The Solid-Phase Racemization of *l-cis*-$[Cr(en)_2Cl_2]Cl\cdot H_2O$[1]

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Abstract: The compound *l-cis*-$[Cr(en)_2Cl_2]Cl\cdot H_2O$ was found to undergo racemization when heated in the solid phase. Studies of both the racemization and dehydration processes indicate that this racemization occurs only during dehydration. The racemization has been interpreted in terms of an aquation–anation pathway. The complexes *d-cis*-$[Co(en)_2Cl_2]Cl\cdot H_2O$, *d*-$[Co(en)_3]I_3\cdot H_2O$, and *d*-$[Co(en)_3](NCS)_3$ also racemize in the solid state when heated, but probably by a different mechanism.

Since it was first noted that $K_3[Cr(C_2O_4)_3]\cdot 2H_2O$ undergoes racemization in the solid phase,[3] frequent references have been made to the solid-state racemizations of the trisoxalato complexes of cobalt(III) and chromium(III). Studies of the racemization of the strychnine salts of $[Cr(C_2O_4)_3]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$ and of $K_3[Cr(C_2O_4)_3]$ have led to a suggestion that lattice water may play an important role in these processes.[4,5] Recently, "$K_3[Rh(C_2O_4)_3]\cdot 3.5H_2O$" has been shown to be $K_6[Rh(C_2O_4)_3][Rh(C_2O_4)_2(HC_2O_4)(OH)]\cdot 6H_2O$.[6] It has been proposed that the optically active oxalato complexes of cobalt(III) and chromium(III) may be analogous.[7]

A recent study of the pressure-induced solid-state racemization of $K_3[Co(C_2O_4)_3]\cdot H_2O$ has shown that increased pressure accelerates this racemization.[8] It was suggested that this is consistent with a trigonal twist mechanism, but again the lattice water may be playing an important role.

We have observed that when *l-cis*-$[Cr(en)_2Cl_2]Cl\cdot H_2O$ is heated in the solid phase, it also undergoes racemization. Preliminary studies on *d-cis*-$[Co(en)_2Cl_2]Cl\cdot H_2O$, *d*-$[Co(en)_3]I_3\cdot H_2O$, and *d*-$[Co(en)_3](NCS)_3$ indicate that they behave similarly, suggesting that such racemization is not uncommon at elevated temperatures provided the complex in question is sufficiently stable toward decomposition. This paper describes studies on the thermal racemization of *l-cis*-$[Cr(en)_2Cl_2]Cl\cdot H_2O$ and suggests a mechanism for this process.

Experimental Section

Preparation of Compounds. The compounds *d-cis*-$[Cr(en)_2Cl_2]Cl\cdot H_2O$,[9] *l-cis*-$[Cr(en)_2Cl_2]Cl\cdot H_2O$,[10] *d-cis*-$[Co(en)_2Cl_2]Cl\cdot H_2O$,[11] and *d*-$[Co(en)_3]I_3\cdot H_2O$[12] were prepared by known methods, and *d*-$[Co(en)_3](NCS)_3$ was prepared from the resolved iodide by metathesis. Elemental analyses and specific rotations are shown in Table I.

Physical Measurements. Infrared and visible spectra, differential thermal analyses (DTA), thermogravimetric analyses (TGA), and X-ray powder patterns are obtained as described previously.[13] Optical activity was measured with a ETL-NPL Bendix automatic polarimeter (Type 143A) using 1-cm sample cells. The specific rotations reported for *l-cis*-$[Cr(en)_2Cl_2]Cl\cdot H_2O$ are extrapolated values. These were obtained for approximately 0.1% solutions in a methanol–water mixture (70% methanol by volume) by extrapolating plots of log $[\alpha]^{25}{}_D$ *vs.* time linearly back to the time when the solutions were prepared. Generally, six to eight readings of optical activity were taken over a 30–45-min period for each extrapolation. The reported uncertainties are deviations from the mean for two such extrapolations. The specific rotation of unheated *l-cis*-$[Cr(en)_2Cl_2]Cl\cdot H_2O$ was $[\alpha]^{25}{}_D$ +427 ± 11° (eight readings taken at various times during the course of this study). The optical rotations reported for other complexes are not extrapolated values.

