

# Investigation of the reaction of cobalt(II) bromide with nitrogen containing compounds in acetic acid

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The reactions of cobalt(II) bromide with nitrogen containing compounds in acetic acid were examined at 20, 60, and 90°C by means of the conductivity and spectroscopic measurements. In the reactions of  $\text{CoBr}_2$  with pyridine, *N,N*-diethylaniline or *n*-hexylamine the conductivity minimum was observed at equimolar concentrations, whilst with ethylenediamine, hexamethylenediamine, and (—)-lysine at a 2 : 1 molar ratio of  $\text{CoBr}_2$  to amine. In both cases the minimum was due to the formation of little soluble ion complexes  $[\text{CoBr}_4]^{2-}$  with the nitrogen containing compounds. Triethanolamine and aminoacetic acid reacted with cobalt(II) bromide in a 2 : 1 ratio yielding predominantly ammonium bromide salts. *N*-Acetylated amines, anthranilic acid, *p*-nitroaniline, and diphenylamine failed to react with cobalt(II) bromide in the investigated temperature range.

С помощью электропроводности и спектральных измерений изучалась реакция бромида двухвалентного кобальта с азотсодержащими соединениями в уксусной кислоте при температуре 20, 60 и 90°C. Минимум электропроводности в реакции  $\text{CoBr}_2$  с пиридином, *N,N*-диэтиланилином или с *n*-гексиламином наблюдался при эквимолярных концентрациях. В случае реакции  $\text{CoBr}_2$  с этилендиамином, гексаметилендиамином и (—)-лисином минимум электропроводности наблюдался при молярном соотношении этих веществ к  $\text{CoBr}_2$  1 : 2. В обоих случаях минимум был вызван возникновением мало растворимых ионных комплексов  $[\text{CoBr}_4]^{2-}$  с соответствующим азотсодержащим соединением. Триэтаноламин и аминокислота с бромидом двухвалентного кобальта взаимодействовали при соотношении 2 : 1 и в результате реакции образовывались в основном аммонийбромидные соли. В интервале изучаемых температур с бромидом двухвалентного кобальта не взаимодействовали *N*-ацетилированные амины, антранильная кислота, *n*-нитроанилин и дифениламин.

Salts of many transition metals soluble in the reaction medium were reported to be very effective oxidation catalysts [1, 2]. Not only their structures, stability, and other characteristic features have been studied, but attention has also been paid to their catalytical properties [3—7]. Less frequent were papers dealing with

the correlation between the catalytic activity and both composition and structure of the metal complexes involved. Such relations enable one to understand the mechanism of the catalyzed reaction and reveal the function of the catalyst in more detail. Therefore, our attention has been paid to the possibility to influence the activity of a homogeneous catalyst by the coordination of the appropriate ligands when studying the oxidation of alkylaromatic hydrocarbons to the respective aromatic carboxylic acids.

As found, cobalt(II) compounds form complexes with nitrogen containing bases in the presence of bromides at certain molar ratios; these complexes display a high catalytic activity and selectivity during oxidation of hydrocarbons [8].

According to *Proll* and *Sutcliffe* [4] solution of cobalt(II) bromide or chloride in acetic acid contains, in addition to neutral forms  $\text{CoX}_2$ , also ions  $\text{CoX}^+$ ,  $\text{CoX}_3^-$ , and  $\text{CoX}_4^{2-}$  ( $\text{X}$  = halogenide). The negatively charged ions prevail in an excess of halide anions. Nitrogen containing bases were either dissolved in a molecular form or form dissociating acetates



To determine the population of neutral, ionized or dissociated form of an amine at a certain temperature is rather complex. *Gyenes* has reported [9] that *e.g.* pyridine, which is a strong base in acetic acid, is present in ionized form  $[\text{C}_5\text{H}_5\text{NH}]^+ \cdot \text{CH}_3\text{COO}^-$  in about 80% and in molecular form in about 20%.

We wish to report the investigation of cobalt(II) compounds formed in acetic acid by reacting cobalt(II) bromide with nitrogen containing compounds as examined by means of conductivity and spectroscopic measurements.

