Inorganica Chimica Acta, 29 (1978) L265–L267
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The Multi-step Reactions between Some *Bis*(Ethylenediamine)cobalt(III) Complexes and Ammonium Salts in the Solid Phase

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Received May 27, 1978

In a previous paper [1] the intermediate products of the thermal reactions between *cis*- or *trans*-[Co(en)$_2$(OCOC$_6$H$_4$R)$_2$]NO$_3$ and NH$_4$Cl in the solid phase were detected showing a two-step substitution of the labile ligands and isomerization reactions.

This paper reports the results of an investigation on the thermal reactions of some diprotic acid cobalt(III) complexes of the type [Co(en)$_2$X]Y (X = carbonato, oxalato, malonato and Y = NO_3^- or Cl^-) to show the effect of ring size and of the added inorganic salts on isomerization and/or substitution reaction of cobalt(III) complexes in the solid phase.

Experimental*

The complexes were prepared with some changes, by the methods reported in the literature: the *trans*- and *cis*- forms of Co(en)$_2$Cl$_2^+$ as chloride and nitrate, according to Bailar [2] and Yamada *et al.* [3], respectively; Co(en)$_2$CO$_3^+$, Co(en)$_2$(ox)$^+$ and Co(en)$_2$(mal)$^+$ as chloride and/or nitrate by the methods outlined for the corresponding perchlorate [4–6], substituting *trans*- dichloro-*bis*(ethylenediamine)cobalt(III) nitrate or chloride for the *trans*- dichloro-*bis*(ethylenediamine)cobalt(III) perchlorate at the appropriate step of the synthesis. Aqueous solutions of all the products gave extinction coefficients which compared well with those reported for the corresponding bromide [7].

The thermal reactions, reflectance spectra and TLC separations were carried out as described in a previous paper [1]. TLC experiments were performed using formamide–methanol–70% perchloric acid –H$_2$O (40:60:0.4:2) as mobile phase (eluent E$_1$). R$_f$ values found: Co(en)$_2$CO$_3^+$: 0.21; Co(en)$_2$(ox)$^+$ and Co(en)$_2$(mal)$^+$: 0.25; *cis*-Co(en)$_2$Cl$_2^+$: 0.43; *trans*-Co(en)$_2$Cl$_2^+$: 0.64.

Non-complexed Co^{2+} was detected in the following manner: the silica gel plates, on which the complexes had been separated with eluent E$_1$, were eluted a second time in the same direction, with eluent E$_2$: NH$_4$CNS (50 g in 50 ml of H$_2$O)–EtOH (1:5). After a few minutes of elution the spot corresponding to Co^{2+} moved from the point of application and was easily visible, owing to its blue color [8].

Visible spectra were measured with a Beckman DK-2A spectrophotometer, using 1 cm cells. High-voltage electrophoresis at 2000 volts was carried out in a Camag apparatus on Whatman No. 1 paper using 0.1*M* LiNO$_3$ as electrolyte.

Results and Discussion

Preliminary studies showed that the complexes under investigation decompose at temperatures above 200 °C. Thus the mixtures of complexes and ammonium salts were heated isothermally at temperatures in the range of 105–180 °C for 1–24 hours. Heating of a 1:10 or 1:50 molar ratio mixture of complex and inorganic salt was found to give the same final product; however, the intermediate products are seen most clearly in the 1:10 ratio, where the rate of their disappearance is slower, while the final products are best seen in the ratio 1:50.

The reaction mixtures and the conditions of thermal experiments are summarized in Table I. The reaction products were mainly identified on the basis of TLC results. Reflectance spectra did not give, as in the case of the thermal reaction of [Co(en)$_2$(OCOC$_6$H$_4$R)$_2$]NO$_3$ and NH$_4$Cl [1], significative results.

