Thermal properties of $[Co(en)_2Cl_2]Cl$ in solid state. *Cis–trans* isomerization of the $[Co(en)_2Cl_2]^+$ complex ion in methanol

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Abstract Thermal decompositions of the *trans*-$[Co(en)_2Cl_2]Cl$ and *cis*-$[Co(en)_2Cl_2]Cl$ complex isomers have been studied using the TG–FTIR and TG–DSC–MS techniques. The measurements were carried out in argon atmosphere over the temperature range 293–873 K. The influence of the configurational geometry on the pathways of thermal transformations was discussed. Furthermore, kinetic studies on the reaction of the *cis–trans* isomerization of the $[Co(en)_2Cl_2]Cl$ complex salt in methanolic solutions were performed using UV–Vis spectrophotometry at five temperatures in the 293–313 K temperature range. The observed rate constants were computed using the "Glint" program based on the global analysis. It has been found that the *cis–trans* isomerization of $[Co(en)_2Cl_2]Cl$ is a first order reaction. Furthermore, the *cis/trans* $[Co(en)_2Cl_2]Cl$ isomerization proceeds according to the dissociative mechanism.

Keywords Isomerization · Mechanism · Kinetics · Cobalt(III) complexes · Thermal decomposition

Introduction

A separation of a mixture of enantiomers is possible using adsorption chromatography and thin layer chromatography (TLC) [1–5]. Retention factor (RF) values of *cis* complexes were found to be greater than those of the *trans* formes. In addition to other factors, solubilities of the complexes have a profound effect on the RF values of these cationic complexes.

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Using chelating ethylenediamine ligands instead of ammonia gives tris (ethylene-diamine) cobalt(III) chloride ([Co(en)$_3$]Cl), which was one of the first coordination complexes that was resolved into optical isomers. The complex exists as both either right- or left-handed form of a "three-bladed propeller". This complex was first isolated by Werner as yellow-gold needle-like crystals [6–8]. The value of the molar extinction coefficient of this "third band" suggests that it is an electron transfer band. It is a characteristic feature for *trans* complexes. Often both isomers are equal or roughly equal in terms of bond energy, and so exist in roughly equal amounts, provided that they can interconvert relatively freely (assuming that the energy barrier between the two isomers is not too high). When the isomerization occurs intramolecularly, it is considered as a rearrangement reaction [9]. However, under certain conditions, one of the isomers can have a longer lifetime. Knowing the thermodynamic properties of compounds, for example of two isomers, it can be determined which one is more stable [10].

Ethylenediamine (en) is a common ligand in cobalt(III) complex compounds [11, 12]. Numerous bio-active compounds contain the N–CH$_2$–CH$_2$–N linkage, includ-ing aminophylline and some antihistamines [13].

Generally, coordination compounds of this type play important roles in the activity of metalloenzymes or during transport processes of metal ions across cell membranes [14]. The [Co(en)$_2$Cl$_2$]Cl complex seems to be especially interesting since the biological tests were carried out with its participation. The interactions of this complex compound with various biological ligands, such as thiourea, methionine, and 5′-GMP (5′-guanosine monophosphate) were examined [15]. The strongest effect was observed with thiourea, whereas the weakest one for the 5′-GMP.

Taking the above into account, it seems that having knowledge about kinetic and physicochemical properties of such complex is crucial issue and, consequently, our studies concerned this matter. Therefore, they were aimed at the determination of the thermal stability in solid state as well as the kinetic stability in solution of both isomers of [Co(en)$_2$Cl$_2$]Cl. The obtained knowledge concerning the kinetic properties of the complex studied will be very useful in further biomedical research.

Experimental section

Reagents

The *cis*-[Co(en)$_2$Cl$_2$]Cl *and* *trans*-[Co(en)$_2$Cl$_2$]Cl complex compounds were prepared by known methods described by Bailar [16]. The purity of each salt was checked by elemental analysis for C and H. The results of analytical calculations for the *trans*-[Co(en)$_2$Cl$_2$]Cl: C 16.81; H 5.60; and for *cis*-[Co(en)$_2$Cl$_2$]Cl: C 16.81; H 5.60; were in agreement with those of the elemental analysis: C 16.53; H 5.60 and C 15.50; H 5.00.

