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The Isomerization and Chloride Exchange of *trans*-Dichlorobis(1,2-diaminopropane)cobalt(III) Diaquohydrogen Chloride, *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$, in the Solid State

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The trans-to-cis isomerization and radiochloride-exchange reactions of solid *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$ were studied in static air. Isomerization occurs by ligand exchange in the presence of H_2O from the dehydration–dehydrochlorination reaction. At 120°, $53 \pm 4\%$ of the ligand exchanges lead to isomerization. The compounds *trans*-$[Co(pn)_2Br_2](H_5O_2)Br_2$, *trans*-$[Co(pn)_2Cl_2](H_5O_2)Br_2$, and *trans*-$[Co(pn)_2Br_2](H_5O_2)Cl_2$ also isomerize. Two possible mechanisms of isomerization are discussed—one an aquation–anation pathway and the second an electron-transfer pathway.

Introduction

There have been a number of coordination compounds of cobalt(III) and chromium(III) reported to undergo stereochemical change in the solid phase. For example, *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$,[1] *d-cis*-$[Co(en)_2Cl_2]Cl$,[1] *d*-$[Co(en)_3]I_3 \cdot H_2O$,[1,2] and a number of salts of $Co(C_2O_4)_3^{3-}$ and $Cr(C_2O_4)_3^{3-}$ [3–8] undergo racemization under various conditions. Trans-to-cis isomerization is found for $[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$,[9,10] $[Co(pn)_2Cl_2](H_5O_2)Cl_2$,[11] and $[Cr(pn)_2Cl_2]Cl \cdot 1.5H_2O$,[12] while cis-to-trans isomerization has been reported for *l-cis-β*-$[Co(LDDL)Cl_2]ClO_4 \cdot 3H_2O$,[13,14] $[Co(stien)_2Cl_2]Cl \cdot H_2O$,[15] and $[Cr(NH_3)_4Cl_2]Cl$.[16]

In solution these reactions are generally thought to involve ligand exchange or one-ended dissociation of a bidentate ligand (as in the racemization of $Cr(C_2O_4)_3^{3-}$).[17,18] In the solid state, ligand exchange involving aquation and anation has been suggested for the racemization of *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$[1] and the isomerization of *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$[10] largely on the basis of the apparent involvement of lattice water in these reactions. However, a twist mechanism has been suggested for the pressure-induced racemizations of *d*-$K_3[Co(C_2O_4)_3] \cdot nH_2O$,[6,7] *l*-$[Fe(phen)_3](ClO_4)_2 \cdot nH_2O$,[19] and *d*-$[Ni(phen)_3](ClO_4)_2 \cdot nH_2O$.[19,20] This mechanism can also give rise to cis–trans isomerization.[21] Even where stereochemical change occurs by ligand exchange, the solid-phase reaction may show more associative character than in solution. Studies of solid-phase anation reactions have led to suggestions that such reactions are essentially associative in nature, taking place by a concerted reaction in which the entering group exerts considerable influence.[22–24] Furthermore, recent work has suggested the importance of electron-transfer processes on thermal annealing of neutron-irradiated complexes and on metal exchange in solids.[25] While thermal annealing and isotopic exchange reactions generally occur with retention of configuration, an appreciable amount of isomerization occurs at least for $[Co(NH_3)_4(NO_2)_2]NO_3$.[26] Thus, stereochemical change within solids might proceed by some mechanism quite different from that involved for similar solution processes.

A study of *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$ was recently undertaken to provide more information about the reactions of coordination compounds within solids. This compound is well suited for such a study since its crystal structure[27] is known as are those of related compounds such as *trans*-$[Co(en)_2Cl_2](H_5O_2)Cl_2$[28,29] which do not isomerize. In addition, radiochloride-exchange studies can readily be conducted, and the solution chemistry of this compound has been extensively studied. Previously, studies of the dehydration–dehydrohalogenation reactions of this compound and related compounds were reported.[30–32] The present paper reports studies of the isomerization process.

