Gluconic lactone was the only one of the derivatives of the sugars submitted to hydrogenolysis which did not react smoothly. A large amount of non-volatile tarry material was obtained. Noteworthy was the formation of ethylene glycol from this lactone as well as a relatively high yield of the 2-(4-hydroxytetrahydrofuryl)-methylcarbinol. The formation of this latter compound is not surprising since gluconic lactone contains the same ring structure as does the tetrahydrofuran derivative represented in Formula I.

Summary

Glucose, sorbitol, mannitol, sucrose, lactose, maltose, α-methyl-*d*-glucoside, pentacetylglucose and gluconic lactone in ethanol solution have been submitted to the action of hydrogen under 300 atmospheres at 250° in the presence of a copper–chromium oxide catalyst. All of the compounds under these conditions undergo a rapid hydrogenolysis to methanol, ethanol, propanediol-1,2 and three additional hydroxy compounds to which the following tentative formulas have been assigned, 2-(4-hydroxytetrahydrofuryl)-methylcarbinol, hexanetriol and hexanetetrol. No attempt is made to formulate the series of reactions involved in the formation of these products because, in our opinion, there is no conclusive evidence on the basis of which a choice may be made between several alternatives. However, the formation of each of the products is understandable in consideration of the behavior toward hydrogenolysis of simpler glycols, aldehydes and ketones which are being studied in this Laboratory.

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The Action of Carbon Monoxide on Iron and Cobalt Complexes of Cysteine

BY MAXWELL P. SCHUBERT

I. Introduction.—In continuation of studies of the iron and cobalt complexes of thiol acids, the reaction of carbon monoxide with these compounds has been taken up. Cremer[1] was the first to observe that solutions of ferrous and cobaltous complexes of cysteine absorb carbon monoxide and from a study of the maximum amount absorbed and the proportion of metal to cysteine under which this takes place, concluded that there must exist in solution the complexes $Fe(cysteine)_2(CO)_2$ and $Co(cysteine)_2(CO)$. The concern of the present paper is the actual isolation of the complexes which occur in solutions of ferrous and of cobaltous biscysteinate after they have absorbed carbon monoxide.

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[1] W. Cremer, *Biochem. Z.*, **206**, 228 (1929).

II. The Ferro Biscysteinate Dicarbonyl Complex.—A solution of potassium ferro biscysteinate, whose isolation has been described previously,[2] was made by mixing the components in the proportions of two moles of cysteine hydrochloride, one mole of ferrous salt and six moles of potassium hydroxide. This amount of alkali is just equivalent to the sum of the iron and acid. Such a solution made in an atmosphere of carbon monoxide absorbs two moles of the gas in two to four hours after which there is no further absorption. The data need not be given as they agree with those of Cremer. Even with double this proportion of alkali the total amount of carbon monoxide absorbed does not change though the rate of absorption is lower. This behavior differs markedly from that of the cobalto biscysteinate complex as will be shown later.

The complex can easily be prepared from its components provided oxygen be carefully excluded during its formation. For this purpose a special flask was constructed. A 250-cc. Erlenmeyer flask is fitted with a side arm having a glass stopcock. Into the neck of the flask is ground a glass stopper carrying a gas inlet tube also fitted with a glass stopcock and a small dropping funnel. In the flask are placed 3.9 g. of $FeSO_4\cdot(NH_4)_2SO_4\cdot 6H_2O$, 3.2 g. of cysteine hydrochloride and 20 cc. of water. The air is swept out with hydrogen freed of oxygen by passage over heated copper. The test described by Von Wartenberg,[3] the disappearance of the phosphorus halo, is used to show when oxygen has been removed. Then 8 cc. of 6.5 *M* potassium hydroxide is admitted through the dropping funnel and the orange color of the ferro biscysteinate complex appears. A stream of carbon monoxide, generated from formic and sulfuric acids and washed with alkaline pyrogallol, is passed through the flask while the mixture is shaken steadily for four hours. The color appears to deepen during this process. Ten cc. of concentrated hydrochloric acid is added, the mixture shaken and set on ice. Precautions against admission of oxygen are no longer necessary as the carbon monoxide complex is stable in air. The mixture rapidly becomes solid with masses of yellow needles. These are filtered off, washed with a little ice cold water and alcohol and dried in a desiccator over sulfuric acid at 1 mm. There is no tendency for carbon dioxide to dissociate in a vacuum as determined by analysis after leaving *in vacuo* for various periods of time.