## Experimental

Ethylenediamine, *n*-hexylamine, pyridine, and *N,N*-diethylaniline were purified by distillation. Pyridinium bromide was prepared from pyridine and an excess of aqueous hydrogen bromide. The  $[\text{CoBr}_4]^{2-} [\text{PyH}]_2^+$  complex was synthesized from equimolecular amounts of cobalt(II) bromide and pyridinium bromide in butanol. The products were crystallized from ethanol and their composition verified by elemental analysis. The cobalt monobromide complex  $[\text{Co}(\text{OAc})\text{Br}]$  was obtained according to [10]. Cobalt(II) acetate tetrahydrate and cobalt(II) bromide hexahydrate were of anal. grade. Acetic acid (anal. grade) was distilled before use. The water content estimated according to Fischer was below 0.1% and did not virtually affect the measurement. Other chemicals also of anal. grade were used without any purification. The electronic spectra were measured with a Specord (Zeiss, Jena) apparatus in acetic acid in 0.5–5 cm cells which were housed in a thermostated cell compartment.

## Conductivity measurements

The electric conductivity was measured in a glass vessel with sealed platinum electrodes. The design of the vessel with platinum electrodes attached to the side made it possible to measure changes of conductivity of such reactions where precipitation took place, or to measure at higher temperatures in a thermostat. The resistance capacity of the cell was approximately  $C_{res} \doteq 0.1 \text{ cm}^{-1}$ . The employed conductometer OK 102/1 (Radelkis, Budapest) was calibrated directly in units of conductance. The operation frequency was 80 Hz. Cobalt(II) bromide was titrated with nitrogen containing substances while shaking; the conductivity reading was registered in one-minute intervals. The molecular fraction

$$N_{Co} = N_{CoBr_2} = \frac{n_{CoBr_2}}{n_{CoBr_2} + n_x},$$

in which  $n_x$  stands for moles of the particular nitrogen containing substance, is plotted on the abscissa, the deviation of the apparatus  $A$  on the coordinate scales (in  $\mu\text{S}$ ). The deviation  $A$  is a function of conductivity  $\varkappa$

$$\varkappa = C_{res} \cdot A.$$

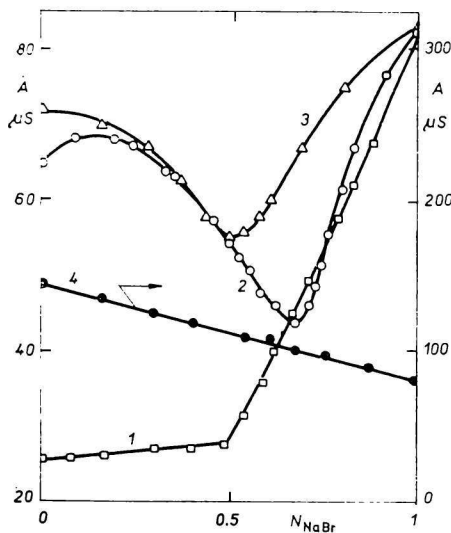


Fig. 1. Conductance titrations of *n*-hexylamine (1), ethylenediamine (2), *N,N*-diethylaniline (3), and *o*-phenanthroline (4) with NaBr in acetic acid.

Concentration of solutions  $4.37 \times 10^{-2} \text{ M}$ .

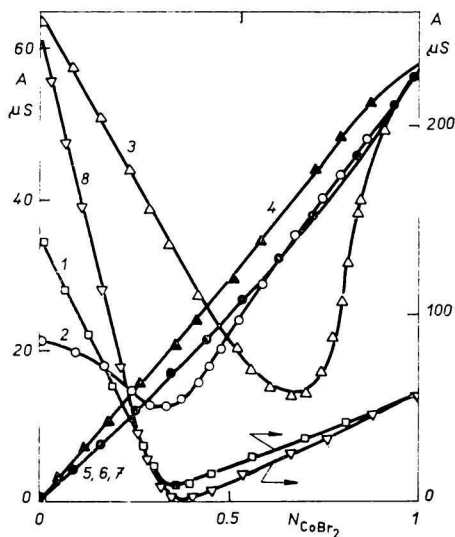


Fig. 2. Conductance titrations of triethanolamine (1), aminoacetic acid (2), (—)lysine (3), anthranilic acid (4), diphenylamine (5), acetanilide (6), *p*-nitroaniline (7), and *o*-phenanthroline (8) with  $\text{CoBr}_2$  in acetic acid.