Experimental Section

The compounds *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$[33,34] and *trans*-

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$[Co(en)_2Cl_2](H_5O_2)Cl$[35] were prepared as described elsewhere; *trans*-$[Co(pn)_2Br_2](H_5O_2)Br_2$ was prepared by analogy to its chloro analog starting with cobalt(II) acetate and using concentrated HBr in place of concentrated HCl. Labeled compounds of the type *trans*-$[Co(AA)_2Cl_2](H_5O_2)^*Cl_2$ were prepared by addition of chlorine-36-labeled hydrochloric acid (General Isotope Processing Co.) to cold concentrated aqueous solutions of *trans*-$[Co(AA)_2Cl_2]Cl$. In order to prepare the covalently labeled compounds, solutions of *trans*-$[Co(AA)_2Cl_2]Cl$ were allowed to aquate to $Co(AA)_2(H_2O)_2{}^{3+}$. Labeled HCl was added and the solutions were evaporated at room temperature to yield *trans*-$[Co(AA)_2{}^*Cl_2](H_5O_2)^*Cl_2$. This was collected by filtration and then dissolved in a minimum of cold water, and a large excess of unlabeled HCl was added to precipitate *trans*-$[Co(AA)_2{}^*Cl]$-$(H_5O_2)Cl_2$. The compound *trans*-$[Co(pn)_2Cl_2](H_5O_2)Br_2$ was prepared by addition of concentrated HBr to a cold concentrated solution of *trans*-$[Co(pn)_2Cl_2]Cl$, while *trans*-$[Co(pn)_2Br_2]$-$(H_5O_2)Cl_2$ was prepared in very low yields by addition of concentrated HCl to *trans*-$[Co(pn)_2Br_2]Br$. Both compounds were recrystallized from cold water by addition of the appropriate hydrohalic acid. Each of the aforementioned compounds was collected by filtration, air-dried prior to study, and analyzed as described elsewhere.[30] The substance *trans*-$[Co(pn)_2Cl_2]Cl$ was precipitated from a methanolic solution of *trans*-$[Co(pn)_2Cl_2]$-$(H_5O_2)Cl_2$ upon addition of ether and was dried *in vacuo* over P_2O_5.

The extent of isomerization of samples of *trans*-$[Co(pn)_2Cl_2]$-$(H_5O_2)Cl_2$ was determined by analysis of their visible spectra in absolute methanol. Three wavelengths, 453, 540, and 610 mμ, were used in routine analyses. The extinction coefficients for *trans*-$Co(pn)_2Cl_2{}^+$ at these wavelengths are 27.5, 8.7, and 38.7, respectively (in agreement with literature values[36]); for *cis*-$Co(pn)_2Cl_2{}^+$ the corresponding extinction coefficients were 21.1, 68.7, and 46.1.[37]

The amount of radioactive chlorine lost as HCl was determined by comparison of the radioactivity of the heated samples with that of a fresh sample from the same batch. The powdered samples were mounted (loosely packed) in an aluminum planchet and covered with Handi-Wrap to prevent disturbing the sample during subsequent handling. For each sample counted, an empirical calibration curve was constructed of activity as a function of relative sample thickness. For this purpose activity was measured as a function of sample mass. Sample densities were then measured and relative sample thickness was calculated assuming that all samples have the same packing characteristics. Several equivalent points along each curve were selected for determining per cent radiochloride retention, and the average percentage was reported.[38] Except where noted, samples used in exchange studies were heated in static air (650 Torr). To determine the amount of covalently bound labeled chloride in the trans-isomer portion of these samples, labeled ionic chlorides were removed by dissolving the compound in a minimum of cold H_2O and adding concentrated HCl to precipitate *trans*-$[Co(pn)_2{}^*Cl_2](H_5O_2)Cl_2$. The radioactivity of this material, when dried, was compared with an equivalent mass of the fresh sample (as described above). The cis isomer remains in solution. Blanks, run on unheated samples, exhibited 0.3–3.0% chloride exchange.