Anal. Calcd. for $Fe(SCH_2CHNH_2COOH)_2\cdot 2CO\cdot H_2O$: Fe, 15.13; S, 17.29; N, 7.57; C, 25.94; H, 3.82. Found: Fe, 15.49; S, 17.28; N, 7.70; C, 26.15; H, 3.86.

The sodium salt can be prepared using sodium hydroxide in place of potassium hydroxide and of course omitting the addition of acid. On cooling in an ice-box overnight fine needles separate. After separating, washing and drying in a vacuum they show the following analysis.

Anal. Calcd. for $Fe(SCH_2CHNH_2COONa)_2\cdot 2CO\cdot 2H_2O$: Fe, 12.96; S, 14.81; Na, 10.65; C, 22.21; H, 3.27. Found: Fe, 13.32; S, 15.18; Na, 10.61; C, 22.08; H, 3.93.

These experiments were carried out in diffuse daylight and it made no apparent difference in the amount of carbon monoxide absorbed whether the contents of the flask were protected from such light or not. This need not contradict Cremer's observation that the complex dissociates carbon monoxide on illumination as no experiments were carried out under intense illumination. Both of these compounds are quite stable in air when dry, the free acid decomposes in solution, within a few days at ice temperature and within an hour on warming. This decomposition is simply a dissociation, the total carbon monoxide being liberated as such and the ferro biscysteinate complex breaking up to ferrous salt and cysteine. As for the structure of this complex there seems to be no reason at present for supposing it other than the same as potassium ferro biscysteinate[2] with two carbonyl groups held by coördinate links directly to the iron:

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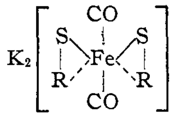
(2) Schubert, THIS JOURNAL, **54**, 4077 (1932).

(3) H. Von Wartenberg, *Z. Elektrochem.*, **36**, 295 (1930).



where R = —CH_2CHNH_2COO—

III. The Action of Carbon Monoxide on Potassium Cobalto Biscysteinate.—Measurements of the amount of carbon monoxide absorbed by potassium cobalto biscysteinate were made as described for the corresponding ferro complex. With the proportions of one mole of cobalt chloride, two of cysteine hydrochloride and six of potassium hydroxide the carbon monoxide absorbed amounted to about one mole in four hours after which there was no further absorption. The data for this are given in Table I, row 2, marked "equiv." But in these mixtures no complex at all analogous to the ferro biscysteinate dicarbonyl just described could be found. Two complexes of cobalt were, however, isolated, of which one contains only cysteine and the other only carbon and oxygen. The first, an oxidation product, is simply the green potassium cobalti triscysteinate, $K_3[Co(RS)_3]$ where R is the divalent radical (—CH_2CHNH_2COO—). The preparation of this complex from cobalt salt and cysteine has already been described.[4] The second complex could only be isolated as the silver and mercuric derivatives whose composition agrees reasonably with the formulas $Ag[Co(CO)_4]$ and $Hg[Co(CO)_4]_2$. In the flask described in the last section are placed 5 g. of cysteine hydrochloride and 15 cc. of 1 *M* cobalt chloride. After the air is completely displaced, 15 cc. of 6.3 *M* potassium hydroxide is added. Carbon monoxide is passed through while the mixture is shaken for four hours. At this point there always remains a small deposit of cobalt hydroxide.

To separate the green potassium cobalti triscysteinate and at the same time to show that its formation is not due to air oxidation occurring during its isolation, the stopcocks on the flask are closed and the whole flask set in the tank described previously[4] for the separation of complexes in the absence of air. After the air has been completely displaced from the tank by nitrogen and hydrogen, the flask is opened, 50 cc. of alcohol added to the contents and the mixture shaken. After an hour the mixture is filtered on a Buchner funnel, the solid dissolved in 40 to 50 cc. of water and reprecipitated with an equal volume of alcohol. After filtering, washing and drying in a vacuum, between 4 and 5 g. of product is obtained.

Anal. Calcd. for $K_3[Co(SR)_3]\cdot 3H_2O$: Co, 10.05; S, 16.35; N, 7.16; K, 19.93. Found: Co, 9.66; S, 16.02; N, 6.92; K, 20.41.

