes containing a rhodano group, it may be assumed with a considerable degree of probability that in cobalt dioximes the thiocyanato group is also attached to the cobalt atom through sulfur.

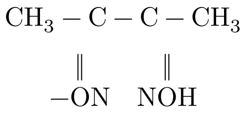
The selenocyanate ion is very similar to the thiocyanate ion. In particular, various complex selenocyanates are known (see, for example, ($^{7-9}$)). It was of interest to determine the possibility of introducing the selenocyanate ion into the inner sphere of cobalt dioximes.

A solution of potassium selenocyanate reacts very readily with trans-chloro-bis-dimethylglyoximatoaquocobalt (^{10,11}), forming small brownish-red crystals of potassium diselenocyanato-bis-dimethylglyoximatocobaltate, $\mathrm{K(Co(DH)_2(SeCN)_2)}$.

The ion $(\mathrm{Co(DH)_2(SeCN)_2})^-$ is very similar to the dirhodano-bis-dimethylglyoximatocobaltate ion (^{2}). Both give sparingly soluble colored salts with various metals. Aqueous solutions of both ions, upon a slight increase in pH, form precipitates of rhodano-, respectively selenocyanato-bis-dimethylglyoximatoaquocobalt. When one mole of an organic amine acts on an alcoholic-aqueous solution of the diselenocyanato-bis-dimethylglyoximatocobaltate ion, one selenocyanato group is likewise split off, with formation of compounds of the type $(\mathrm{CoAmine(DH)_2(SeCN)})$. A similar reaction is also shown by the dirhodano-bis-dimethylglyoximatocobaltate ion.

The thiocyanato and selenocyanato ions behave very similarly also toward nitro-bis-dimethylglyoximatoaquocobalt (^{12}). On heating nitro-bis-dimethylglyoximatoaquocobalt with potassium selenocyanate, taken in equimolecular ratios, the selenocyanatonitro-bis-dimethylglyoximatocobaltate ion $(Co(DH)_2(NO_2)(SeCN))^-$ is formed. Its formation was proved by precipitation as the salt $(CoPy_2(DH)_2)(Co(DH)_2(NO_2)(SeCN))$. Just as the rhodanonitro-bis-dimethylglyoximatocobaltate ion ([12]), the selenocyanato-bis-dimethylglyoximatocobaltate ion in a slightly alkaline medium splits off the nitro group and passes into a selenocyanato-aquo compound—

* DH is the residue of dimethylglyoxime,



$$CH_3-\underset{\underset{-ON}{\|}}{C}-\underset{\underset{NOH}{\|}}{C}-CH_3$$

This fact indicates that in cobalt dioximes the selenocyanato group, like the rhodano group, has a greater trans influence than the nitro group.

It should be especially noted that the diselenocyanato-bis-dimethylglyoximatocobaltiate ion is exceptionally stable toward acids. This is all the more interesting because the free selenocyanate ion is exceptionally unstable in the presence of hydrogen ions. This may serve as an indication that the selenocyanato group in dioximes is bound to cobalt through selenium.

It is known that selenourea, like thiourea, is prone to forming complexes with salts of heavy metals ([13,14]). We found that selenourea can also be introduced into the inner sphere of cobalt dioximes. Thus, on the action of selenourea on chloro-bis-dimethylglyoximato-aquocobalt, chloro-bis-dimethylglyoximatoselenocarbamidocobalt is obtained exceptionally readily.

Experimental Part

Potassium diselenocyanato-bis-dimethylglyoximatocobaltiate $K(Co(DH)_2(SeCN)_2)$. 1.7 g (5 mmol) of trans-chloro-bis-dimethylglyoximato-aquocobalt $CoH_2O(DH)_2Cl$* is poured over with 75 ml of hot 50% alcohol, and a solution of 1.44 g (10 mmol) of potassium selenocyanate in 25 ml of alcohol is added. On heating on a water bath for several minutes, the gray-green chloro-aquo compound changes into a reddish-brown crystalline mass, which is filtered off on a glass filter and washed with water, alcohol, and ether. Yield 60-70% of theory. Under the microscope the crystals have the form of yellow thin plates.