Thermal analysis

Thermal decompositions of *cis*-[Co(en)$_2$Cl$_2$]Cl and *trans*-[Co(en)$_2$Cl$_2$]Cl have been studied using the TG–FTIR and TG–DSC–MS techniques [17]. The TG–MS

measurements in argon (Ar 5.0) were run on a STA 449 *F3 Jupiter*® thermal analyzer (Netzsch) coupled with a QMS 403 C *Aëolos*® quadrupole mass spectrometer. The measurements were carried out in an argon atmosphere over a temperature range of 293–873 K (Al crucible with a small central hole, sample mass 5–10 mg, heating rate 10 K min^{-1}, flow rate of the carrier gas 20 mL min^{-1}). The TG–FTIR analyses in argon (Ar 5.0) were run on a Netzsch TG 209 apparatus coupled with a Bruker IFS 66 spectrometer (Al crucible with a small central hole, sample mass 10–15 mg, flow rate of the carrier gas 15 mL min^{-1}, range 308–700 K, heating rate 10 K min^{-1}).

Kinetic measurements

Kinetic studies consisted of the spectrophotometric observation of the isomerization of *cis*-[Co(en)$_2$Cl$_2$]Cl complex salt dissolved in methanol. Measurements were conducted at five temperatures: 293, 298, 303, 308 and 313 K. Experiments started with the preparation of appropriate mass of the salt studied, *i.e.* 0.00565 g. Next, into each of two measuring trays 2 mL of CH$_3$OH was poured and the trays were kept at constant temperature for 20 min. Afterwards, in one of trays (the second tray with the methanol was used as the reference), the prepared sample of *cis*-[Co(en)$_2$Cl$_2$]Cl was dissolved by stirring and the measurement started. The concentration of the complex in the solution prepared in this way was 0.0125 M. Changes in the absorption of the solutions caused by the progress of the *cis–trans* isomerization reaction of the complex studied were monitored spectrophotometrically in the range of 350–700 nm.

Instrumentation and simulations

Spectral measurements were carried out in the UV–Vis region using a Perkin-Elmer Lambda 650 instrument with the scan accuracy of 1 and 1 nm slit width at a scanning rate 120.00 nm min^{-1}. The pH of the solution was measured using pH-meter CX-731 ELMETRON.

Results and discussion

Thermal analysis

Results of thermal analyses of *trans*-[Co(en)$_2$Cl$_2$]Cl and *cis*-[Co(en)$_2$Cl$_2$]Cl are collected in Table 1. The TG and DSC curves of the compounds studied recorded at a heating rate of 10 K min^{-1} are shown in Fig. 1.

Both examined isomers exhibit comparable thermal stabilities. Their decomposition is preceded by the desorption of surface bound water molecules. This is shown by losses in the weight of both samples starting at the temperature of 373 K with accompanying endothermic energy effects registered during the simultaneous DSC analysis. The presence of water in the first step of the decomposition is confirmed by both IR spectra of gas products, on which characteristic vibrational

Table 1 Thermal characteristics of *trans*-[Co(en)$_2$Cl$_2$]Cl and *cis*-[Co(en)$_2$Cl$_2$]Cl in argon

Formula	Ranges of decomposition/K	DSC[a]	Mass loss/%
trans-[Co(en)$_2$Cl$_2$]Cl	373–407	395 (endo)	0.6
	500–560	516 (endo), 543 (exo)	16
	560–647	641 (exo)	22.3
	647–702	648 (exo)	22.2
cis-[Co(en)$_2$Cl$_2$]Cl	376–432	422 (endo)	3.5
	500–555	516 (endo), 540 (exo)	15.2
	555–655	648 (exo)	21.5
	655–702	665 (exo)	21.3