Elemental analyses were carried out in the University of Illinois laboratories by Mr. Josef Nemeth and his staff.

Racemization and Dehydration Studies. An Abderhalden apparatus containing xylene was used to maintain a temperature of 138 ± 2°. Other temperatures were maintained within ±1–2° by use of the temperature control device and oven of the previously described thermobalance.[13] Generally, 0.1–0.3 g of sample was employed in each experiment. Samples heated in the Abderhalden apparatus were contained in uncapped 5-ml vials unless otherwise specified. The rate of dehydration was followed at several different temperatures by measuring loss of weight on the thermobalance.

Two separate preparations of *l-cis*-$[Cr(en)_2Cl_2]Cl\cdot H_2O$ were used in this investigation. The samples were not pulverized unless otherwise stated and were stored between experiments in dark, tightly stoppered bottles. They were not evacuated or stored in a desiccator, since it was thought that perhaps dehydration under desiccation would lead to racemization.

Results

Racemization. When *l-cis*-$[Cr(en)_2Cl_2]Cl\cdot H_2O$ was kept in dark, stoppered bottles at room temperature, it showed no loss of optical activity even after 4 years. However, when this compound was heated in an open vial at 120° or above, racemization was evident. The specific rotation of this complex as a function of time at 120, 138, 140, 160, and 180° is shown in Figure 1.

At each temperature, racemization stopped before complete loss of optical activity. At 120 and 140°, there was an initial increase in specific rotation apparently due to the loss of lattice water (molecular weight decreases).

Although fairly good agreement in final rotations was obtained at each temperature, the rates of racemization were not always the same for seemingly duplicate experiments. Furthermore, the results of the experiments at 138° appear to be inconsistent with those at 140 and 160°; while the data for the runs at 120, 140, 160, and

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Table I. Elemental Analyses and Specific Rotations

	Calcd, %				Found, %				
	C	H	N	H_2O	C	H	N	H_2O	$[\alpha]^{25}D$,[a] deg
dl-cis-$[Cr(en)_2Cl_2]Cl \cdot H_2O$	16.19	6.12	18.88	6.07	16.02	6.08	18.93	6.05	...
l-cis-$[Cr(en)_2Cl_2]Cl \cdot H_2O$	16.19	6.12	18.88	6.07	16.25	6.12	18.46	6.09	+422
d-cis-$[Co(en)_2Cl_2]Cl \cdot H_2O$	15.82	5.93	18.45	5.93	15.87	5.92	18.15	5.94	+741
d-$[Co(en)_3]I_3 \cdot H_2O$	11.27	4.07	12.98	2.82	11.48	3.96	13.11	2.86	+80.5
d-$[Co(en)_3](NCS)_3$	26.13	5.81	30.53	...	26.01	5.79	30.59	...	+123.8

[a] The specific rotations for *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ and *d-cis*-$[Co(en)_2Cl_2]Cl \cdot H_2O$ were obtained using approximately 0.1% solutions in a 70% methanol–30% water mixture. The values for *d*-$[Co(en)_3]I_3 \cdot H_2O$ and *d*-$[Co(en)_3](NCS)_3$ were obtained using approximately 0.4% aqueous solutions.

180° suggest greater racemization at higher temperatures, the degree of racemization at 138° was greater than that at any of the other temperatures except 180°. However, the rate and extent of racemization were found to depend not only on temperature, but also on the thickness of the sample bed. This appears to explain why more racemization occurred at 138° than at 140 or 160° in earlier experiments. When *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot HCl$ was heated at 120, 140, 160, or 180°, it was held in a relatively shallow cup having a large opening. In the experiment in which it was heated at 138°, it was contained in a narrow sample vial having a small opening. Effectively, this led to greater sample thickness and hence more racemization. For samples of equal thickness, the extent and rate of racemization increase with increasing temperature.