NH$_4$Cl

In the reaction between [Co(en)$_2$CO$_3$]NO$_3$ and NH$_4$Cl (1:10 molar ratio) an intermediate species was put in evidence together with the final product, identified as *trans*-[Co(en)$_2$Cl$_2$]Y. The intermediate species was found to have the same R$_f$ value as *cis*-Co(en)$_2$Cl$_2^+$ and was eluted together with it when this complex was added to the reaction products as a carrier. On the basis of the above results the reaction may be postulated in two steps:

$$\mathrm{Co(en)_2CO_3^+} \longrightarrow cis\text{-}\mathrm{Co(en)_2Cl_2^+} \longrightarrow trans\text{-}\mathrm{Co(en)_2Cl_2^+}$$

the first of which is faster than the second one.

The reactions of [Co(en)$_2$CO$_3$] Cl or [Co(en)$_2$(mal)]NO$_3$ in the presence of NH$_4$Cl at 165 °C for 1–24 hours occur more slowly than in the case of

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*abbreviations used: en = ethylendiamine; ox = oxalato, mal = malonato, *cis* or *trans*-dichloro = *cis*- or *trans*-[Co(en)$_2$Cl$_2$]Y; carbonato, oxalato, and malonato complexes = [Co(en)$_2$CO$_3$]Y, [Co(en)$_2$(ox)]Y, [Co(en)$_2$(mal)]Y, respectively.

TABLE I. Solid–Solid Reactions of Some Ethylenediamine Complexes of Cobalt(III) with Ammonium Salts.

Complex[a]	Salt	Reaction Temp. (°C)	Heating Time	Main Products
$[Co(en)_2CO_3]Y$	–	165	24 hours	no reaction
$[Co(en)_2(ox)]Y$	–	180	24 hours	no reaction
$[Co(en)_2(mal)]NO_3$	–	165	24 hours	no reaction
$[Co(en)_2CO_3]Y$	NH_4Cl	165	1–4 hours	*cis*-$Co(en)_2Cl_2^+$, *trans*-$Co(en)_2Cl_2^+$
$[Co(en)_2(ox)]Y$	"	180	24 hours	no reaction
$[Co(en)_2(mal)]NO_3$	"	165	1–5 hours	*cis*-$Co(en)_2Cl_2^+$, *trans*-$Co(en)_2Cl_2^+$
$[Co(en)_2CO_3]Cl$	NH_4NO_3	20	a week	aquo- and/or chloroaquo-species, *trans*-$Co(en)_2Cl_2^+$
$[Co(en)_2CO_3]NO_3$	"	120	30 min	unidentified species
$[Co(en)_2(ox)]Y$	"	160	24 hours	no reaction
$[Co(en)_2(mal)]NO_3$	"	160	24 hours	no reaction
$[Co(en)_2CO_3]Y$	$(NH_4)_2SO_4$	165	24 hours	Co^{2+}
$[Co(en)_2(ox)]Y$	"	180	24 hours	no reaction
$[Co(en)_2(mal)]NO_3$	"	165	24 hours	Co^{2+}

[a] $Y = NO_3^-, Cl^-$.

$[Co(en)_2CO_3]NO_3$ and the same intermediate species is formed. It is interesting to note that *trans*-$Co(en)_2Cl_2^+$ is the product of $[Co(en)_2CO_3]Cl$ and NH_4Cl mixtures. This may mean that, in this case, both the NO_3^- and NH_4^+ ions are not necessary for a *trans*-preferred reaction [9]. A detailed study concerning this unusual behaviour is the subject of a separate paper [10]. For the oxalato complexes, in spite of heating for 24 hours and to 180 °C, only the starting compound was visible after the chromatographic development, demonstrating that, under our experimental conditions, no reaction occurred.