[a] *peak temperature* temperature at which a maximum of the thermal effect emerges (*endo* endothermic, *exo* exothermic effect)
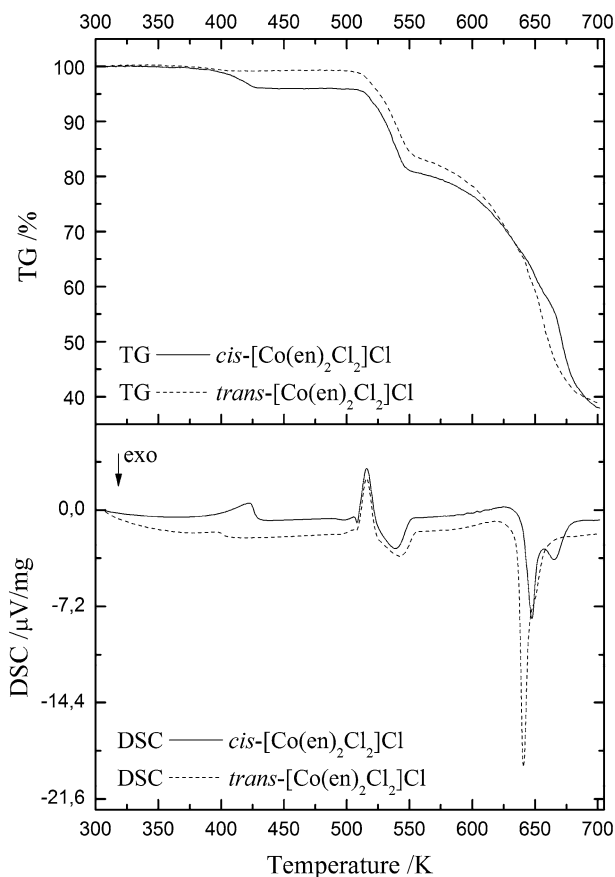
Fig. 1 TG (*top*) and DSC (*bottom*) curves of thermal decomposition of *trans*-[Co(en)$_2$Cl$_2$]Cl and *cis*-[Co(en)$_2$Cl$_2$]Cl in argon, β = 10 K min^{-1}

bands are present over the ranges of 4,000–3,500 and 1,750–1,400 cm^{-1}, as well as the increase of the intensity of ion currents m/z = 17 and 18, registered during the TG–MS analysis. It is worth noting that the *cis* isomer shows higher adsorptive abilities compared with the *trans* isomer, which is confirmed by greater loss in weight of the first step registered on the TG curve (Table 1, Fig. 1). The process of the adsorption of water molecules by complexes of this type is probably their distinctive feature [18].

The measurements performed show that there are four stages of the thermal decomposition of both complexes: *trans*-[Co(en)$_2$Cl$_2$]Cl and *cis*-[Co(en)$_2$Cl$_2$]Cl. *Cis*-[Co(en)$_2$Cl$_2$]Cl isomer has a greater amount of water at 395 K. The remaining three stages of the thermal decomposition are similar for both complex molecules related to the surface of substance (Table 1), because in the first stage of the thermal decomposition, the *cis* isomer loses more of its mass than the *trans* isomer. In other words, *cis*-[Co(en)$_2$Cl$_2$]Cl loses more molecules of water at 422 K than the *trans*-[Co(en)$_2$Cl$_2$]Cl isomer, the percentage amounts of the weight loss have similar values for both isomers.

The geometrical configuration of both examined complexes does not influence the course of their decomposition. After the stage of the desorption, both isomers are stable thermally up to the temperature of approximately 500 K. Their decomposition is not preceded by melting of the sample. On the DSC curve, there is also the lack of signals showing the possibility of the presence of the isomerization processes. At temperatures higher than 500 K, both complexes studied undergo thermal decomposition with the accompanying destruction of their geometric structure. The mass loss over the temperature range of 500–560 K (the second mass loss on the TG curve) is accompanied by two following immediately one by one energy effects, first of which is due to an endothermic process and the second one owing to the exothermic process (Table 1, Fig. 1). During this step, the decomposition reaction rates of both processes are so high so that it is very difficult to determine the temperatures of the start and the end of both individual transformations. This makes it impossible to define the equations of chemical reactions describing the proceeding processes.