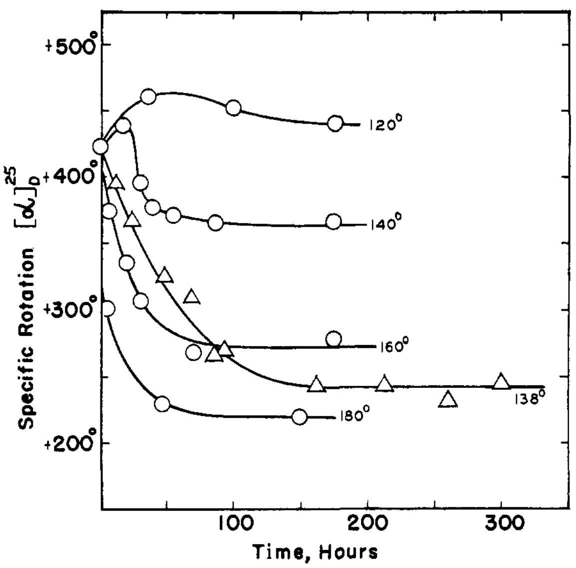

Figure 1. The temperature dependence of the thermal racemization of *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$.

The cessation of racemization after a certain time and the effects of temperature, particle size, and sample thickness all suggest that evolved lattice water plays a dominant role in the reaction. A further indication of this is observed when a sample is heated in a closed container. Under these conditions, nearly complete racemization occurs.

When partially racemized samples were allowed to cool to room temperature, they picked up water from the atmosphere. When reheated (to 180° at a rate of 2–5°/min), they underwent a slight additional loss of optical activity. In contrast, when samples which had not been previously heated were raised to the temperature of 180° at a rate of 1–2°/min, nearly complete racemization occurred.

No conclusive evidence of racemization was obtained when *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ was left in a vacuum desiccator at room temperature. After 2 months *in vacuo* over phosphorus(V) oxide, one sample had a specific rotation of +419 ± 11°. However, it is possible that racemization might occur if sufficient amounts of complex were employed for an extended length of time.

Dehydration. The results described in the previous section seem to indicate that the dehydration of *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ is related in some fashion to its racemization. Because of this, the dehydration of this complex was investigated in some detail.

Table II shows the loss of mass of *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ as a function of time at 140°. This experiment was conducted on the same sample as the study of the racemization at 140° shown in Figure 1. After the sample had been heated for 17.2 hr on the thermobalance, a portion was removed and its rotation measured. Similarly, other portions were removed at each of the subsequent times listed in Table II and their optical activities measured. The mass loss shown for those samples is a calculated value and is that which would have been observed had no material been removed. In this fashion a final per cent loss of mass of 6.11 was obtained. A loss of 1.00 mole of water per mole of complex corresponds to a per cent mass loss of 6.07.

Table II. The Dehydration of *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ as a Function of Time at 140°

Time, hr	Mass loss, g[a]	% mass loss
0.25	0.0101	3.86
0.5	0.0128	4.89
1.0	0.0137	5.23
1.5	0.0138	5.27
5.2	0.0141	5.39
17.2	0.0142	5.42
29.2	0.0147 (calcd)[b]	5.62
41.1	0.0152 (calcd)	5.81
54.6	0.0160 (calcd)	6.11
90.7	0.0164 (calcd)	6.26
175.0	0.0160 (calcd)	6.11

[a] Sample mass = 0.2618 g. [b] For method of calculation, see text.

Similar experiments were conducted at 120, 160, and 180°. In each case, loss of mass was much more rapid than racemization. At 160°, a 5.92% loss of mass was observed within 35 min, at which time $[\alpha]^{25}D$ +468 ± 14°. Significantly, at 140° the racemization and the

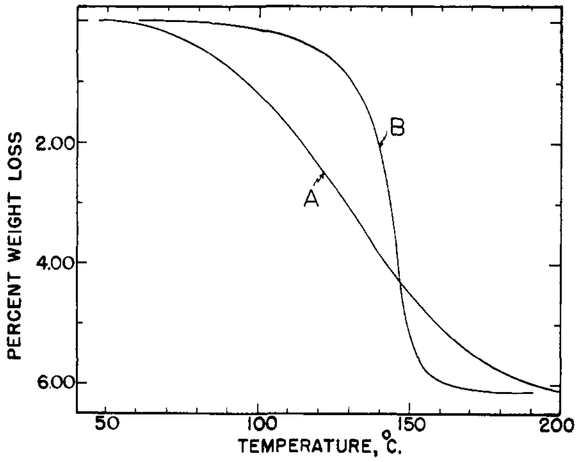

Figure 2. The TGA curves of *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ (A) and *dl-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ (B).

loss of mass both came to a stop between 41.1 and 54.6 hr. Seemingly, racemization occurs only during dehydration, but not all of the evolved water takes part in the racemization.