To show the presence of the second complex the following procedure was found best. To the mixture described above, after the absorption of carbon monoxide, there is added 100 cc. of acetone. After fifteen minutes the whole is filtered, and the filtrate quickly evaporated *in vacuo* to about 15 cc. To this is added a solution of a gram of mercuric chloride in 20 cc. of water and then after a few minutes 15 cc. of 6 *M* hydrochloric acid A yellow, more or less crystalline precipitate is obtained which is washed with dilute hydrochloric acid and then water. It can be recrystallized easily by dissolving in a small volume of acetone, filtering if necessary and then adding two volumes of water. The precipitate slowly crystallizes to yellow needles or rectangular yellow plates. It is dried *in vacuo* and protected from light; yield 0.5 g.

Anal. Calcd. for $Hg[Co(CO)_4]_2$: Hg, 37.00; Co, 21.78; C, 17.71; H, none. Found: Hg, 37.37, 37.52; Co, 21.16, 21.51; C, 17.38; H, 0.25.

This mercury salt is quite stable. It darkens when exposed to sunlight. It is very insoluble in water and non-oxidizing acids but dissolves readily in alcohol, ether, chloroform and acetone. It melts without apparent decomposition at 82°.

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[4] Schubert, THIS JOURNAL, **55**, 3336 (1933).

To separate the silver salt, the procedure given above for the isolation of the mercury salt is followed as far as the evaporation of the acetone *in vacuo*. To the clear solution remaining after this evaporation there is added 5 cc. of concentrated ammonium hydroxide and as much of a solution of 2 g. of silver nitrate in 10 cc. of water plus 5 cc. of concentrated ammonium hydroxide as is necessary to cause complete precipitation. The precipitate, at first liquid, crystallizes rapidly. This is filtered off, washed with dilute ammonia, then with water, and dried in a desiccator over concentrated sulfuric acid at 1 mm. The product is light yellow and consists of needle-like crystals. It is not very stable, especially in air or when exposed to light, turning first gray, then black within an hour after its separation from solution. For this reason the analyses here given were run on samples which had been left in the desiccator only ten minutes. The water is probably residual moisture and the formula is not to be understood as implying the existence of a hydrate.

Anal. Calcd. for $Ag[Co(CO)_4]\cdot{}^1/_2H_2O$: Ag, 37.45; Co, 20.48; C, 16.66; H, 0.35. Found: Ag, 36.32; Co, 20.20; C, 16.42; H, 0.2.

Another preparation was apparently wetter.

Anal. Calcd. for $Ag[Co(CO)_4]\cdot 2H_2O$: Ag, 34.21; Co, 18.74; C, 15.42; H, 1.27. Found: Ag, 32.42; Co, 19.26; C, 14.89; H, 1.29.

This silver salt can be recrystallized from acetone just like the mercury salt. Its solubilities are similar to those of the mercury salt but it has no melting point, merely turning black when heated to about 90°. The yield of silver salt after recrystallization is about 400 mg.

IV. The Action of Carbon Monoxide on Potassium Cobalti Triscysteinate.—If larger quantities of potassium hydroxide are used in the experiment described in the last section, the absorption of carbon monoxide does not reach an end-point even after twenty-four hours and the amount of carbon monoxide absorbed in this period increases with the amount of potassium hydroxide used, as shown in Table I. In casting about for a possible explanation of this remarkable phenomenon it was found that potassium cobalti triscysteinate, one of the products of the reaction described in the last section, will itself absorb large quantities of carbon monoxide when in strongly alkaline solution and that this absorption is much slower than that discussed in the previous section, requiring twenty-four to forty-eight hours to approach completion. Table II shows that with a sufficient amount of alkali, one mole of this cobalti triscysteinate will absorb as much as five to six moles of carbon monoxide. One of the products of this reaction is potassium carbonate which was separated as barium carbonate while the other product is the same new complex described above, $Hg[Co(CO)_4]_2$, again separated as silver and mercury derivatives. In this reaction as in the preceding there again appears an oxidation product, the carbonate which could only have come from the carbon monoxide used.

The volume of carbon monoxide consumed was measured in a 500-cc. suction flask connected to a calibrated gas reservoir provided with a leveling tube and an outlet. In the bottom of the flask were placed small beakers containing the components of the mixtures described in Tables I and II. After sealing the connections with paraffin, carbon monoxide is passed into the suction flask, out the side arm through the gas reservoir, finally escaping through the outlet of the latter. When all the air has been displaced the whole apparatus is closed off by stopcocks and set on a shaking machine in a room kept at 30 ± 0.2°. When the system has come to temperature equilibrium the volume of gas in the reservoir is read, the beakers in the flask upset, mixing the components, and the shaking machine started.