Analyses of IR and MS spectra of volatile products of the decomposition show that *en* ligands decompose to NH$_3$ (m/z = 16, 17), C$_2$H$_4$ (m/z = 26, 27, 28) and to N$_2$ (m/z = 14, 28) (Figs. 2, 3). However, a part of *en* ligands dissociate in their molecular form (m/z = 30). The presence of ammonia (Fig. 2) in the volatile products of the decomposition is confirmed by the presence in the IR spectra of the oscillatory-rotational absorption bands characteristic for this compound. However, these bands partly hide the C$_2$H$_4$ absorption bands, thus the explicit identification of the last molecule based on IR spectra is not easily accessible.

A characteristic feature of cobalt(III) coordination compounds is a change of the oxidation state of the central atom accompanying the reaction of the decomposition [19–23]. A reducing factor can be Cl$^-$ ligands, which reduce cobalt(III) in the process of an intramolecular electron transfer. Reducing properties of halogen ligands were observed in reactions of the intramolecular reduction of iron(III) ions present in the tetrachloridoferrate(III) complexes [24–27]. There is also a possibility of an intermolecular mechanism of the reduction of Co(III), in which chloride ions
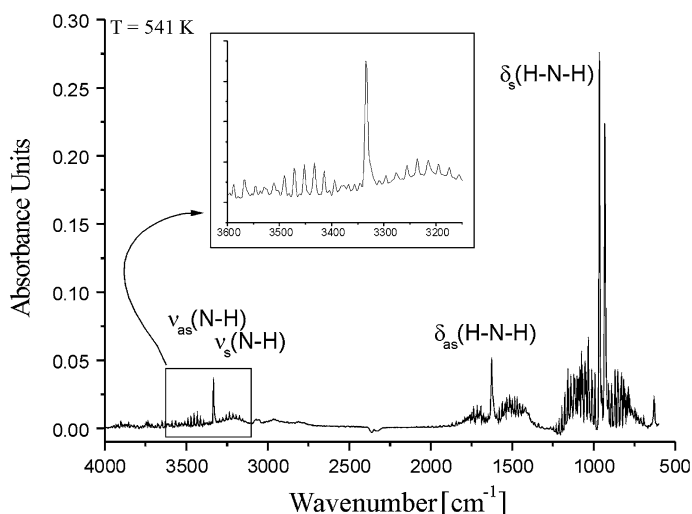
Fig. 2 IR spectra of the volatile products of the thermal decomposition of *trans*-[Co(en)$_2$Cl$_2$]Cl at 541 K in argon
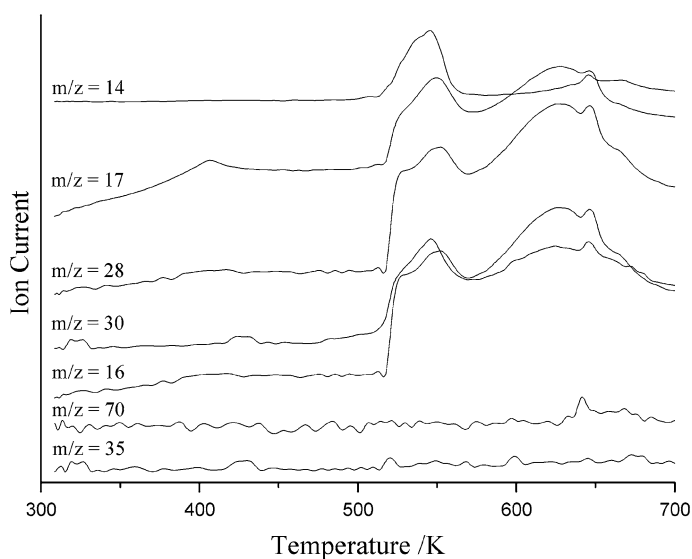
Fig. 3 Ionic current profiles recorded during TG–MS analysis of *cis*-[Co(en)$_2$Cl$_2$]Cl in argon, $\beta = 10$ K min^{-1}

present outside the inner coordination sphere of the metal ion participate. In both cases, chloride ions are oxidized to Cl$_2$.

