

PHOTOCHEMICAL DECOMPOSITION AND CARBON MONOXIDE INSERTION IN ORGANOMETALLIC COBALT CHELATES

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SUMMARY

From photoreaction of $\text{RCo}(\text{Salen}) \cdot \text{H}_2\text{O}$ [$\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$; $\text{Salen} = \text{bis}(\text{salicylaldehyde}) \text{ ethylenediiminato}$] with carbon monoxide in $\text{R}'\text{OH}$ as solvent ($\text{R}' = \text{CH}_3, \text{C}_2\text{H}_5, \text{iso-C}_3\text{H}_7$) and in the presence of oxygen $(\text{R}'\text{OCO})\text{Co}(\text{Salen}) \cdot \text{H}_2\text{O}$ is produced.

The reaction occurs in two steps, photoreaction of $\text{RCo}(\text{Salen}) \cdot \text{H}_2\text{O}$ giving $\text{R}'\text{OCO}(\text{Salen})$ being followed by a true insertion of carbon monoxide into the cobalt-oxygen bond. In anaerobic conditions, even in presence of carbon monoxide, only a homolytic cleavage of carbon-cobalt bond takes place giving $\text{Co}^{\text{II}}(\text{Salen})$.

When other planar chelate tetradentate systems are used in place of Salen the same kind of reaction occurs.

INTRODUCTION

Carbon monoxide insertion into metal-carbon bonds was first observed in $\text{CH}_3\text{Mn}(\text{CO})_5^1$, and has since been observed with several alkyl- or arylmetal carbonyls. Among cobalt compounds the reaction has been observed for $\text{RCo}(\text{CO})_4$, which gave the corresponding cobalt acyl derivative².

We have previously reported several remarkably stable alkyl- and acylcobalt complexes of the type $\text{RCo}(\text{Chel}) \cdot \text{L}$ and $\text{R}'\text{COCo}(\text{Chel}) \cdot \text{L}$ [$\text{Chel} = \text{bis}(\text{acetylacetonate}) \text{ ethylenediiminato dianion (BAE)}$ or $\text{bis}(\text{salicylaldehyde}) \text{ ethylenediiminato dianion (Salen)}$; $\text{R} = \text{alkyl, aryl}$; $\text{R}' = \text{alkyl}$; $\text{L} = \text{Lewis base}$]³, and have also investigated the reactions of carbon monoxide with $\text{RCo}(\text{Chel}) \cdot \text{L}$. Attempts to obtain the acyl derivatives by CO insertion into the Co-C bond in the dark at room temperature and atmospheric pressure were unsuccessful, but under action of light in $\text{R}'\text{OH}$ solution ($\text{R}' = \text{alkyl}$) we obtained instead the alkoxycarbonyl derivatives⁴.

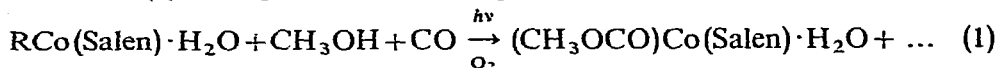
In the present paper the formation of $(\text{CH}_3\text{OCO})\text{Co}(\text{Salen}) \cdot \text{H}_2\text{O}$ starting from complexes of the type $\text{XCo}(\text{Salen}) \cdot \text{H}_2\text{O}$, $\text{RCo}(\text{Salen}) \cdot \text{H}_2\text{O}$, $\text{Co}^{\text{II}}(\text{Salen})$, $\text{NaCo}^{\text{I}}(\text{Salen})$ is studied to throw light on the reaction mechanism and on the nature of the common intermediate.

Extension of the scope of the carbon monoxide insertion, involving use of complexes of the type $\text{XCo}(\text{Salen}) \cdot \text{L}$, $[\text{Co}(\text{Salen})\text{L}_2]^+\text{X}^-$ ($\text{L} = \text{Lewis base}$; $\text{X} = \text{halogen}$), $\text{CH}_3\text{Co}(\text{BAE})$, and $\text{XCo}(\text{DH}_2)_2 \cdot \text{L}$ [$\text{DH}_2 = \text{bis}(\text{dimethylglyoximate}) \text{ dianion}$] is also reported.