NH_4NO_3

The reaction between $[Co(en)_2CO_3]Cl$ or $[Co(en)_2CO_3]NO_3$ and NH_4NO_3 began to occur at room temperature. At 160 °C a decomposition reaction took place, with formation of Co^{2+}. In the reaction between $[Co(en)_2CO_3]Cl$ and NH_4NO_3, at room temperature, chromatographic results give good evidence for the formation of various products, one of which seems to be *trans*-$Co(en)_2Cl_2^+$, although the characteristic green colour of the last did not appear in any experiment. This may indicate that the substitution reaction was not complete, due to a lack of Cl^- ions, twice as many Cl^- ions being required to obtain all *trans*-$Co(en)_2Cl_2^+$. This would be consistent with the results obtained in the presence of an excess of Cl^- ions (*i.e.* in the reaction between $Co(en)_2CO_3^+$ and NH_4Cl), where *trans*-$Co(en)_2Cl_2^+$ is the main final product. The formation of *trans*-$Co(en)_2Cl_2^+$ from the solid–solid reaction between $[Co(en)_2CO_3]Cl$ and NH_4NO_3 may involve the displacement of carbonato ligand due to the counter ion or to the aquation–anation reaction, accompanied in both cases by a structural change from a *cis*- to a *trans*-configuration. A similar thermal behaviour in the presence of NH_4NO_3 was reported for *cis*-$[Co(en)_2(OH_2)_2]Cl_3 \cdot 2H_2O$ [9].

In the case of $[Co(en)_2CO_3]NO_3$ and NH_4NO_3 at room temperature only a slight change of colour was visible, even after a week. At 120 °C, after 30 minutes, the mixture (1:50 molar ratio) was orange-red and TLC evidenced the progressive formation of +2 or +3 charged species. In order to obtain further information on the products generated in these thermal reactions, electrophoretic and spectrophotometric analysis on aqueous solutions of heated samples at convenient concentrations were performed. The electrophoretic experiments showed that Co^{2+} was not present and that two complexed species with a charge > +1 were clearly visible. A reversible change of the visible absorption spectrum with pH was observed, which may indicate the presence of aquo-species [11]. From the information available in the literature it was not possible to establish the composition of the orange–red mixture. It is probably a mixture of aquo-nitrato and diaquo species.

$[Co(en)_2(ox)]Cl$, $[Co(en)_2(ox)]NO_3$ and $[Co(en)_2(mal)]NO_3$ heated at 160 °C for 24 hours in the presence of NH_4NO_3 (molar ration 1:5) appeared not to react. Increasing the ratio complex: NH_4NO_3, after some hours Co^{2+} began to form.

$(NH_4)_2SO_4$

A yellow brown colour appeared after samples of this salt and $[Co(en)_2CO_3]Cl$, $[Co(en)_2CO_3]NO_3$

or $[Co(en)_2(mal)]NO_3$ (molar ratio 10:1) had been heated for an extensive time at 165 °C.

The presence of Co^{2+} is suggested by the chromatographic results obtained, which are consistent with the diminution of the temperature of decomposition of the complexes due to the presence of $(NH_4)_2SO_4$. On the other hand, experiments performed at lower temperatures were not successful. As in the case of these complexes with NH_4Cl, at temperature <160 °C no reactions seem to occur.

When $[Co(en)_2(ox)]Cl$ or $[Co(en)_2(ox)]NO_3$ were heated in the presence of $(NH_4)_2SO_4$ no reactions seemed to occur even at 180 °C.

Conclusion

From the comparison of the above results we may deduce that, under our experimental conditions, $Co(en)_2(ox)^+$ complexes are less reactive than $Co(en)_2(mal)^+$ and $Co(en)_2CO_3^+$. The former do not give either substitution or decomposition products with any of the examined ammonium salts, even at 180 °C. $[Co(en)_2(mal)]NO_3$, on the contrary, reacts at a rather high temperature (165 °C) although only in the presence of NH_4Cl does a substitution reaction occur, whereas a decomposition reaction is the main process in the presence of $(NH_4)_2SO_4$. $[Co(en)_2CO_3]Cl$ and $[Co(en)_2CO_3]NO_3$ are the most reactive: chloro- and aquo-intermediate species may be formed and decomposition products may be obtained depending on the ammonium salt, the temperature and the time of heating.

As to the leaving groups, the reactivity sequence of the complexes (ox < mal < CO_3) is consistent with their different stability, depending on the chelating ring size and on the different ability of the leaving groups to be protonated on reacting with NH_4^+

Acknowledgement

The authors wish to thank Mr. A. Cristalli for valuable technical assitance.

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