A different mechanism of the reduction of the center of the coordination of Co(III) complexes takes place when the nitrogen atoms of such ligands like e.g.

NH_3 or *en* participate in the process, which are oxidized to N_2 at the same time. The analysis of MS spectra of gas products of the decomposition of the *trans*-$[Co(en)_2Cl_2]Cl$ and *cis*-$[Co(en)_2Cl_2]Cl$ complexes suggests that the nitrogen atoms of *en* ligand can be a factor reducing the Co(III) ions. This suggestion is strengthened by the increase in the intensity of the $m/z = 14$ and 28 ion currents characteristic for N_2 and the lack of changes in the intensity of the $m/z = 35, 70$ ion currents characteristic for Cl_2 (Fig. 3). The reduction of Co(III)–Co(II) takes place already over the temperature range of 500–560 K and probably can be attributed to an intramolecular process.

The two last steps of the decomposition of both complexes studied run exothermically. Due to the high speed of the transformations occurring subsequently, which are probably accompanied by the complicated oxidation and reduction reactions, a thorough definition of the reaction equations is not possible.

Kinetic studies

The isomerization reaction of the $[Co(en)_2Cl_2]Cl$ complex can be presented as follows:

$$cis\text{-}\big[Co(en)_2Cl_2\big]Cl \xrightarrow{\text{ k }} trans\text{-}\big[Co(en)_2Cl_2\big]Cl \qquad (1)$$
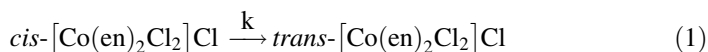
Studies on reaction rates with the use of the UV–Vis spectrophotometric method were carried out at 550 nm wavelength due to the fact that at this wavelength there are present the most significant changes in the absorption observed. Kinetic measurements were conducted at five temperatures: 293, 298, 303, 308 and 313 in methanol. As seen on the electronic spectra (Fig. 4), the *cis/trans*-$[Co(en)_2Cl_2]^+$ complex ions have absorption maxima at different positions. In the course of reaction 1, a shift of the absorption maximum towards longer wavelengths was observed.

Kinetic experiments performed allowed the determination of the order of the reaction studied. The results obtained enable the conclusion that the reaction of the *cis/trans* isomerization of $[Co(en)_2Cl_2]Cl$ is of the first-order (Fig. 5) and proceeds according to the scheme:

$$A \xrightarrow{\text{ k }} B \qquad (2)$$

Based on the kinetic experimental data, the rate constants for the isomerization reaction were determined. Table 2 shows the influence of the temperature on the rate constants of the *cis/trans* isomerization.

As seen from Table 2, with a rise in the temperature a value of the rate constant of reaction studied increases. The activation parameters for the isomerization reaction of *cis/trans*-$[Co(en)_2Cl_2]Cl$ are as follows: $E_a = 28.44$ kJ, $\Delta H = 25.93$ kJ/mol and $\Delta S = 25.9$ J/K.

Based on the kinetic data obtained, the dissociative mechanism for the studied coordination compound has been proposed (Scheme 1). A substrate of the reaction is the *cis*-$[Co(en)_2Cl_2]Cl$ (Scheme 1a). In the first phase of the isomerization