When *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ was heated at a rate of 1°/min, mass loss began at approximately 60°. There was an inflection point in the TGA curve at 130–140°, and the dehydration process was complete at 190–200°. In contrast, *dl-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$[14] began to lose water at 80°, an inflection occurred at 145°, and the loss of mass ceased at approximately 170°. The TGA curves of both compounds are shown in Figure 2. The DTA curves of *dl-* and *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ are shown in Figure 3. The optically active complex shows a very broad endothermic peak centered at approximately 150°. This coincides roughly with dehydration and racemization. A sharp exothermic peak of unknown origin occurs at 206°. Since no decomposition was evident at this temperature, the peak may correspond to a lattice change. Since this transition did not appear to be related to the racemization process, it was not investigated further.

Dehydration of *dl-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ resulted in a relatively sharp endothermic peak centered at 140–145°. No exothermic peak was noted at 206°, but one began to appear at approximately 240°. This might have been indicative of decomposition since the sample began to take on a brown cast at that temperature.

The nonisothermal kinetic methods of Freeman and Carroll[15] and of Fuoss, Salyer, and Wilson[16] were applied to the TGA data. For the dehydration of *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$, the activation energy, E_a, was found to be 12 ± 1 kcal mole^{-1}, while for the optically inactive compound, $E_a = 40 \pm 3$ kcal mole^{-1} (where the uncertainties are estimated). Clearly, the process of dehydration is markedly different for these two substances.

X-Ray and Spectral Data. No evidence was found for any decomposition during the course of these thermal studies. The visible solution spectra of optically active, racemic, and racemized *cis*-$[Cr(en)_2Cl_2]Cl$ agreed with each other and with literature values[16,17] within experimental error. Absorption maxima were found at 528 mμ (log ε 1.90) and 402 mμ (log ε 1.91). The visible mull spectra of each of these complexes exhibited maxima at 528–530 and 403 mμ, in agreement with literature values for the reflectance spectrum of this compound (maxima at 530 and 403 mμ).[18,19]

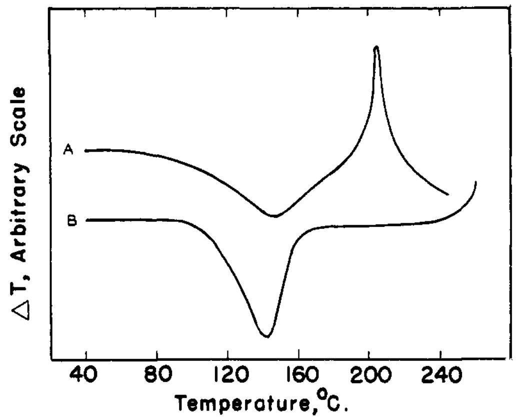

Figure 3. The DTA curves of *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ (A) and *dl-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ (B).

The main reflections from X-ray powder patterns of a series of *cis*-$[Cr(en)_2Cl_2]Cl$ complexes are shown in Table III. As can be seen, *dl-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ and *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ have different crystal structures. It was found that, as *dl-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ was dehydrated, only moderate changes occurred in its X-ray powder pattern. However, as *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ was heated, much greater changes were evident in the powder patterns. In this case, the crystal change seemed to parallel racemization rather than dehydration. As noted previously, dehydration was initially very rapid at high temperatures, but racemization proceeded slowly (in open containers). The observed changes in the powder patterns were also slow except when the complex was heated in a closed container (under which conditions racemization was rapid).