Samples were heated in a thermostated oil bath or on the sample pan of a thermobalance and were maintained within ±0.5°. Visible spectra were obtained on a Cary 14 recording spectrophotometer using 5-cm cells. Radioactivity levels were measured using a Tracorlab Versa/matic II Scaler with a thin-window Geiger–Müller tube. Other measurements made use of techniques and equipment previously described.[30]

Results

Isomerization Behavior.—Typical behavior for *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$ when it is heated isothermally is shown in Figure 1. Tga's of samples at various stages of heating indicate that the plateaus of Figure 1 correspond to complete dehydration–dehydrochlorination of the samples (yielding $[Co(pn)_2Cl_2]Cl$). This apparent cessation of isomerization usually occurs prior to complete isomerization.

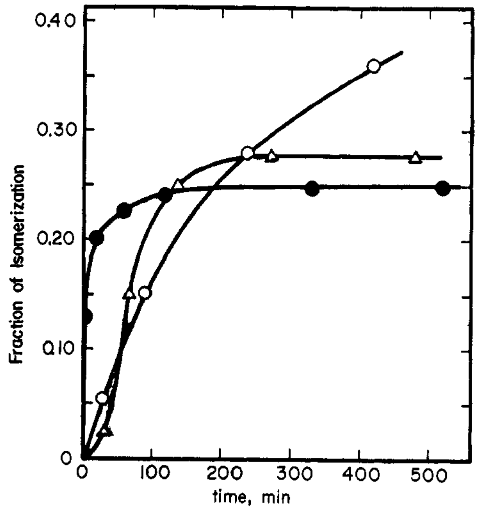

Figure 1.—The fraction of isomerization, α, as a function of time for *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$ heated in shallow sample beds: ○, 75°; △, 90°; ●, 110°.

Several factors were found to affect both the position of the plateau and the rate of isomerization. The lower the temperature for an isothermal study, the lower the rate of isomerization but the higher the plateau (Figure 1). As the sample bed is made thicker, the rate of isomerization slows, while the fraction of isomerization (α) levels at a higher value. In a very deep sample bed (as when the sample is heated in an nmr tube) isomerization is first observed at the top of the sample. *In vacuo*, the sample-bed thickness has a much smaller influence on rate and α than in static air. Reduction of pressure causes the rate of isomerization to increase, but the extent of isomerization decreases. The rate of isomerization increases as particle size is reduced, and the extent of isomerization increases if the samples are not completely dried.

These observations parallel dehydration–dehydrochlorination behavior, and they suggest that water plays an important role in the isomerization process. In fact, a linear correlation between per cent isomerization and per cent dehydration–dehydrochlorination has been reported recently for *trans*-$[Co(pn)_2Cl_2]$-$(H_5O_2)Cl_2$.[39] We have also found that when *trans*-$[Co(pn)_2Cl_2]Cl$ is allowed to pick up water from the atmosphere and then heated in a sealed vial, nearly complete isomerization occurs. The isomerization of *trans*-$[Cr(pn)_2Cl_2]Cl\cdot 1.5H_2O$ probably also involves H_2O.[12] In fact, we have observed isomerization of *trans*-$[Co(pn)_2Cl_2]Cl$ only when at least small amounts of water were present. On the other hand, *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$ will not isomerize when heated in a sealed vial which suggests that the isomerization is retarded by HCl.[40]

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[37] Based on these extinction coefficients, the spectrum reported for *cis*-$Co(pn)_2Cl_2{}^+$ (R. Tsuchiya, K. Murai, A. Uehara, and E. Kyuno, *Bull. Chem. Soc. Jap.*, **43**, 1383 (1970)) contains about 23% of the trans isomer. There may also be some trans isomer in the "*cis*"-$Co(pn)_2Cl^+$ of the present study. The isomerization percentages may therefore be high, but that does not affect the arguments presented.

[38] In initial experiments on *trans*-$[Co(pn)_2{}^*Cl_2](H_5O_2)Cl_2$, the evolved radiochloride was also precipitated as AgCl and counted.

[39] R. Tsuchiya, K. Murai, A. Uehara, and E. Kyuno, *Bull. Chem. Soc. Jap.*, **43**, 1383 (1970).