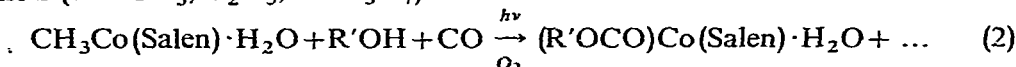
RESULTS

Alkoxy carbonyl derivatives from organometallic and Co^{III} complexes

When $\text{RCo}(\text{Salen}) \cdot \text{H}_2\text{O}$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{n-C}_3\text{H}_7, \text{n-C}_4\text{H}_9$) is irradiated with visible or UV light in methanol and in the presence of carbon monoxide/air mixture, reaction (1) takes place under atmospheric pressure and room temperature.



Other alkoxy carbonyl derivatives were obtained by using different solvent alcohols ($\text{R}' = \text{CH}_3, \text{C}_2\text{H}_5, \text{iso-C}_3\text{H}_7$):

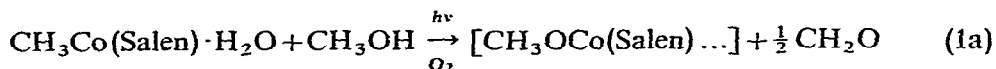


The $(\text{R}'\text{OCO})\text{Co}(\text{Salen}) \cdot \text{H}_2\text{O}$ complexes ($\text{R}' = \text{CH}_3, \text{C}_2\text{H}_5$) were identical to the products of the reactions of $\text{R}'\text{OCOC}\text{Cl}$ with $\text{NaCo}(\text{Salen})^{3c}$; $(\text{iso-C}_3\text{H}_7\text{OCO})\text{Co}(\text{Salen}) \cdot \text{H}_2\text{O}$ has not previously been reported.

The exactly parallel reaction takes place also starting from the pentacoordinate $\text{CH}_3\text{Co}(\text{BAE})$.

There was no evidence that reactions (1) or (2) occur in the dark even after a week.

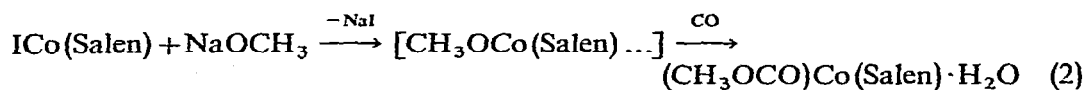
The reaction of $\text{CH}_3\text{Co}(\text{Salen}) \cdot \text{H}_2\text{O}$ in CH_3OH was chosen as a typical example and studied in more detail. Reaction (1) can be effected in two steps [(1a) and (1b)], only the first of which requires irradiation.



The solution (I), obtained by aerobic irradiation of $\text{CH}_3\text{Co}(\text{Salen}) \cdot \text{H}_2\text{O}$ reacts readily with CO even in the absence of oxygen and in the dark yielding the methoxycarbonyl derivative:



Solutions yielding $(\text{CH}_3\text{OCO})\text{Co}(\text{Salen}) \cdot \text{H}_2\text{O}$ by reaction with CO in the dark and in the absence of oxygen and showing the same visible spectrum as solution (I) are also obtained by treating $\text{ICo}(\text{Salen})^5$ with NaOCH_3 in CH_3OH .