To carry out the reaction described in this section, 5 g. of potassium cobalti triscysteinate, prepared as described elsewhere,[4] and 15 cc. water are placed in the flask described in the preceding section. After air has been removed by carbon monoxide

TABLE I

Millimoles of carbon monoxide absorbed by a mixture of 3.2 g. (20 mml.) of cysteine hydrochloride, 9.6 cc. of 1 *M* $CoCl_2$ solution and the number of cc. of 6.3 *M* KOH solution shown in column 1. The total solution volume is made up to about 40 cc. with water. Temperature 30°. The mixtures were shaken mechanically for the time indicated

Cc. of 6.3 KOH *M*	Millimoles of CO absorbed after the indicated number of hours 1	2	4	8	24	32
7.1	4.2	5.5	6.1	6.9	7.5	..
9.5 (equiv.)	7.8	9.0	9.4	9.5	9.7	9.7
10.0	8.3	11.0	12.1	12.2	12.4	12.3
15	3.6	6.9	10.8	15.8	25.9	27.8
20	3.5	7.0	12.0	19.1	34.9	36.3
25	4.7	9.0	13.2	22.4	38.5	42.0
30	3.8	7.6	12.3	21.7	39.6	43.2

TABLE II

Millimoles of carbon monoxide absorbed by a solution of 1 g. of the green potassium cobalti triscysteinate in 10 cc. of water with the addition of the number of cc. of 6.3 *M* KOH shown in column 1. One gram of this complex is 1.7 millimoles. The mixtures were shaken mechanically for the time indicated. Temperature, 30°

6.3 *M* KOH, cc.	Millimoles of CO absorbed after the indicated number of hours 1	2	4	8	24	32
0	0	0	0	0	0	0
1	0.2	0.6	1.7	3.3	5.1	5.3
2	.2	.5	1.6	3.8	7.1	7.6
3	.4	1.0	2.8	5.0	7.6	8.1
4	.4	1.3	3.6	6.9	8.9	9.0

20 cc. of 6.3 *M* potassium hydroxide, freed of carbonate by saturation with barium hydroxide, is added. The flask is then connected to a calibrated reservoir of carbon monoxide under slightly more than atmospheric pressure and shaken for about forty hours. Forty-five millimoles of carbon monoxide are absorbed. The very dark green color of the solution disappears in this time, only a light brown clear solution remaining. To separate the carbonate formed this solution is diluted with some water and about 25 cc. 1 *M* barium chloride added. The precipitate is filtered off, washed and dried and can be shown by a few simple tests and by barium analysis to be practically pure barium carbonate. Three and one-tenth grams is obtained.

The silver and mercury salts of the complex $H[Co(CO)_4]$ can be separated by extraction of the solution resulting from the carbon monoxide absorption with three 80-cc. portions of acetone and treatment of this acetone extract as already described. Two grams of the silver salt or 1.7 g. of the mercury salt is recovered after purification by recrystallization from acetone by addition of water. The properties and analyses of these two salts agree completely with those resulting from the reaction described in the preceding section.

V. **The Formation of Cobalt Tetracarbonyl.**—If either of the reaction mixtures produced by the absorption of carbon monoxide as described in the last two sections be diluted with two volumes of water and then acidified with hydrochloric acid, some gas is liberated and an extremely choking odor is produced strongly suggestive of impure acetylene. At the same time a yellow precipitate of plate-like crystals forms, extremely insoluble in water, dilute acids or alkalies. These are filtered off, washed with much water and set in a vacuum desiccator. They are very unstable in a dry state, so, like the silver salt described above, they must be analyzed after only a few minutes drying. Like the silver salt, they fortunately dry very quickly. The analysis and properties of these crystals correspond to those of cobalt tetracarbonyl.

Anal. Calcd. for $Co(CO)_4 \cdot {}^1/_2H_2O$: Co, 32.79; C, 26.67; H, 0.56. Found: Co, 32.70, 32.38; C, 25.88, 26.07; H, 0.48, 0.52.