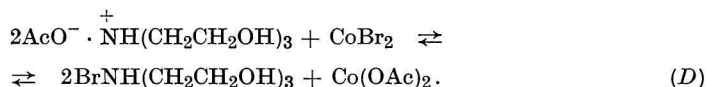
Concentration of solutions  $4.37 \times 10^{-2} \text{ M}$ .

## Results and discussion

As seen in Fig. 1, the conductance minimum of the titration of amines with sodium bromide appeared, with the exception of *o*-phenanthroline, always at a molar ratio corresponding to the formation of the respective ammonium bromide. The identity of ammonium bromide, formed according to reaction *C*, was checked by elemental analysis



The reaction of amines with cobalt(II) bromide in acetic acid should proceed in accordance with eqn *C* with the only difference that the conductivity minimum should appear after addition of half a mole of cobalt(II) bromide. The reaction course according to eqn *D* was observed *e.g.* with the titration of alkanolamines and some amino acids (Fig. 2)

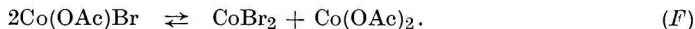


Figs. 2 and 3 show that hexamethylenediamine, (–)-lysine, pyridine as well as many other alkylamines, diamines, aniline, *N,N*-diethylaniline, and picolinic acid reacted in a different manner. Seemingly, the bromine anion is "saturated" during the reaction of nitrogen containing substances with cobalt(II) bromide only to the first step



One-donor and also multi-donor nitrogen containing substances reveal conductivity minimum at an equimolecular ratio. The ratio is constant even at 90°C (Fig. 3), under this reaction condition, however, the conductivities are substantially higher and with pyridine even the formation of a maximum occurred.

The possibility that the reaction *E* would occur was checked by the titration of pyridine with a solution of  $\text{Co}(\text{OAc})\text{Br}$ . This complex gave, when reacted with pyridine, a very distinct minimum of conductivity at molar ratio 2 : 1 (Fig. 4). The reaction of pyridine with  $\text{Co}(\text{OAc})\text{Br}$  indicates that the cobalt(II) bromide complex did not react with amines in acetic acid according to the assumed reaction *E*. The  $\text{Co}(\text{OAc})\text{Br}$  complex is in this solvent presumably in equilibrium with the cobalt(II) bromide and acetate



The such formed cobalt(II) bromide reacts in turn with pyridine, whereby the equilibrium of the reaction *F* is shifted to the right side. The complex  $\text{Co}(\text{OAc})\text{Br}$  is not the final product of the reaction of cobalt(II) bromide with pyridine what consequently excludes the reaction according to eqn *E*.

Pyridinium bromide and other ammonium bromides are not in all cases the final products of the reaction of amines with cobalt(II) bromide in acetic acid. Fig. 4 demonstrates that pyridinium bromide reacts with both cobalt(II) bromide and acetate under formation of a light blue precipitate. The conductivity minimum

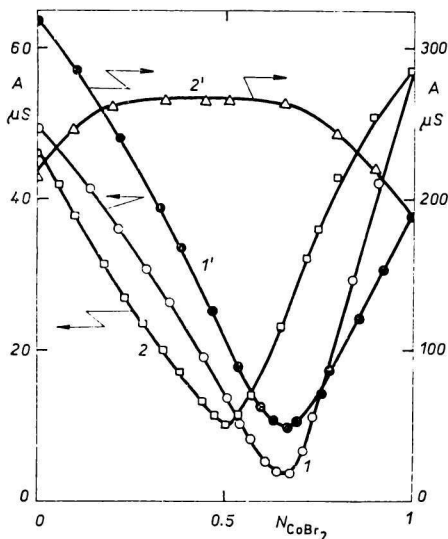


Fig. 3. Titration of hexamethylene diamine (1) and pyridine (2) with  $\text{CoBr}_2$  in acetic acid at 20 and 90°C (1' and 2'), respectively.  
Concentration of solutions  $4.37 \times 10^{-2}$  M.