[40] The isomerization could also be retarded by high partial pressures of water. However, it is known that *trans*-$Co(pn)_2Cl_2{}^+$ isomerizes when aqueous solutions are evaporated to dryness in the absence of HCl but not in its presence. Furthermore, recent work has shown that *cis*- and *trans*-$[Co(en)_2(H_2O)_2]Cl_3$ yield *cis*-$[Co(en)_2Cl_2]Cl$ during normal deaquation–anation, but the trans isomer is obtained in the presence of HCl from NH_4Cl: F. C. Chang and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, **32**, 3535 (1970).

Attempts to reduce data such as those in Figure 1 to a common rate law were complicated by the effects of sample-bed thickness and particle size. However, the rate law $-\log(1 - F) = kt^{1/2} + c$, where $F = \alpha_t/\alpha_\infty$,[41] gives a reasonable fit of data. This law was previously observed for dehydration–dehydrobromination of small particles of *trans*-[Co(pn)$_2$Br$_2$](H$_5$O$_2$)Br$_2$ under reduced pressure at low temperatures.[31] Sherriff and Galwey[42] have reported this rate law for the deammination of [Ni(NH$_3$)$_6$](ClO$_4$)$_2$ in a constant-volume system and have suggested that it may indicate a diffusion-controlled process. Except for a run at 75° for which k = 0.032 min$^{-1/2}$, the rate constants found in the present study fell in the range 0.10–0.18 min$^{-1/2}$ and showed no systematic variation with reaction temperature.[43] Sherriff and Galwey's results are similar.

Evidence was found for isomerization of *trans*-[Co(pn)$_2$Br$_2$](H$_5$O$_2$)Cl$_2$, *trans*-[Co(pn)$_2$Cl$_2$](H$_5$O$_2$)Br$_2$, and *trans*-[Co(pn)$_2$Br$_2$](H$_2$O$_5$)Br$_2$ but not for *trans*-[Co(en)$_2$Cl$_2$](H$_5$O$_2$)Cl$_2$ or *trans*-[Co(en)$_2$Br$_2$](H$_5$O$_2$)Br$_2$. The aforementioned propylenediamine complexes take on an olive brown coloration when heated. These olive brown materials exhibit spectra with more absorption in the 550-mμ region and less in the 450- and 600-mμ regions than the unheated samples, consistent with trans-to-cis isomerization. In addition, methanolic solutions of these olive brown substances gradually revert quantitatively to the trans isomers as evidenced by changes in their visible absorption spectra.[44] Such cis-to-trans isomerization for Co(pn)$_2$Cl$_2^+$ and Co(en)$_2$Cl$_2^+$ in methanol is well documented.[45–47]

Mass loss studies of *trans*-[Co(pn)$_2$Cl$_2$](H$_5$O$_2$)Br$_2$ and *trans*-[Co(pn)$_2$Br$_2$](H$_5$O$_2$)Cl$_2$ indicate scrambling of chloride and bromide ions during the dehydration and dehydrohalogenation which accompanies their apparent isomerization. For *trans*-[Co(pn)$_2$Cl$_2$](H$_5$O$_2$)Br$_2$ the higher the temperature used for isothermal dehydration–dehydrohalogenation, the lower the observed mass loss. This indicates loss of HCl in increasing amounts relative to HBr as the temperature is increased. In the same fashion *trans*-[Co(pn)$_2$Br$_2$](H$_5$O$_2$)Cl$_2$ loses more mass as the temperature used for dehydration–dehydrohalogenation is increased.