The water in the formula is probably simply a residue of moisture and is calculated in this way merely for convenience. The yellow crystals are very unstable in air, usually turning black within an hour after their separation in a dry condition. They are volatile and have been sublimed *in vacuo*. No melting point could be obtained as the crystals sinter and decompose at 48 to 50° even under nitrogen. They dissolve readily in alcohol, ether, chloroform and benzene and such solutions show a slow evolution of gas and soon deposit a black amorphous precipitate. The crystals even after long washing with water persist in emitting traces of the choking acetylenic odor mentioned above and it cannot be decided at present whether this is the odor of the crystals themselves or of a product of their decomposition.

If the mixture described in section III be used to prepare the carbonyl a yield of 200 to 250 mg. is obtained, while from the mixture described in section IV 700 mg. results. Made from the mixture of section IV the carbonyl is never as pure as when made from the mixture of section III. This may be due to the fact that the reaction of section IV requires forty hours in the presence of strong alkali so that some decomposition or secondary reaction occurs, making it impossible to obtain as pure a product as from the mixture of section III where the conditions are milder.

VI. The Reaction of Cobalt Tetracarbonyl with Cysteine.—A half gram of freshly prepared cobalt tetracarbonyl is added to a solution of 2 g. of cysteine hydrochloride in 15 cc. water, 6 cc. 6.3 *M* potassium hydroxide and 15 cc. alcohol. The alcohol must be added as the carbonyl is too insoluble in water for any reaction to occur. With this mixture the carbonyl slowly goes into solution and at the same time a gas is evolved; 2.2 millimoles of gas are evolved, all of which is absorbed by ammoniacal cuprous chloride. The solution itself slowly deposits the characteristic green crystals of potassium cobalti triscysteinate even when the whole reaction is conducted under nitrogen in the tank used for the preparation of oxygen-sensitive compounds. Under these conditions 0.33 g. of the green complex have been obtained after recrystallization from water by addition of alcohol. Finally there was separated by the method described in section III, between 0.4 and 0.5 g. of the compound $Hg[Co(CO)_4]_2$.

VII. Discussion of Results.—The mixture discussed in section III has been shown[4] to give rise to the following reaction in the absence of air: $CoCl_2 + 2HSRH \cdot HCl + 6KOH \longrightarrow K_2[Co(SR)_2] + 4KCl + 6H_2O$ where R has the meaning defined in section III. When carbon monoxide is passed through this solution, it is quite possible that the first reaction is the same as that described in section II for the corresponding iron complex where potassium ferro biscysteinate dicarbonyl is the product. But whereas the iron complex is stable in this ferrous state the cobalt in the analogous hypothetical complex, having a greater tendency to assume the trivalent condition, does so at the expense of reducing some other reactant. The equation for the total reaction can be written

$$9K_2[Co(SR)_2] + 8CO + 2H_2O \longrightarrow 6K_3[Co(SR)_3] + 2H[Co(CO)_4] + Co(OH)_2 \qquad (1)$$

The formation of carbonate in the reaction of section IV means that this is also an oxidation-reduction reaction. It can be represented thus

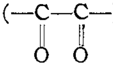
$$K_3[Co(SR)_3] + 6CO + 7KOH \longrightarrow H[Co(CO)_4] + 2K_2CO_3 + 3K_2(RS) + 3H_2O \qquad (2)$$

The assumptions and reasoning made use of for arriving at equations (1) and (2) cannot be given here for lack of space but a study of the data given in sections III and IV will show that all the products and only those demanded by these equations were actually found. Furthermore, the quantities of reactants and products will be found to be in fair agreement with these equations particularly considering that wherever possible products were purified by recrystallization.

No adequate formulation of the reaction described in section V can be given as it has been impossible so far to account for the hydrogen which it has been assumed occurs in the cobalt tetracarbonyl hydride. When this compound is, in part at least, converted to cobalt tetracarbonyl either free hydrogen or some reduction product, possibly of carbon monoxide, would be expected to result but none such could be found.