Found, %: Co 10.85; 10.97; Se 29.10;
Se 29.28 29.12

$K(Co(C_4H_7O_2N_2)_2(CNSe)_2)$. Calculated, %: Co 10.93;

Ammonium diselenocyanato-bis-dimethylglyoximatocobaltiate $NH_4(Co(DH)_2(SeCN)_2) \cdot 3H_2O$. 1.7 g of trans-chlorobisdimethylglyoximato-aquocobalt and 1.44 g of potassium selenocyanate are poured over with 75 ml of water, and the mixture is heated on a water bath for several minutes. The potassium diselenocyanatocobaltiate formed thereby dissolves. Ammonium chloride is added to the filtered solution. After some time a brown crystalline precipitate separates. The cold mixture is transferred to a glass filter, washed with cold water, then with alcohol and ether. Yield 70-80% of theory. Under the microscope the crystals have the form of rhombic prisms beveled at the bases. The salt dissolves in water. For analysis, the air-dry substance was taken.

Found, %: Co 10.33; 10.29; Se 27.52; N 17.04; loss in weight at 105° 9.8; 10.01
$NH_4(Co(C_4H_7O_2N_2)_2(CNSe)_2) \cdot 3H_2O$. Calculated, %: Co 10.31; Se 27.64; N 17.16
H_2O 9.46

A solution of this salt gives precipitates with various cations: Co^{2+} —a precipitate of dark-brown, almost black color; under the microscope —a finely crystalline powder. Ni —a brown crystalline precipitate; under the microscope the crystals have the form of quadrangular prisms. Cu^{2+} —a dark-brown crystalline precipitate. Cd —a finely crystalline brown precipitate. Fe^{2+} —a brown precipitate; under the microscope —triangular prisms. Fe^{3+} —a yellow crystalline precipitate; under the microscope they have the form of plates. Ca —a yellow-orange crystalline precipitate; under the microscope the crystals have the form of long yellow needles. Mg —orange long prisms.

* To obtain dioximes of trivalent cobalt containing the selenocyanate ion, the starting substances must not contain even traces of acids.

Diselenocyanato-bis-dimethylglyoximatocobaltic acid $H(Co(DH)_2(SeCN)_2)$. Potassium or ammonium diselenocyanato-bis-dimethylglyoximatocobaltate is dissolved in a small amount of hot water, filtered, and HCl is added. After some time a brown-red crystalline precipitate begins to separate from the solution. After cooling to room temperature, the precipitate is transferred onto a glass filter and washed with water, alcohol, and ether. Yield 70-80% of theory.

Diselenocyanato acid can also be obtained from 1,6-$(Co(H_2O) \cdot (DH)_2OH) \cdot H_2O$ (15) and potassium selenocyanate. For this purpose the reacting substances are taken exactly in a ratio of 1 : 2, heated for 15-20 min on a water bath with a small amount of water, and precipitated with HCl. Yield 80% of theory. Diselenocyanato-bis-dimethylglyoximatocobaltic acid is sparingly soluble in water, somewhat better in ethyl alcohol. Under the microscope the crystals have the form of brown-red prisms.

$H(Co(C_4H_7O_2N_2)_2(CNSe)_2)$.
Found, %: Co 11.60; 11.65; Se 31.30; N 16.78; 16.44
Calculated, %: Co 11.79; Se 31.57; N 16.67

Selenocyanato-bis-dimethylglyoximatoaquocobalt $(Co(H_2O)(DH)_2(SeCN)) \cdot H_2O$. To a solution of the ammonium salt of diselenocyanatobisdimethylglyoximatocobaltic acid or, more simply, to a solution obtained by the interaction of the hydroxo-aquo compound and potassium selenocyanate, taken in a ratio of 1 : 2, several drops of concentrated ammonia or alkali are added. On stirring, a pale-yellow microcrystalline precipitate immediately forms; it is washed on the filter several times with water, alcohol, and ether. Yield 90% of theory. The substance is sparingly soluble in water and organic solvents.