Infrared spectral changes also accompanied the dehydration and racemization of *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$. However, the changes are small and the spectra of *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$, *rac-cis*-$[Cr(en)_2Cl_2]Cl$, *dl-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$, and *dl-cis*-$[Cr(en)_2Cl_2]Cl$ are essentially the same.

It should be noted that the infrared spectra of *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ taken immediately after extended heating (racemization had ceased) frequently showed the presence of water. This might suggest that dehydration sometimes stops before all the lattice water has been evolved. However, it is possible that the water noted in the infrared spectrum was picked up from the atmosphere between the time the sample was removed from the heating apparatus and the time the spectrum was obtained.

Racemization of Other Complexes. In order to gain some idea of how typical the racemization of solid

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(14) Since the unresolved *cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ and the racemic *cis*-$[Cr(en)_2Cl_2]Cl$ obtained by solid-phase racemization of *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ differ in some respects, the first is designated by the prefix *d-* while the prefix *rac-* is used for the second.

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(18) L. E. Slaten and C. S. Garner, *J. Phys. Chem.*, **63**, 1214 (1959).

(19) W. W. Wendlandt and C. H. Stembridge, *J. Inorg. Nucl. Chem.*, **27**, 575 (1965).

Table III. The Prominent Lines of the X-Ray Powder Patterns of Several *cis*-$[Cr(en)_2Cl_2]Cl$ Complexes[a]

d, Å	*d*, Å
dl-cis-$[Cr(en_2Cl_2]Cl \cdot H_2O \xrightarrow{\Delta}$	*dl-cis*-$[Cr(en)_2Cl_2]Cl$
10.28 (s)	10.60 (s)
7.10 (m)	6.97 (s)
5.95 (s)	6.00 (s)
5.31 (w)	5.28 (s)
5.15 (w)	4.87 (m)
4.87 (w)	3.57 (m)
4.77 (w)	3.50 (m)
4.12 (m)	3.35 (m)
3.54 (m)	3.10 (w)
3.45 (w)	2.98 (w)
3.30 (w)	2.37 (w)
3.21 (w)	2.29 (w)
3.04 (s)	
2.88 (m)	
2.74 (m)	
2.41 (w)	
2.32 (w)	
2.26 (w)	
2.23 (w)	
l-cis-$[Cr(en)_2Cl_2]Cl \cdot H_2O \xrightarrow{\Delta}$	*rac-cis*-$[Cr(en)_2Cl_2]Cl$
11.86 (s)	6.89 (s)
8.41 (m)	5.33 (s)
6.41 (w)	5.17 (s)
6.16 (s)	4.22 (m)
5.84 (m)	3.63 (s)
5.66 (s)	3.48 (w)
5.38 (w)	3.23 (m)
4.76 (w)	3.05 (w)
4.56 (w)	2.95 (w)
4.30 (w)	2.76 (s)
4.15 (w)	2.34 (w)
3.91 (w)	2.30 (w)
3.79 (w)	2.25 (w)
3.47 (m)	2.11 (w)
3.26 (w)	1.98 (w)
3.10 (w)	
2.93 (s)	
2.85 (w)	
2.71 (w)	
2.64 (w)	
2.38 (w)	

[a] s = strong, m = medium, w = weak.

l-cis-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ is, several other complexes were investigated. The cobalt compound, *d-cis*-$[Co(en)_2Cl_2]Cl \cdot H_2O$, was found to undergo racemization. When heated to 160° at a rate of 1°/min, this complex lost all of its lattice water (5.94% mass loss as compared to a calculated value of 5.93%). After this heating, the specific rotation was $[\alpha]^{25}\text{D}$ +720 ± 12° compared with an initial value of +714 ± 8°. During an additional 24.0 hr at 160°, no further mass loss was observed. However, nearly complete racemization resulted, $[\alpha]^{25}\text{D}$ +9.3 ± 0.1°. Visible spectra and elemental analyses indicated that no conversion to the *trans* isomer or decomposition had taken place.