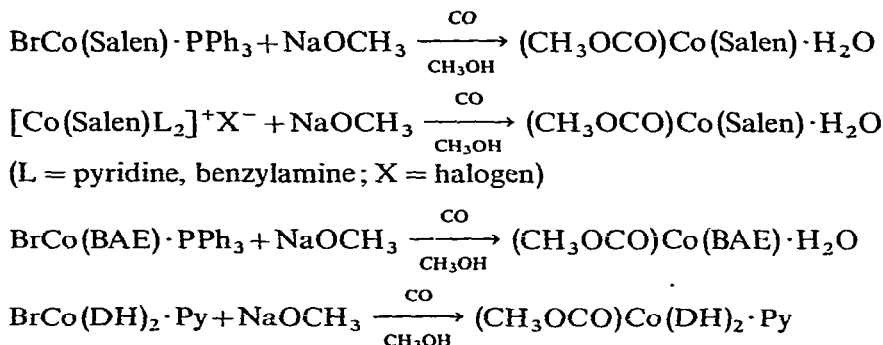
The methoxycobalt intermediate was not isolated, but the hydroxo complex $\text{HOCo}(\text{Salen}) \cdot \text{H}_2\text{O}$ was obtained from the irradiated solution as a dark brown solid. The same product was obtained also from the reaction of $\text{ICo}(\text{Salen})$ with NaOH in anaerobic conditions. The product is slightly soluble in water. The visible spectrum in methanol is identical with that of solution (I), while in water it shows a shift of 1 kK in the absorption maximum.

On the other hand, when $\text{HOCo}(\text{Salen}) \cdot \text{H}_2\text{O}$ is dissolved in CH_3OH and

treated with CO, even in anaerobic conditions, the $(\text{CH}_3\text{OCO})\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}$ is formed in quantitative yield.

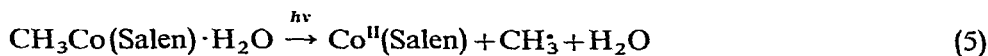
From the above evidence it is suggested that the very easily hydrolysable methoxycobalt intermediate is formed either by ligand exchange on Co^{III} complexes [from $\text{ICo}(\text{Salen})$ and $\text{HOCO}(\text{Salen})\cdot\text{H}_2\text{O}$ in CH_3OH] or by aerobic photolysis in CH_3OH from $\text{CH}_3\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}$.

The scope of the above reaction was extended by the preparation of the methoxycarbonyl derivatives from different cobalt complexes of Salen and even of other cobalt complexes containing a planar tetradentate conjugate chelating system as BAE and $(\text{DH})_2$.



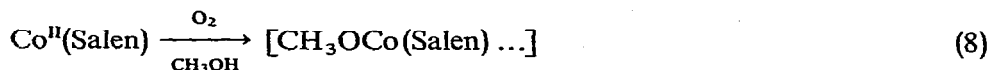
The photochemical reaction of $\text{CH}_3\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}$ in anaerobic conditions

Under helium the photochemical decomposition of the complex is much slower and parallels the homolytic thermal cleavage of the cobalt-carbon bond yielding $\text{Co}^{\text{II}}(\text{Salen})^3$. In CH_3OH solution the former reaction is accompanied by the formation of the stoichiometric amount of CH_2O from the CH_3^{\cdot} radical



In the absence or even with traces of oxygen the $\text{Co}^{\text{II}}(\text{Salen})$ is also the product of the photochemical decomposition of $\text{HOCO}(\text{Salen})\cdot\text{H}_2\text{O}$ or $\text{ICo}(\text{Salen})$ in CH_3OH . Under carbon monoxide atmosphere free from oxygen the product is still $\text{Co}^{\text{II}}(\text{Salen})$ and the CO insertion does not take place. This evidence confirms that the oxidation of Co^{II} to Co^{III} is required before the CO insertion.

When the oxidation of $\text{Co}^{\text{II}}(\text{Salen})$ is carried out at room temperature by atmospheric oxygen in methanol, the solution shows the same visible spectrum as that obtained from photochemical decomposition of $\text{CH}_3\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}$ in aerobic conditions:

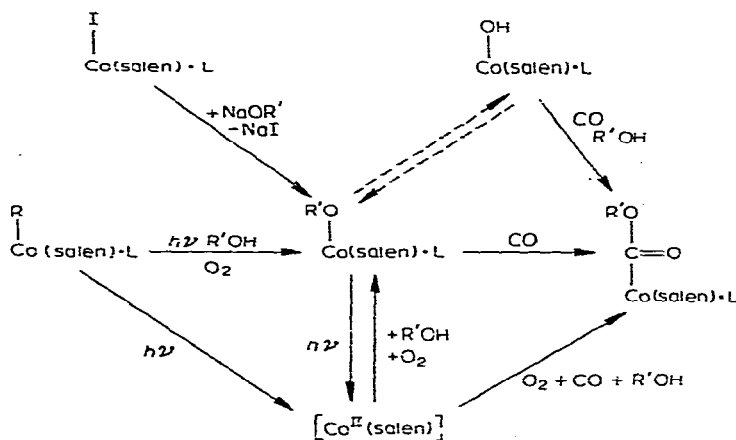


The oxidised solution reacts with carbon monoxide yielding $(\text{CH}_3\text{OCO})\text{Co}(\text{Salen})$ [reaction (1a)].

The scope of this reaction was also extended including other Co^{II} chelates of the type $\text{Co}^{\text{II}}(\text{Chel})$ [$\text{Chel} = \text{BAE}$, Salen , bis(*o*-hydroxyacetophenone) ethylenediiminato, bis(salicylaldehyde) bis(3,3'-diiminatopropyl)amine and bis(salicylaldehyde)-*o*-phenylenediiminato].

DISCUSSION

All the above reactions are set out in Scheme 1.



The photochemical homolytic cleavage of the cobalt-carbon bond takes place in the absence or in the presence of traces of oxygen. The formation of $\text{CH}_3\text{O}^\bullet$ [reaction (7)] involves hydrogen abstraction by the CH_3 radical from the OH group of the alcohol [reaction (6)] instead of the abstraction from the CH_3 -group which should yield the $\cdot\text{CH}_2\text{OH}$ radical and ethylene glycol. The former process could be understood if the abstraction takes place from an oriented methanol molecule within the coordination sphere of the cobalt atom. The same mechanism was proposed for the thermal decomposition of solid CuCH_3 in CH_3OH ⁶.

The enhanced photochemical cleavage in the presence of traces of O_2 could be attributed to the interaction of the oxygen molecule as a radical acceptor in the homolytic bond breaking step yielding $\text{CH}_3\text{OO}^\bullet$ species and $\text{Co}^{\text{II}}(\text{Salen})$. The formation of alkyl peroxide radicals has already been proposed in the aerobic photolysis of alkylcobalamins⁷.

At higher oxygen concentrations probably all of the methyl radicals are abstracted as methyl peroxide while the $\text{Co}^{\text{II}}(\text{Salen})$ is irreversibly oxidized by oxygen to the hydroxo or methoxo derivatives. Oxygen adducts of $\text{Co}^{\text{II}}(\text{Salen})$ might be the reactive intermediate in this oxidation process, although there is no proof of the existence of such adducts in alcohols. Alternatively the accelerating effect of oxygen on photolysis might be explained through an interaction of alkyl and cobaltous radicals (formed by photolysis) with the biradicalic oxygen molecules. If the low photolysis rate in anaerobic conditions is due to recombination of alkyl and $\text{Co}^{\text{II}}(\text{Salen})$ radicals, the interaction with oxygen molecule may prevent the recombination.

As far as carbon monoxide insertion is concerned, this molecule cannot be inserted into the cobalt-carbon bond in our $\text{RCo}(\text{Chel})\cdot\text{L}$, while a true carbonyl

insertion into the cobalt-oxygen bond takes place when $\text{ROCo}(\text{Chel})\cdot\text{L}$ is reacted with CO to give $(\text{ROCO})\text{Co}(\text{Chel})\cdot\text{L}$. This type of reaction has been previously proposed to explain the formation of tert-butoxycarbonyl cobalt derivative from $\text{NaCo}(\text{CO})_4$ and $(\text{CH}_3)_3\text{COCl}$ in presence of CO⁸. This reaction is probably a true insertion, but a direct attack of a coordinated carbonyl group on the oxygen cannot be excluded. In our case the latter mechanism can be ruled out considering that the methoxy carbonyl derivative is obtained also from the methoxycobalt bis(salicylaldehyde) *o*-phenylenediiminato chelate where, owing to the rigidity of the planar ligand, the coordination of the CO group in a *cis*-position to the CH_3O group is prevented.