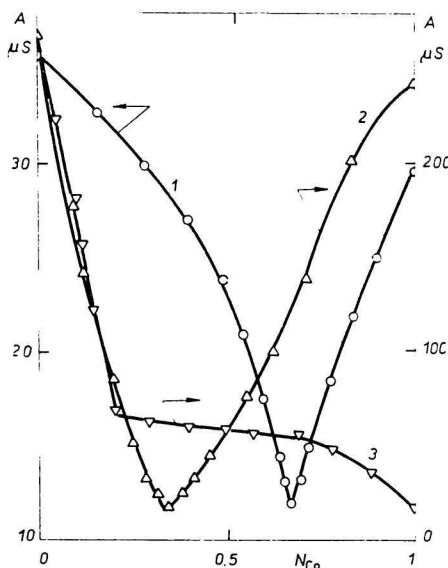


Fig. 4. Titration of pyridine with  $\text{Co(OAc)Br}$  (1).  
Concentration  $4.37 \times 10^{-2}$  M.  
Titration of pyridinium bromide with  $\text{CoBr}_2$  (2) and  $\text{Co(OAc)}_2$  (3) in acetic acid at 20°C.  
Concentration 0.1 M.

has been found at a molar ratio 2 : 1 and 4 : 1, respectively. As will be shown, the reaction of  $\text{Co(OAc)Br}$  and  $\text{CoBr}_2$  complexes with pyridine or other nitrogen containing bases could not be explained in terms of a simple "saturation" of bromine with pyridine to yield pyridinium bromide, which is furnished by the reaction of sodium bromide (reaction C), because complexes of cobalt with pyridine might be involved.

Derivatives of aniline with electron-accepting groups as anthranilic acid, *o*- and *p*-nitroaniline and diphenylamine have a very low conductivity in acetic acid and do not exhibit the expected changes with cobalt(II) bromide (Fig. 2). The change in conductivity upon titration is similar to that of a bromide diluted with acetic acid. The conductivity of the solutions of aniline derivatives is virtually equal to that of acetic acid and it could be, therefore, presumed that these substances are not dissociated or ionized. The low conductivity can be rationalized by the formation of hydrogen bonds. Intramolecular structures are formed in the case of anthranilic acid and *o*-nitroaniline, whereas polymeric intermolecular ones with *p*-nitroaniline. The inflections on the conductivity curves were not observed even at 90°C. This bears out evidence for the presence of either original hydrogen bonds or secondarily formed ones between the solvent and nitrogen containing bases after their decomposition.

The unreactivity of diphenylamine with cobalt(II) bromide can be explained

by its very low basicity or by a steric hindrance. The latter could cause that also *N*-acetylated compounds, as *e.g.* acetanilide and dimethylformamide, do not react with cobalt(II) bromide (Fig. 2). Such nitrogen containing compounds behave in the same manner as their *N*-unsubstituted analogues when the carbonyl group becomes more distant from the reactive nitrogen atom by *N*-acetylacetylation. *o*-Phenanthroline displays a very distinctive conductivity minimum with cobalt(II) bromide solution at a molar ratio of phenanthroline to  $\text{CoBr}_2$  2 : 1, although sodium bromide does not cause changes in conductivity. Phenanthroline is bound in this cobalt complex as a neutral molecule.

The formation of complexes with nitrogen containing compounds was investigated by spectral means in acetic acid; the original absorption spectra of cobalt(II) bromide complexes underwent alteration in many cases (Fig. 5). The reaction between hexamethylenediamine (HMDA) and cobalt(II) bromide at lower temperature is accompanied with precipitation. If HMDA is added in more than double excess, the precipitate is redissolved and at the 3 : 1 or a greater ratio the solution becomes homogeneous. Spectra of solutions were recorded after filtration, since at certain ratios of reactants precipitation takes place. The enhancement of the HMDA concentration decreases the absorption of bands in the 14 000 to 16 000  $\text{cm}^{-1}$  range and increases it in the 18 000 to 19 000  $\text{cm}^{-1}$  range. The minimal value of the band extinction at 14 650  $\text{cm}^{-1}$  and the greatest amount of precipitate is formed at the HMDA to cobalt(II) bromide ratio 1 : 2 (Fig. 6). The elemental analysis of the precipitate showed the composition of the complex to be



Another evidence confirming the composition of such an ion complex have brought the electronic spectra. The spectrum of the original cobalt(II) bromide complex gets more complex with an increase of the HMDA concentration and consists of some absorption bands. The structure of the spectrum of saturated solution of such a complex in acetic acid is identical with that of tetrahedral  $\text{CoBr}_4^{2-}$  complexes [11, 12]. Considering both the conductance and spectral measurements, it is possible