When *d*-$[Co(en)_3]I_3 \cdot H_2O$ was heated to 110° at a rate of 1°/min, a loss of mass of 2.86% was observed (calculated for one molecule of water per complex molecule, 2.82%). After this, the specific rotation at the sodium D line was +79.4° compared to an initial value of +80.5°. After heating at 140–143° for 18–20 hr, the specific rotation was +37.9°. After heating at 170° for 14–16 hr, the complex was completely racemized. This racemization was not unexpected, since this compound had previously been reported to racemize when heated at 110° in a sealed tube.[12]

The complex *d*-$[Co(en)_3](NCS)_3$ lost 0.06% in mass when heated to 100° at a rate of 1°/min. The specific rotation changed from +123.8 to +114.2°. After an additional 16 hr at 145°, the specific rotation fell to +84.2°. No mass loss was observed during this additional heating, and the visible spectrum and an elemental analysis gave no evidence of decomposition.

Discussion

The behavior of *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ is similar to that found for the racemization of $(stry)_3$-*d*-$[Cr(C_2O_4)_3] \cdot 12H_2O$ in the solid state.[5] In the case of this oxalato complex, it has been suggested that the lattice water takes part in the reaction in some manner. Exactly how this occurs is not known. Studies on the pressure-induced racemization of $K_3[Co(C_2O_4)_3] \cdot 2.6H_2O$ have led to the suggestion that a trigonal twist mechanism might be involved in the solid-phase racemization of the oxalato complexes. If so, the water could simply assist this twist either by providing the required energy or by some type of intermolecular interaction. However, it is by no means conclusive that a twist mechanism is operative. It is just as plausible that the water actually enters the coordination sphere, as it does in the racemization of these complexes in the aqueous solution[20] (although aquation would be followed by anation in the solid-phase racemization).

Likewise, *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ might racemize *via* a twist mechanism. However, it seems more probable that the mechanism involves the entrance and emission of water from the coordination sphere. Three steps are proposed. In the first step, the lattice water begins to escape from the crystal. Reaction 2 then occurs, followed by anation and racemization.

$$l\text{-}cis\text{-}[Cr(en)_2Cl_2]Cl \cdot H_2O \longrightarrow l\text{-}cis\text{-}[Cr(en)_2Cl_2]Cl + H_2O \tag{1}$$

$$l\text{-}cis\text{-}[Cr(en)_2Cl_2]Cl + H_2O \longrightarrow l\text{-}cis\text{-}[Cr(en)_2(H_2O)Cl]Cl_2 \tag{2}$$

$$l\text{-}cis\text{-}[Cr(en)_2(H_2O)Cl]Cl_2 \longrightarrow rac\text{-}cis\text{-}[Cr(en)_2Cl_2]Cl + H_2O \tag{3}$$

Thermoanalytical studies of the deaquation of *cis*-$[Cr(en)_2(H_2O)_2]Cl_3 \cdot 2H_2O$ and *cis*-$[Cr(en)_2(H_2O)Cl]Cl_2$ indicate that anation could proceed readily (and rapidly) under conditions which lead to the racemization of *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$.[21] Racemization could occur in the second step as well as the third. However, in aqueous solution, this aquation reaction proceeds with retention of configuration and hence only mutarotation.[10]

Apparently, as *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ is heated at temperatures below 120° (at least in a loosely packed sample), reaction 1 occurs but not reactions 2 and 3. At higher temperatures, ample energy is provided and a sufficiently high water vapor pressure builds up in the sample so that reaction 2 can take place. However, much of the water escapes without reacting. Because water escapes from the system without entering into reaction 2, only partial racemization occurs.

At higher temperatures, more energy is provided so that aquation can occur more readily. When a sample is heated in a closed container, the water vapor is in contact with *l-cis*-$[Cr(en)_2Cl_2]Cl$ for a longer period,

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(20) D. R. Stranks and R. G. Wilkins, *Chem. Rev.*, **57**, 743 (1957).

(21) W. W. Wendlandt and W. R. Robinson, *J. Inorg. Nucl. Chem.*, **26**, 531 (1964).

and reactions 2 and 3 occur to a greater extent. More contact between this complex and the water vapor is also possible when the water is forced to travel through more sample to escape. Hence, more aquation and racemization occur when there is a thicker sample bed.