EXPERIMENTAL

Photochemical reaction of $\text{RCo}(\text{Salen})\cdot\text{H}_2\text{O}$ with CO in $\text{R}'\text{OH}$ (aerobic)

In a typical reaction, $\text{CH}_3\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}$ (500 mg) is dissolved in CH_3OH (200 ml), saturated with CO and irradiated under CO at atmospheric pressure and room temperature with a high pressure, Osram 500 W mercury lamp for about 30 h. The solution is concentrated under vacuum and 100 ml H_2O are added. The precipitated orange-yellow solid is recrystallized from methanol/water. (Found: C, 53.62; H, 4.89; N, 7.10. $\text{C}_{18}\text{H}_{19}\text{CoN}_2\text{O}_5$ calcd.: C, 53.74; H, 4.76; N, 6.96%.) The IR spectrum is identical to that of the product of the reaction of $\text{CH}_3\text{OCOC}\text{Cl}$ with $\text{NaCo}(\text{Salen})^{3c}$.

The same product is obtained by the above photochemical reaction starting from $\text{C}_2\text{H}_5\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}$, *n*- $\text{C}_3\text{H}_7\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}$ and *n*- $\text{C}_4\text{H}_9\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}$.

The same procedure was employed starting from $\text{CH}_3\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}$ but using $\text{C}_2\text{H}_5\text{OH}$ and *iso*- $\text{C}_3\text{H}_7\text{OH}$ as solvents. In the former solvent the product is $(\text{C}_2\text{H}_5\text{OCO})\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}$ (Found: C, 55.00; H, 5.21; N, 6.83. $\text{C}_{19}\text{H}_{21}\text{CoN}_2\text{O}_5$ calcd.: C, 54.81; H, 5.08; N, 6.73%.) The IR spectrum is identical to that of the product of the reaction of $\text{C}_2\text{H}_5\text{OCOC}\text{Cl}$ with $\text{NaCo}(\text{Salen})^{3c}$. When *iso*- $\text{C}_3\text{H}_7\text{OH}$ is used as solvent, the product is $(\text{iso-C}_3\text{H}_7\text{OCO})\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}$ (Found: C, 56.26; H, 5.61; N, 6.64. $\text{C}_{20}\text{H}_{23}\text{CoN}_2\text{O}_5$ calcd.: C, 55.82; H, 5.39; N, 6.51%.)

Photolysis of $\text{CH}_3\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}$ in CH_3OH (aerobic)

$\text{CH}_3\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}$ (40 mg) dissolved in CH_3OH (50 ml) was photolysed as before for 90 min in the presence of air yielding solution (I). CH_2O was determined by the chromatropic acid method⁹. Found: CH_2O (2.4 mg). Molar ratio $\text{CH}_2\text{O}/\text{CH}_3\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}=0.7$. CH_2O (0.5 mg) was found after photolysis of 50 ml CH_3OH in the same conditions.

Reaction of solution (I) with CO

Carbon monoxide is bubbled briefly (20 sec) through solution (I) obtained as above. The colour changes from brownish-yellow to deep orange. The solution is concentrated under vacuum. After addition of water the precipitated solid is recrystallized from water/methanol: $(\text{CH}_3\text{OCO})\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}$ (IR spectrum).

Reaction of $\text{ICo}(\text{Salen})$ with NaOCH_3

$\text{ICo}(\text{Salen})^5$ (100 mg) is suspended in anhydrous disaerated CH_3OH (80 ml) and

treated with NaOCH_3 in CH_3OH under He to give a brownish-yellow solution. Carbon monoxide is bubbled through the solution (20 sec) and $(\text{CH}_3\text{OCO})\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}$ is isolated as above.