Fig. 4 Absorbance changes for the isomerization reaction of *cis/trans*-[Co(en)$_2$Cl$_2$]Cl (C = 004 M, T = 313 K)
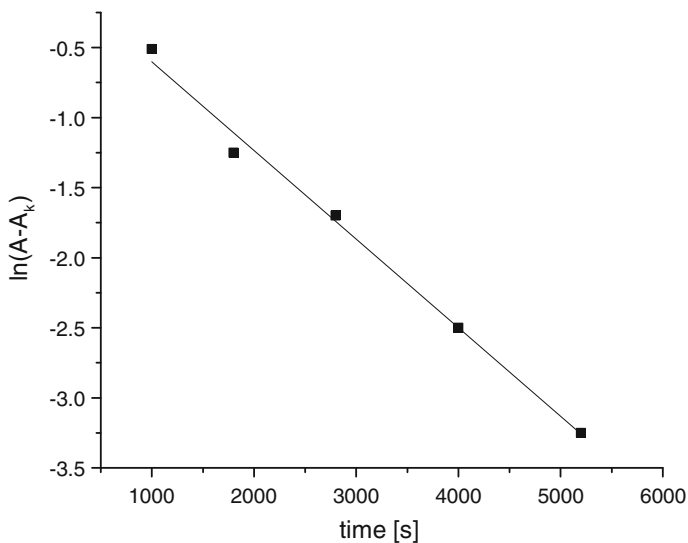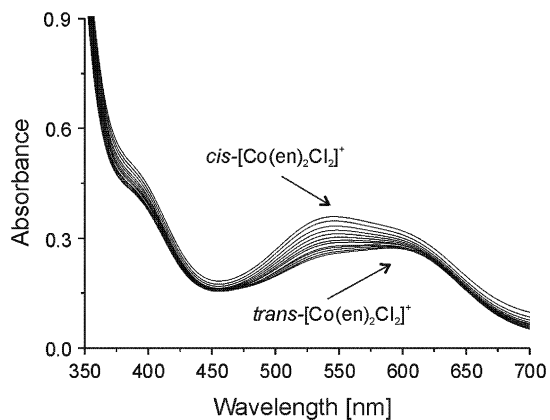
Fig. 5 The linear function of ln(A–A$_k$) versus time for the isomerization reaction of [Co(en)$_2$Cl$_2$]Cl complex

Table 2 The rate constants for the isomerization reaction *cis/trans*-[Co(en)$_2$Cl$_2$]Cl

| c (mol/L)	T (K)	k$_{obs}$ (s^{-1})
0.01	293	$2.62 \times 10^{-4} \pm 0.50 \times 10^{-4}$
0.01	298	$3.30 \times 10^{-4} \pm 0.03 \times 10^{-4}$
0.01	303	$3.51 \times 10^{-4} \pm 0.02 \times 10^{-4}$
0.01	308	$4.57 \times 10^{-4} \pm 0.04 \times 10^{-4}$
0.01	313	$5.75 \times 10^{-4} \pm 0.05 \times 10^{-4}$

reaction, the bond between the nitrogen atom derived from ethylenediamine and cobalt(III) ion is broken (Scheme 1b). The complex compound with the reduced coordination number changes the bond angle between central atoms. Ligands change their position to some extent as a result of the turnover (Scheme 1c). In the next step of the process the nitrogen atom derived from ethylenediamine is coordinated to cobalt(III). Ligands are in the *trans* position (Scheme 1d). During the whole process, bonds between cobalt(III) and chloride ions remain indissoluble.

The isomerization reaction of $[Co(en)_2Cl_2]Cl$ has been already studied [28] by Watts and Lantzke in non-aqueous solvents such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and N,N-dimethylacetamide (DMA) at five temperatures ranging from 293 to 313 K. They found that the bond between ethylenediamine and cobalt(III) ion in *cis*-$[Co(en)_2Cl_2]Cl$ complex becomes more stable in the order DMSO > DMF > DMA. This series of solvents has been arranged on the basis of the rate constants of reactions. The solvents order can be explained taking into account that a process of solvation has a big impact on the rate of reaction. The highest bond stability in DMSO can be explained in terms of the strongest solvating properties of DMSO molecules due to the DMSO smaller steric structure in comparison with DMF and DMA. When comparing DMF and DMA solvating properties, it turned out that the most important factor is an energy of hydrogen bonds, which is higher in DMA than in DMF. It was proven by Tomikawa and co-workers [29] on example of the clathrate compounds.

Moreover, from the comparison of values of the reaction rates and activation parameters for the *cis*-$[Co(en)_2Cl_2]Cl$ isomer it is apparent that for each complex values of E_a and ΔS are solvent dependent [29]. They decrease in the order DMF > DMA > H_2O > DMSO in the case of DMF being exceptionally high. However, when comparing the results obtained in the work [29] and the results obtained in in this work in methanolic solutions it turns out that in methanol the value of E_a is even higher being 28.44 kJ/mol than that characteristic for DMF (24.2 kJ/mol).