As reported earlier, *trans*-[Co(en)$_2$Cl$_2$](H$_5$O$_2$)Cl$_2$ yields crystalline *trans*-[Co(en)$_2$Cl$_2$]Cl by what appears to be a topotatic reaction.[30] Similarly, *trans*-[Co(en)$_2$Br$_2$](H$_5$O$_2$)Br$_2$ and *trans*-[Rh(en)$_2$Cl$_2$](H$_5$O$_2$)Cl$_2$ both yield crystalline products. This behavior contrasts that of the propylenediamine complexes studied here which all yield disorganized or microcrystalline product lattices. The X-ray powder pattern of [Co(pn)$_2$Br$_2$]Br obtained by dehydration–dehydrobromination shows only a single broad reflection peak at d = 9.21 Å and is similar to that of [Co(pn)$_2$Cl$_2$]Cl reported previously.[30] It is thought that disruption of the crystal lattice is a consequence of isomerization rather than of dehydration–dehydrohalogenation.

Radiochloride-Exchange Studies.—Studies of *trans*-[Co(pn)$_2$Cl$_2$](H$_5$O$_2$)*Cl$_2$ and *trans*-[Co(pn)$_2$*Cl$_2$](H$_5$O$_2$)Cl$_2$ indicate that ligand exchange occurs during isomerization. For example, when these compounds are heated at 120° for at least 90 min in a moderately shallow sample bed (0.5–1.0-cm thickness), complete chloride scrambling is observed.[48] Thus each of these compounds loses only 25% radioactivity (as H*Cl) under these conditions (see Table I). By contrast, *trans*-[Co(en)$_2$*Cl$_2$](H$_5$O$_2$)Cl$_2$ loses no radiochloride and *trans*-[Co(en)$_2$Cl$_2$](H$_5$O$_2$)*Cl$_2$ loses 50% when heated indicating the absence of scrambling. Ettle and Johnson[49] have previously reported that *trans*-[Co(en)$_2$*Cl$_2$](H$_5$O$_2$)Cl$_2$ loses no radiochloride upon heating. Schmidt and Rössler[50] have studied chloride exchange in *trans*-[Co(en)$_2$Cl$_2$]Cl and according to their data only about 1% ligand exchange should occur under our reaction conditions. Interestingly, Rössler[51] reported that chloride exchange in *trans*-[Co(pn)$_2$*Cl$_2$]Cl occurs initially at a very rapid rate ($t_{1/2}$ = 3.5 min at 150°) but then slows to a rate only slightly faster than that of *trans*-[Co(en)$_2$Cl$_2$]Cl ($t_{1/2}$ = 150 min).[50] The initial rapid ligand exchange might have been due to traces of water which we have found enhances both isomerization and ligand exchange.

TABLE I

PERCENTAGE RADIOCHLORIDE RETAINED DURING DEHYDRATION AND DEHYDROCHLORINATION AT 120°

	Total %* Cl$^-$ retention	%* Cl$^-$ retention in covalent positions of trans product
trans-[Co(pn)$_2$Cl$_2$](H$_5$O$_2$)*Cl$_2$	77.8 ± 3.5[a]	51.2 ± 2.6[a]
	74.2 ± 2.0	. . .
trans-[Co(pn)$_2$*Cl$_2$](H$_5$O$_2$)Cl$_2$	71.8 ± 2.2	49.5 ± 1.6
	73.1 ± 3.1	. . .
trans-[Co(en)$_2$Cl$_2$](H$_5$O$_2$)*Cl$_2$	48.0 ± 2.2	0.2 ± 0.4
trans-[Co(en)$_2$*Cl$_2$][H$_5$O$_2$)Cl$_2$	97.0 ± 4.7	97.2 ± 4.7

[a] All error limits are standard deviations calculated from sample counts.

The effects of particle size, sample-bed thickness, temperature, pressure reduction, and presence of moisture on the exchange parallel their effects on isomerization—greater ligand exchange being accompanied by greater isomerization. Although no isomerization is observed when *trans*-[Co(pn)$_2$Cl$_2$](H$_5$O$_2$)*Cl$_2$ is heated in a closed container, ligand exchange occurs.