$\text{HOCo}(\text{Salen})\cdot\text{H}_2\text{O}$ from solution (I)

Solution (I) obtained as above from $\text{CH}_3\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}$ (40 mg) was concentrated under vacuum at room temperature. The dark brown solid was recrystallized from water and identified as $\text{HOCo}(\text{Salen})\cdot\text{H}_2\text{O}$ by IR spectrum comparison with an authentic sample.

Oxidation of $\text{Co}^{\text{II}}(\text{Salen})$ in CH_3OH

$\text{Co}^{\text{II}}(\text{Salen})$ (100 mg) was oxydized in CH_3OH (100 ml) by a stream of air. The visible spectrum of the solution was identical to that of solution (I). From the solution $\text{HOCo}(\text{Salen})\cdot\text{H}_2\text{O}$ was recovered and recrystallized from water. (Found: C, 52.83; H, 4.75; N, 7.85. $\text{C}_{16}\text{H}_{17}\text{CoN}_2\text{O}_4$ calcd.: C, 53.03; H, 4.75; N, 7.76%.)

The presence of OH ligand was confirmed also by the OH absorption band at 3550 cm^{-1} .

$\text{HOCo}(\text{Salen})\cdot\text{H}_2\text{O}$ from $\text{ICo}(\text{Salen})$

$\text{ICo}(\text{Salen})$ (128 mg) suspended in CH_3OH (80 ml) under He were treated with the stoichiometric amount of aqueous KOH (2 ml). From the solution $\text{HOCo}(\text{Salen})\cdot\text{H}_2\text{O}$ was isolated as above, and identified by the IR spectrum.

Reaction of $\text{HOCo}(\text{Salen})\cdot\text{H}_2\text{O}$ with CO in CH_3OH

$\text{HOCo}(\text{Salen})\cdot\text{H}_2\text{O}$ (80 mg) was dissolved under He in disaerated methanol and reacted with CO for 3 h. From the concentrated (under vacuum) solution orange crystals were precipitated by addition of disaerated water. Recrystallized from methanol/water. The IR spectrum was identical to that of $(\text{CH}_3\text{OCO})\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}$.

Photochemical reaction of $\text{CH}_3\text{Co}(\text{BAE})$ with CO in CH_3OH

By the above method $(\text{CH}_3\text{OCO})\text{Co}(\text{BAE})\cdot\text{H}_2\text{O}$ was obtained. Recrystallized from acetone/water. (Found: C, 46.54; H, 6.51; N, 7.78. $\text{C}_{14}\text{H}_{23}\text{CoN}_2\text{O}_5$ calcd.: C, 46.93; H, 6.47; N, 7.81%.)

$(\text{CH}_3\text{OCO})\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}$ from the reaction of $\text{XCo}(\text{Salen})\cdot\text{L}$ and $[\text{Co}(\text{Salen})\cdot\text{L}_2]^+\text{X}^-$ with NaOCH_3 in the presence of CO

$\text{BrCo}(\text{Salen})\cdot\text{PPh}_3$ (600 mg) is suspended in anhydrous methanol (50 ml) and treated in the dark with the stoichiometric amount of NaOCH_3 in CH_3OH . Carbon monoxide is then bubbled through the brownish-green solution until it becomes orange-yellow (10–15 min). After addition of water the solution is concentrated under vacuum and $(\text{CH}_3\text{OCO})\text{Co}(\text{Salen})\cdot\text{H}_2\text{O}$ is isolated, recrystallized from methanol/water, and identified by the IR spectrum.

The same product is obtained also starting from $[\text{Co}(\text{Salen})\cdot\text{L}_2]^+\text{X}^-$ (L = pyridine, benzylamine; X = halogen).