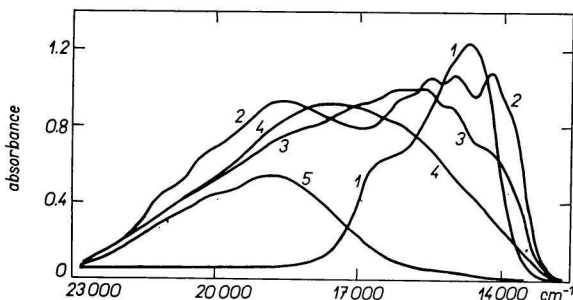
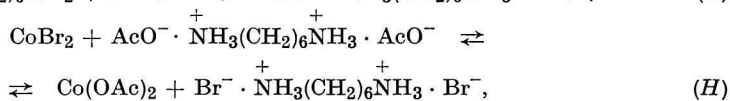
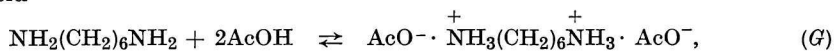


Fig. 5. Electronic spectra of cobalt(II) complexes in the presence of hexamethylenediamine HMDA.

1.  $2 \times 10^{-3}$  M- $\text{CoBr}_2$ ; 2.  $1.6 \times 10^{-2}$  M- $\text{CoBr}_2$  +  $1.6 \times 10^{-2}$  M-HMDA; 3.  $1.6 \times 10^{-2}$  M- $\text{CoBr}$  +  $6.4 \times 10^{-2}$  M-HMDA; 4.  $1.6 \times 10^{-2}$  M- $\text{CoBr}_2$  +  $1.12 \times 10^{-1}$  M-HMDA; 5.  $1.6 \times 10^{-2}$  M- $\text{Co}(\text{OAc})_2$ .

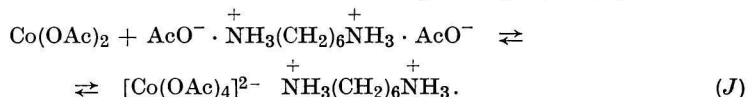
Temperature 20°C, 2 cm cell length excepting (2) (5 cm).

to formulate equations referring to the reactions of cobalt(II) bromide with HMDA in acetic acid

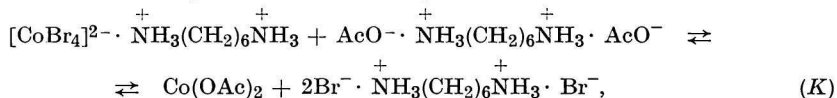


This complex is formed by reacting one mole of HMDA with two moles of cobalt(II) bromide, whereby one mole of cobalt(II) acetate is liberated. The conductance minimum (Fig. 3) and the lowest value of the absorption band at  $14\,650\text{ cm}^{-1}$  (Fig. 6) was estimated at the given ratio of reactants.

The spectrum of the  $[\text{CoBr}_4]^{2-} \cdot \overset{+}{\text{NH}}_3(\text{CH}_2)_6\overset{+}{\text{NH}}_3$  complex is partly overlapped by the concurrently formed spectrum of cobalt(II) acetate and possibly other complexes (Fig. 5). Cobalt(II) acetate resulting in the reaction *H* reacts with acetate ions in the excess of HMDA to furnish tetraedric complexes  $[\text{Co}(\text{OAc})_4]^{2-}$