If scrambling occurred before dehydration, reduction of pressure would not be expected to affect the per cent exchange. If it occurred after dehydration is complete, *trans*-[Co(pn)$_2$Cl$_2$](H$_5$O$_2$)*Cl$_2$ should lose 50% of its activity while *trans*-[Co(pn)$_2$*Cl$_2$](H$_5$O$_2$)Cl$_2$ loses none. Since 25% activity is lost, chloride exchange in *trans*-[Co(pn)$_2$Cl$_2$](H$_5$O$_2$)Cl$_2$ must occur during dehydration. Because chloride exchange and isomerization both occur during dehydration and because of the parallels noted (*vide supra*), we are led to conclude that isom-

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[41] α_t equals the fraction of isomerization at any time, t, and α_∞ equals the fraction of isomerization corresponding to the isomerization plateaus.

[42] R. A. Sherriff and A. K. Galwey, *J. Chem. Soc. A*, 1705 (1967).

[43] The temperatures studied, besides 75°, were 90, 104, 108, and 110°. Rate constants reported in ref 39 cannot be compared with those of the present study because no rate law was given. The 10 kcal mol^{-1} activation energy reported for isothermal mass loss, however, is probably low because of sample self-cooling (see ref 31 and 32). Furthermore, the assignment of an exothermic dta peak to trans–cis isomerization is highly speculative and deserves further study.

[44] A statistical scrambling of halides occurs.

[45] D. D. Brown and C. K. Ingold, *J. Chem. Soc.*, 2680 (1953); D. D. Brown and R. S. Nuholm, *ibid.*, 2696 (1953).

[46] B. Bosnich, C. K. Ingold, and M. L. Tobe, *ibid.*, 4074 (1965).

[47] R. C. Brasted and C. Hirayama, *J. Amer. Chem. Soc.*, **80**, 788 (1958).

[48] Complete dehydration–dehydrochlorination occurs under these conditions. However, only about 50% isomerization was generally observed. Thus both the cis and trans isomers are completely scrambled.

[49] G. W. Ettle and C. H. Johnson, *J. Chem. Soc.*, 1490 (1939).

[50] G. B. Schmidt and K. Rössler, *Radiochim. Acta*, **5**, 123 (1966).

[51] K. Rössler, Doctoral Thesis, University of Cologne, 1967; see also K. Rössler and W. Herr, *Angew. Chem., Int. Ed. Engl.*, **6**, 993 (1967).

erization occurs by ligand exchange (although the data do not exclude the possibility of a second, less important pathway).

The *trans*-$Co(pn)_2Cl_2^+$ remaining after partial dehydration of *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$ always shows some radiochloride exchange. The relative amounts of isomerization and chloride scrambling found for *trans*-$[Co(pn)_2Cl_2](H_5O_2)^*Cl_2$ at 120° are summarized in Table II. The results indicate that chloride scrambling leads to isomerization about 50% of the time, if it is assumed that the cis product is completely scrambled and contains 75% of the activity of *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$. No consistent correlation between this percentage and sample-bed thickness was observed. By comparison, 80% of the ligand exchange of *cis*-$[Co(en)_2Cl_2]Cl$ in methanol gives the trans product.[45,46]

TABLE II

COMPARISON OF PERCENTAGE ISOMERIZATION AND LIGAND EXCHANGE FOR *trans*-$[Co(pn)_2Cl_2](H_5O_2)^*Cl_2$ AT 120°

% isomerization	% covalent $^*Cl^-$ in *trans*-$Co(pn)_2Cl_2^+$	% Cl^- scrambling giving isomerization[b]
4.1 ± 0.3[a]	1.8 ± 0.3[a]	54.0 ± 5.5[a]
8.5 ± 0.4	5.2 ± 0.4	47.2 ± 2.9
13.4 ± 1.0	8.4 ± 0.8	47.9 ± 4.6
17.4 ± 0.4	8.6 ± 1.4	55.1 ± 4.0
21.1 ± 0.3	10.4 ± 0.8	56.2 ± 1.9
26.6 ± 0.4	16.8 ± 1.4	51.8 ± 2.1
26.7 ± 1.1	10.2 ± 0.4	64.0 ± 3.3
29.0 ± 0.9	19.8 ± 1.5	50.8 ± 2.6

[a] All error limits are standard deviations. [b] Method of calculation is shown for the last entry. The original *trans*-$[Co(pn)_2Cl_2](H_5O_2)^*Cl_2$ yields 29.0% cis (completely scrambled) and 71.0% trans (39.6% scrambled). Total chloride scrambling is then 29.0% + (0.710)(39.6%) or 57.1%. Thus 29.0/57.1 or 0.508 of the chloride exchanges lead to isomerization.