Finally, the following equation agrees very well both qualitatively and quantitatively with the products found for the reaction of section VI.

$$4Co(CO)_4 + 3H_2RS + 3KOH \longrightarrow 3H[Co(CO)_4] + K[Co(RS)_3] + 4CO + 3H_2O \quad (3)$$

Although equations (1), (2) and (3) seem to summarize correctly the experimental findings, there remains the ambiguity attaching to the unformulated constitution of $H[Co(CO)_4]$. An assumption that has been found useful as a working hypothesis in dealing with these unusual reactions is that in the formation of the new complex the carbon monoxide has been reduced to a divalent negative radical $(C_2O_2)^{=}$. The only two plausible structure which can be suggested for this radical are $(\text{—}OC{\equiv}CO\text{—})$ and  $(\text{—}\underset{\underset{O}{\|}}{C}\text{—}\underset{\underset{O}{\|}}{C}\text{—})$. The first has already been suggested by Reihlen[5] in his studies on iron carbonyls and their derivatives. The second has been suggested by Joannis,[6] who isolated the compound $K_2C_2O_2$ by the action of carbon monoxide on a liquid ammonia solution of potassium.

On this view the new complex would be a cobalti complex of a divalent pseudo acid radical, $H[Co(C_2O_2)_2]$ which in alkaline solution might exist as a potassium salt. This suggests the interpretation of the oxidation-reduction reactions (1) and (2). In fact if the essential part of (2) is written alone, we have: $3CO + 4(OH)^- \longrightarrow (C_2O_2)^{=} + CO_3^{=} + 2H_2O$. It thus resembles a Cannizzaro reaction on a free carbonyl group occurring appropriately in strong alkali.

Cobalt carbonyl has usually been regarded like most of the metal carbonyls as being a pure coördination compound, that is, as being composed of zero valent cobalt and coördinatively bound carbon monoxide. Reaction (3) which can be carried out completely in the absence of air and in which no stronger oxidant than water is present gives as products one complex, the cobalti triscysteinate, in which the cobalt is certainly trivalent and another in which it is probably trivalent. With this reaction in mind it seems difficult to regard the cobalt in the carbonyl as zero valent. The

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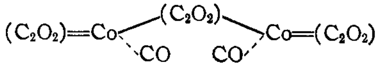
(5) Reihlen and co-workers, *Ann.*, **465**, 72 (1928); **472**, 268 (1929).

(6) M. A. Joannis, *Compt. rend.*, **116**, 1518 (1893); **158**, 874 (1914).

following structure involving trivalent cobalt would be much more in agreement with the experiments described here.



This formula in addition to accounting for reaction (3) would explain why cobalt tetracarbonyl is dimolecular and why it loses two moles of carbon monoxide rather easily to form cobalt tricarbonyl.

Hieber[7] describes a reaction of acid with tricarbonyl-*o*-phenanthroline cobalt among the products of which is cobalt tetracarbonyl and a carbonyl compound with hydrogen attached directly to the cobalt, $[Co(CO)_4H]$, as well as a volatile unstable cobalt compound with an evil odor. The cobalt carbonyl hydrogen compound, for whose existence Hieber defers giving any evidence, might be one assumed here from which the mercury and silver compounds are derived.

Hieber[8] has also described a reaction of $Fe(CO)_5$ in strong alkali which bears some resemblance to the reaction of section IV. He formulates it as: $Fe(CO)_5 + 2(OH)^- \longrightarrow [Fe(CO)_4H_2] + CO_3^{=}$. The hydrogen in the iron carbonyl hydride is regarded as being attached directly to the iron by a peculiar kind of bond.

Further study of these compounds would no doubt add to our knowledge of valence.

Mr. G. Bitterlich of this Laboratory carried out all the analytical work described here.

Summary

The complex ferro biscysteinate dicarbonyl has been crystallized as a free acid and as its sodium salt. The action of carbon monoxide on potassium cobalto biscysteinate has been shown to involve oxidation and reduction, the products being the green potassium cobalti triscysteinate and a new complex, isolated as the silver and mercury compound, apparently derived from $H[Co(CO)_4]$. The action of carbon monoxide on the green potassium cobalti triscysteinate in strong alkali also involves oxidation and reduction, the products being carbonate and the new complex $H[Co(CO)_4]$. The complex $H[Co(CO)_4]$, on treatment with acid, gives cobalt tetracarbonyl. Cobalt tetracarbonyl on treatment with cysteine and alkali gives potassium cobalti triscysteinate and $H[Co(CO)_4]$.

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(7) W. Hieber, F. Muhlbauer and E. A. Ehmann, *Ber.*, **65**, 1090 (1932).

(8) W. Hieber and F. Leutert, *Z. anorg. allgem. Chem.*, **204**, 155 (1932).