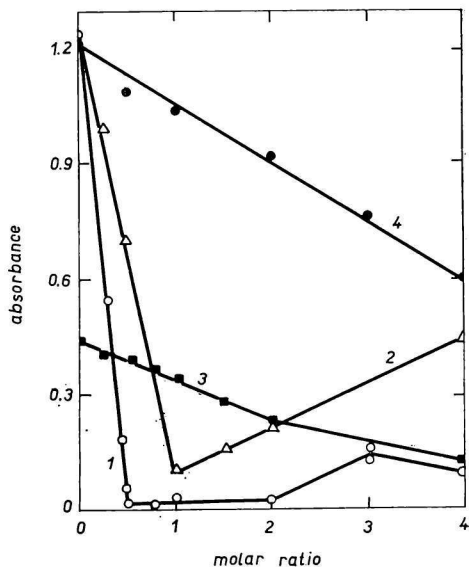
In the excess of HMDA, *i.e.* in the excess of acetate ions, the absorption band maximum of cobalt(II) acetate is shifted from  $18\,800\text{ cm}^{-1}$  to the  $17\,500\text{ cm}^{-1}$  region; the absorption intensity is also enhanced (Fig. 5). The same dependence has been observed even in the presence of sodium acetate [3]. Due to different dissociation constants of acetates of nitrogen containing bases, the concentration of  $[\text{Co}(\text{OAc})_4]^{2-}$  complexes differs from that of sodium acetate [13]. Cobalt(II) acetate and bromide can produce, in addition to reaction *J*, a cobalt monobromide complex (reaction *F*), having a spectrum consisting of some absorption bands shifted to the shorter wave-length side. With an alteration of the molar ratio HMDA to cobalt(II) bromide, changes of the  $\text{CoBr}_4^{2-}$  complex took place. This complex precipitates from acetic acid at a molar ratio 1 : 2 as a little soluble precipitate, which is gradually dissolved in an excess of diamine and at the 3 : 1 ratio the solution becomes homogeneous. The little soluble  $\text{CoBr}_4^{2-}$  complex is transformed in an excess of HMDA into more soluble forms of cobalt complex. The absorption bands of the latter lie in the shorter wave-length region and have lower extinction coefficients. These changes are likely due to reactions *J* and *K*, proceeding through partial reactions *H* and *I*



or alternatively, complexes are formed in which the nitrogen containing compound is not bound in ionic form but as a neutral molecule. Further investigation would be necessary to put more light on this point.

Pyridine reacts with cobalt(II) bromide in the same manner as HMDA excepting that the minimal absorption value appears at equimolar concentrations (Fig. 6). Under these reaction conditions the complex  $[\text{CoBr}_4]^{2-} \cdot [\text{PyH}]_2^+$  precipitates from

Fig. 6. The dependence of absorption band at  $14\ 650\text{ cm}^{-1}$  and  $20^\circ\text{C}$  on the molar ratio of HMDA to  $\text{CoBr}_2$  (1), pyridine to  $\text{CoBr}_2$  (2), and pyridine to  $\text{Co(OAc)Br}$  (3). The curve (4) refers to the dependence (3) at  $60^\circ\text{C}$ .



the reaction mixture. The origin of such a complex in the reaction system can be described by reactions *L* and *M*



The molar ratio of the starting material was found to be the same in the summarized equation both by conductivity and spectral measurements. If the reaction is examined at  $60^\circ\text{C}$  the precipitate is not formed at any ratio of reactants. The structure of the spectra resembles that of the preceding case. The extinction of the absorption band at  $14\ 650\text{ cm}^{-1}$  is gradually lowered with the increased concentration of pyridine without forming a minimum (Fig. 6). Under these reaction conditions complexes  $\text{CoBr}_2\text{Py}_2$  and  $\text{CoBr}_2\text{Py}_4$  might exist in the solution in addition to ion complex  $[\text{CoBr}_4]^{2-} \cdot [\text{PyH}]_2^+$ .

Pyridine reacts with the  $\text{Co(OAc)Br}$  complex without formation of precipitates. The structure of the spectra is like that of pyridine with cobalt(II) bromide. The absorption band at  $14\ 650\text{ cm}^{-1}$  shows a decreasing tendency when the concentration of pyridine increases (Fig. 6).

Aminoacetic acid and triethanolamine react with cobalt(II) bromide to yield little soluble ammonium bromide salts (reaction *E*). The equilibrium of the reaction is almost totally shifted to the right side at about  $20^\circ\text{C}$ . The particular ammonium bromide forms a white precipitate. The solution remains pink and its spectrum is identical with that of cobalt(II) acetate. The consecutive reactions *I* or *M* leading to the formation of  $[\text{CoBr}_4]^{2-}$  proceed at higher temperatures.

Diphenylamine, *N*-phenylanthranilic acid, and *N*-acetylated amines do not affect the electronic spectrum of cobalt(II) bromide at all, or only sparingly even at high concentrations.



Considering the results of spectral measurements it can be said that the conductivity minima obtained from conductance titration of nitrogen containing compounds with cobalt(II) bromide in acetic acid at certain molar ratios of reactants are associated with the formation of little soluble ion complexes  $[\text{CoBr}_4]^{2-}$  as a result of reactions analogous to *H*, *I* and *L*, *M*. The conductance minima of alkanolamines and some aminoacids is due to ammonium bromide compounds which do not undergo further reactions at lower temperatures.

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