$(Co(H_2O)(C_4H_7O_2N_2)_2(CNSe)) \cdot H_2O$.
Found, %: Co 13.46; 13.58; 13.42; Se 18.15; 18.20
Calculated, %: Co 13.70; Se 18.35

Selenocyanato-bis-dimethylglyoximatopyridinecobalt $(CoPy(DH)_2SeCN)$. 0.85 g of the chloro-aquo compound $(Co(H_2O) \cdot (DH)_2Cl)$ and 0.72 g of potassium selenocyanate are heated on a water bath with 75 ml of 50% ethyl alcohol until complete dissolution. To the filtered solution, 0.2 ml (1 mole) of pyridine is added. A yellow crystalline precipitate, sparingly soluble in water, alcohol, and ether, immediately separates from the solution. Under the microscope the crystals have the form of long quadrangular prisms.

$Co(C_5H_5N)(C_4H_7O_2N_2)_2CNSe$.
Found, %: Co 12.46; 12.48; Se 16.55
Calculated, %: Co 12.46; Se 16.69

Selenocyanato-bis-dimethylglyoximatoanilinecobalt $Co(C_6H_5NH_2)(DH)_2SeCN$. To an alcohol-water solution of potassium diselenocyanato-bis-dimethylglyoximatocobaltate, obtained by the method described above, aniline (1 mole) is added. A fine-crystalline yellow precipitate forms; it is filtered off on a glass filter and thoroughly washed with water, alcohol, and ether. Yield 70% of theory.

$Co(C_6H_7N)(C_4H_7O_2N_2)_2CNSe$.
Found, %: Co 11.48; 11.52; N 17.30; 17.28
Calculated, %: Co 11.66; N 17.25

Action of pyridine on rhodano-bis-dimethylglyoximatocobaltic acid. When pyridine is added to an alcohol-water solution of a small amount of pyridine, a yellow fine-crystalline precipitate of rhodano-bis-dimethylglyoximatopyridinecobalt separates, with a yield of 80% of theory.

$CoC_5H_5N(C_4H_7O_2N_2)_2CNS$.
Found, %: Co 13.68; S 7.40; N 19.65
Calculated, %: Co 13.82; S 7.50; N 19.71

Selenocyanatonitro-bis-dimethylglyoximatocobaltate of bis-dimethylglyoximato-di-pyridinecobalt $(CoPy_2(DH)_2)(Co(DH)_2NO_2(SeCN))$. Mixed···

solutions of 1.75 g of nitro-bis-dimethylglyoximatoaquocobalt in 50 ml of alcohol and 0.77 g of potassium selenocyanate in 20 ml of alcohol, and the mixture is heated for 20 min on a water bath. To the filtered solution is added 2.5 g of nitric-acid bis-dimethylglyoximato-di-pyridinecobalt in 40 ml of water. After some time a yellow crystalline precipitate forms, which is filtered off on a glass filter and washed several times with water, alcohol, and ether. Yield 70% of theory.

Under the microscope the substance has the appearance of long yellow plates. It is sparingly soluble in water, somewhat better in alcohol.

$$(Co(C_5H_5N)_2(C_4H_7O_2N_2)_2)(Co(C_4H_7O_2N_2)_2CNSeNO_2).$$

Found, %: Co 13.15; Se 8.80; 13.04 9.00
Calculated, %: Co 13.29; Se 8.90

On adding to the alcoholic solution obtained by heating nitro-bis-dimethylglyoximatoaquocobalt and potassium selenocyanate, as described above, a few drops of dilute alkali or ammonia, a precipitate of selenocyanato-bis-dimethylglyoximatoaquocobalt $(CoH_2O(DH)_2SeCN) \cdot H_2O$ is formed.

Found, %: Co 13.62; Se 18.25
Calculated, %: Co 13.70; Se 18.55

Chloro-bis-dimethylglyoximato-selenocarbamidocobalt $Co(SeCN_2N_4)(DH)_2Cl$. 3.4 g of chloro-bis-dimethylglyoximatoaquocobalt and 1.23 g of selenourea are treated with 75 ml of water. Already at room temperature, on stirring, the gray-green chloro-aquo compound passes completely into a yellow-brown substance. To complete the reaction, the precipitate is heated for 15 min on a water bath, then filtered off on a glass filter and washed with water, alcohol, and ether. Yield 80% of theory.

Under the microscope the substance has the appearance of a yellow fine-crystalline powder.

$$CoCH_4N_2Se(C_4H_7O_2N_2)_2Cl.$$

Found, %: Co 13.06; 12.94; 13.15; 13.10; N 18.69; 18.72
Calculated, %: Co 13.17; N 18.76

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