Discussion

Comparison with Solution Reactions.—The behavior of *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$ is similar to that of $[Co(pn)_2Cl_2]Cl$ and $[Co(en)_2Cl_2]Cl$ in solution[18,47] where isomerization also occurs by ligand exchange. In alcohols, where cis-to-trans isomerization is observed, water accelerates the isomerization and the rate of isomerization is less than that of ligand exchange just as in the solid. Evaporation of aqueous solutions yields the cis isomer in the absence of HCl while *trans*-$[Co(AA)_2Cl_2](H_5O_2)Cl_2$ is obtained in the presence of HCl. Since these stereochemical changes involve aquation and anation, it is tempting to propose an aquation–anation pathway for the solid-phase reaction. In this view aquation could result from the high effective concentration of water in the lattice due to its high mobility relative to charged species. This would permit a large number of encounters between H_2O and *trans*-$Co(pn)_2Cl_2^+$ or some reactive intermediate. Anation reactions within solids are, of course, well documented and can give rise to stereochemical change as in the cases of *d-cis*-$[Co(en)_2(H_2O)Cl]Cl_2$[52] and *cis*-$[Co(trien)(H_2O)Cl]Cl_2$.[53]

The *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$ undergoes ligand exchange at an appreciable rate while H_2O is being evolved, but ligand exchange for *trans*-$[Co(en)_2Cl_2](H_5O_2)Cl_2$ occurs at a significant rate only after H_2O has been evolved. Ligand exchange appears to lead to isomerization only in the presence of H_2O. The more rapid ligand exchange of *trans*-$Co(pn)_2Cl_2^+$ is also observed in solution and has been attributed to steric crowding at the reaction site caused by the methyl group of the propylenediamine ligand.[18,47]

The apparent lack of isomerization in the absence of water suggests an important energetic role for the water. It is difficult to see what this might be, but entering groups appear to be important in determining the rate of solid-phase anation reactions,[22–24] and they could also be important in determining the stereochemistry of the product. The presence of an acceleration caused by steric crowding on the one hand and the involvement of the entering group in determining steric course on the other suggest an I_d process.

The rate law found for isomerization suggests the importance of H_2O diffusion. However, it is surprising that this rate law differs from that previously reported for dehydration–dehydrohalogenation of *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$ in static air.[30] The different rate laws may reflect the larger sample sizes or higher temperatures used in the present study. It could also reflect the fact that the reaction is retarded by HCl while promoted by H_2O. The balance of these last two factors could give a rate law different from that for mass loss.

Comparison with Other Solid-Phase Reactions.—While the behavior of *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$ makes comparisons with solution processes compelling, there are also some similarities to thermal annealing processes in solids which are evident.

Rössler[50,51] has studied the ligand-exchange reactions of a number of complexes of the type *cis*- and *trans*-$[Co(en)_2X_2]X$ in connection with studies of Co^{2+} exchange and thermal annealing of neutron-irradiated complexes. These cobalt complexes exhibited nearly identical rates of halide exchange, and irradiation with X-rays or γ rays accelerates exchange. It was concluded that halide exchange takes place *via* anion vacancies which increase in number upon irradiation. It has also been suggested that these defects may be electron acceptors.[54] The exchange might be promoted by electron transfer from anion vacancy to cobalt(III) giving a labile cobalt(II) complex which readily exchanges ligands. It was observed that electrical conductivity of the solids parallels their exchange behavior—conductivity increases with temperature and also increases upon irradiation.[51]