Conclusions

The TG–MS, TG–FTIR as well as DSC techniques have successfully been applied to determine thermal properties of the *cis*-$[Co(en)_2Cl_2]Cl$ and *trans*-$[Co(en)_2Cl_2]Cl$ complex compounds. It has been found that the geometrical configurations of both complexes studied do not influence the way of their thermal transformations. Their decompositions are multistep processes accompanied by the complex reduction and oxidation reactions. According to the TG–FTIR and TG–DSC–MS results concerning thermal decompositions of the *trans*-$[Co(en)_2Cl_2]Cl$ and *cis*-$[Co(en)_2Cl_2]Cl$ complexes both isomers demonstrate the tendency to bound the surface water, however, the *cis* isomer has a greater sorption ability. The analysis of MS spectra shows that a factor which reduces Co(III) to Co(II) is a nitrogen atom of ethylenediamine, which is simultaneously oxidized to molecular N_2. Thus, it can be supposed that redox processes undergoing in the case of isomers studied consist of the intramolecular processes of the electron transfer.

(a) **(b)**

(d) **(c)**
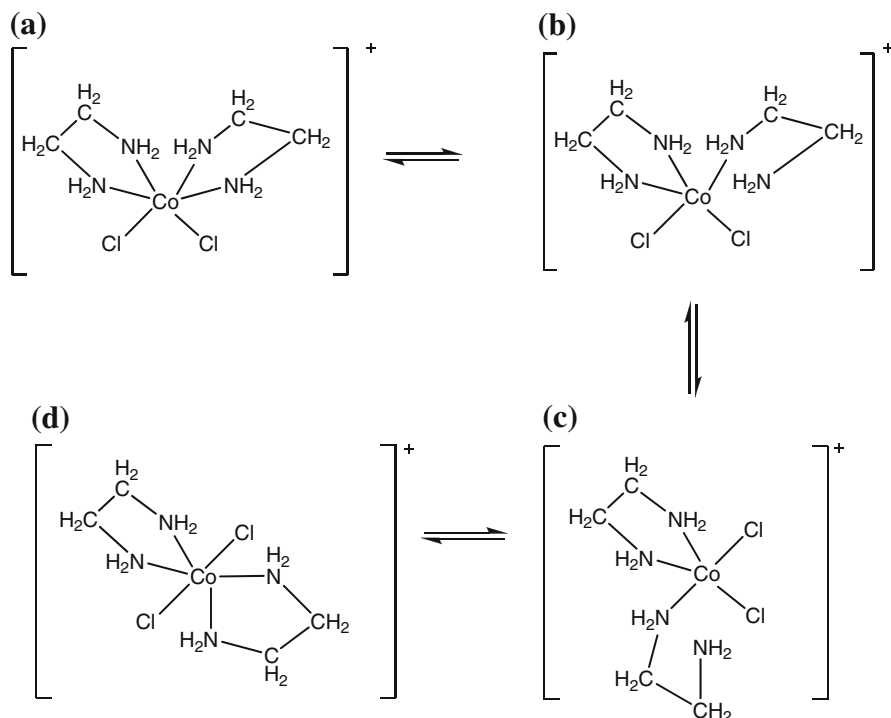
Scheme 1 The isomerization reaction of *cis/trans*-[Co(en)$_2$Cl$_2$]Cl

On the basis of the kinetic data, it has been found that the *cis–trans* isomerization of [Co(en)$_2$Cl$_2$]Cl is the first order reaction. The rate constant increases with the temperature. Among the parameters of activation, the change of entropy is positive and contributes to the transition of the isomer *cis* in *trans*. The changes of enthalpy and entropy of the activation have similar positive values. A positive enthalpy of activation hinders the reaction. However, the entropy change has a greater impact and, therefore, it is possible to observe the proceeding reaction. Furthermore, it has been found that the *cis/trans* [Co(en)$_2$Cl$_2$]Cl isomerization proceeds according to the dissociative mechanism.

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