It is more difficult to explain why nearly complete racemization occurs when a sample is heated slowly (1–2°/min) to 180° while only partial racemization takes place when the sample is rapidly heated to this temperature and then kept there for an extended period. The explanation may be as follows. As the complex is heated, a certain amount of dehydration occurs at a particular temperature, but, before this water has escaped into the atmosphere, the temperature has increased. At the higher temperature aquation and anation are more rapid than at the lower temperature. Had the entire process occurred at the higher temperature, the water would have escaped more readily leaving less to react in the aquation step.

The racemization could proceed through the formation of a trigonal bipyramid intermediate or transition state. Such an intermediate has been postulated to explain the behavior of *cis*-$[Cr(en)_2Cl_2]^+$ and its cobalt analog, *cis*-$[Co(en)_2Cl_2]^+$, in solution. In water, *l-cis*-$[Cr(en)_2Cl_2]^+$ undergoes mutarotation with the formation of *l-cis*-$[Cr(en)_2(H_2O)Cl]^{2+}$.[10] Complete loss of optical activity then occurs as this aquo complex isomerizes. This is the same mode of racemization as observed for *d-cis*-$[Co(en)_2Cl_2]^+$ in aqueous solutions.[22] In methanol, *cis*-$[Cr(en)_2Cl_2]^+$ has been found to undergo a direct *cis*-to-*trans* isomerization. The racemization process has not been studied; however, it is probably like that of *d-cis*-$[Co(en)_2Cl_2]^+$ which also undergoes a *cis*-to-*trans* isomerization in methanol. In the case of the cobalt compound, racemization has been found to occur at the same rate as radiochloride exchange.[22,23] Thus racemization is accompanied by *cis–trans* isomerization and a dissociative process involving a symmetrical five-coordinate intermediate has been postulated. The formation of the *trans* isomer in methanol is probably the result of thermodynamic factors.

Likewise, the formation of *cis*- rather than *trans*-$[Cr(en)_2Cl_2]Cl$ in the solid-phase aquation–anation of *l-cis*-$[Cr(en)_2Cl_2]Cl$ could be due to the thermodynamic factors (greater thermodynamic stability of the *cis* salt). However, the reaction course could be controlled by topochemical factors. It is noteworthy that *d-cis*-$[Co(en)_2(H_2O)Cl]Cl_2$ racemizes with the formation of *dl-cis*-$[Co(en)_2Cl_2]Cl$ when heated to 100° in the solid phase, and no *trans* isomer is formed.[24] The heat of formation of solid *dl-cis*-$[Co(en)_2Cl_2]Cl$ is $\Delta H^\circ_{298} = -175.1$ kcal mole^{-1}.[25]

In order to completely characterize the solid phase racemization of *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$, the question of how the reaction begins and proceeds through the solid should be answered. Since no color changes accompany either dehydration or racemization, this process could not be studied in any detail by optical methods. Furthermore, detailed kinetic studies have not been carried out. Therefore, any conclusions regarding these processes would necessarily be speculative.

Lest it now be concluded that all solid-phase racemizations require the presence of water, preliminary studies of *d-cis*-$[Co(en)_2Cl_2]Cl \cdot H_2O$, *d*-$[Co(en)_3]I_3 \cdot H_2O$, and *d*-$[Co(en)_3](NCS)_3$ should be considered. Although the racemization of *d-cis*-$[Co(en)_2Cl_2]^+$ in solution seems to be like that of *l-cis*-$[Cr(en)_2Cl_2]^+$, the solid-phase racemizations of the chloride salts of these two complex cations appear to be different. While the chromium compound was found to undergo racemization only during dehydration, the cobalt compound racemized largely after dehydration. Likewise, *d*-$[Co(en)_3]I_3 \cdot H_2O$ continued to racemize after all weight loss had been recorded at 110°. The anhydrous complex *d*-$[Co(en)_3](NCS)_3$ also racemized with no accompanying loss of weight.

Therefore, while the possibility of an aquation–anation path should be considered whenever racemization involving a hydrated solid complex is observed, this need not be the only path for such racemization. Further studies need to be undertaken to elucidate other modes of reaction.

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