$(\text{CH}_3\text{OCO})\text{Co}(\text{BAE})\cdot\text{H}_2\text{O}$ from the reaction of $\text{BrCo}(\text{BAE})_2\cdot\text{PPh}_3$

By the above procedure $(\text{CH}_3\text{OCO})\text{Co}(\text{BAE})\cdot\text{H}_2\text{O}$ is obtained, and identi-

fied by comparison of IR spectrum with that of an authentic sample.

(CH₃OCO)Co(DH)₂·Py from the reaction of BrCo(DH)₂·Py

BrCo(DH)₂·Py (500 mg) was suspended in anhydrous methanol (100 ml) and treated as before with stoichiometric amount of NaOCH₃ in CH₃OH. The solution is saturated with CO and allowed to react for 48 h. After addition of H₂O (10 ml) the solution is concentrated under vacuum. The precipitated yellow solid is recrystallized from petroleum ether/pyridine: (CH₃OCO)Co(DH)₂·Py. (Found: C, 42.43; H, 5.19; N, 16.3. C₁₅H₂₂CoN₅O₆ calcd.: C, 42.16; H, 5.19; N, 16.4%.)

Photochemical decomposition of CH₃Co(Salen)·H₂O in anaerobic conditions

CH₃Co(Salen)·H₂O (63 mg) is dissolved under He in deaerated CH₃OH (80 ml). The solution is photolyzed during 80 h in a closed water jacketed pyrex vessel by an Osram 500 W high pressure mercury lamp. Methane was determined by gas chromatography and IR spectrum. Formaldehyde was determined in the photolyzed solution by chromotropic acid reaction⁴. Mole ratio CH₂O/CH₃Co(Salen)·H₂O=0.54. From the concentrated solution Co^{II}(Salen) was recovered and identified by IR spectrum.

Photolysis of HCo(Salen)·H₂O and ICo(Salen) in anaerobic conditions

1.5 mg of either material were photolyzed in deaerated CH₃OH (50 ml) under He. After 12 h both solutions show the visible spectrum of Co^{II}(Salen).

Photolysis of CH₃Co(Salen)·H₂O under CO, free from oxygen

CH₃Co(Salen)·H₂O (50 mg) were irradiated as above in accurately deaerated CH₃OH under carbon monoxide for 80 h. The solvent was removed under vacuum. The solid product is a mixture of Co^{II}(Salen) and CH₃Co(Salen)·H₂O without any appreciable amount of methoxy carbonyl derivative as ascertained by the IR spectrum [no trace of absorption at $\nu(\text{CO}) = 1673 \text{ cm}^{-1}$].

Reaction of Co^{II}(Chel) with CO in the presence of air in CH₃OH

Chel=BAE, Salen, bis(*o*-hydroxyacetophenone) ethylenediiminato⁸, bis(salicylaldehyde) bis(3-iminatopropyl)amine⁸, and bis(salicylaldehyde) *o*-phenylenediiminato.

As a typical example Co^{II}(Salen) (1 g) is suspended in CH₃OH (100 ml) and a 50% mixture of CO and air is bubbled through the suspension. After 4 h the original solid is completely dissolved and (CH₃OCO)Co(Salen) is precipitated. Recrystallized from methanol/water.

(Methoxycarbonyl)[bis(*o*-hydroxyacetophenone)ethylenediiminato]cobalt·H₂O. (Found: C, 56.35; H, 5.25; N, 6.45. C₂₀H₂₃CoN₂O₅ calcd.: C, 55.82; H, 5.39; N, 6.51%.) (Methoxycarbonyl)[bis(salicylaldehyde) bis(3-iminatopropyl)amine]-cobalt. (Found: C, 57.92; H, 5.69; N, 9.55. C₂₂H₂₅CoN₃O₄ calcd.: C, 58.02; H, 5.76; N, 9.23%.) (Methoxycarbonyl)[bis(salicylaldehyde) *o*-phenylenediiminato]cobalt·H₂O. (Found: C, 58.84; H, 4.27; N, 5.96. C₂₂H₁₉CoN₂O₅ calcd.: C, 58.67; H, 4.25; N, 6.22%.)

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