Although the question of the mechanism of thermal annealing reactions is still an open one, it has been proposed that free electrons are important in thermal annealing of neutron-irradiated $[Co(dipy)_3](ClO_4)_3$ and $[Co(phen)_3](ClO_4)_3$ and also in the thermal exchange of radioactive Co^{2+}-doped complexes.[25,55] Such an electron-transfer mechanism would explain why *trans*-$[Rh(en)_2Cl_2]Cl$ undergoes much slower ligand exchange than its cobalt analog.[50,51] It is also noteworthy that cis-to-trans isomerization of $Co(en)_2Cl_2^+$ has been reported to take place *via* a redox mechanism in methanol at low temperatures.[56]

Water has been found to accelerate these annealing and Co^{2+}-exchange reactions.[57,58] Presumably the

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higher dielectric constant of the hydrate telescopes the electron-trapping levels, and hence release of electrons requires less energy. Electron emission has been observed to accompany dehydration of salts.[59]

Such annealing reactions generally take place with retention of configuration.[60,61] However, neutron-irradiated *cis*- or *trans*-$[Co(NH_3)_4(NO_2)_2](NO_3)_2$ has been found to give rise to a considerable percentage of the other isomer.[26]

Since electron transfer can lead to isomerization and since electron transfer may be important in the solid-phase reactions discussed above, it appears possible that the isomerization of *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$ involves electron transfer. Within the framework of this mechanism it is easy to see how ligand exchange occurs faster for the "hydrated" form, but it is not evident why isomerization should occur only while water is present or why *trans*-$[Co(en)_2Cl_2](H_5O_2)Cl_2$ should not also isomerize. Therefore, at the present time the mechanism developed by analogy to solution reactions gives the most ready explanation of the isomerization and ligand-exchange behavior of *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$.

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The Kinetics and Steric Course of the Spontaneous Aquation of the *cis*-Dibromobis(ethylenediamine)cobalt(III) Cation

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The aquation of the complex cation *cis*-dibromobis(ethylenediamine)cobalt(III) has been reexamined kinetically and the steric course of substitution determined. A complete spectrophotometric analysis of the system has revealed both *cis*- and *trans*-$Co(en)_2OH_2Br^{2+}$ in the initially formed products. At 25° and an ionic strength of 0.1 the complex aquates directly to give 72% *cis*- and 28% *trans*-$Co(en)_2OH_2Br^{2+}$. Close examination of the substitution processes showed that the observed products do not result from 100% stereoretentive aquation followed by rapid isomerization. Rate constants for the aquation of *cis*-$Co(en)_2Br_2^+$ and the isomerization of the products have been determined over a 25° temperature range. While the values found for the latter are in good agreement with those already reported,[1] the rates presented below for the aquation process are somewhat lower than those previously found.[2] Activation parameters have been calculated for the aquation. The temperature independence of the equilibrium constant for the isomerization of the products has been confirmed; the value found for the constant agrees with the literature figures.[1] The sensitivity of the steric course to temperature and the nonstereoretentivity of the aquation of this complex are discussed.

Introduction

It is now generally agreed that the mechanism of hydrolysis of Werner-type complexes of cobalt(III) is basically dissociative.[3-5] One interesting observation is that while trans Co(III) substrates with anionic leaving groups often display steric change during spontaneous aquation only in one case has a cis complex been previously reported to do so.[6] Recently we have found another cis Co(III) complex, the *cis*-dibromobis(ethylenediamine)cobalt(III) cation, where the acid hydrolysis of its anionic leaving group leads initially to both cis and trans products. It was found impossible to reconcile the spectra observed during its aquation with the published rates of aquation[2] and isomerization of product(s)[1] and the assumed stereoretentivity of the reaction. Thus the rates of the processes involved and the equilibrium constant for the isomerization were redetermined. We now report our results for these together with the steric course of the aquation and the temperature dependence of this course.

Experimental Section

Preparation of Compounds.—All the complexes prepared were stored either in a vacuum desiccator over anhydrous magnesium perchlorate or in tightly sealed tubes. Due to the inability to store some of the compounds without decomposition, freshly prepared materials were generally used; light was excluded as a routine precaution. Carbonatobis(ethylenediamine)cobalt(III) chloride was prepared by the method of Dwyer, *et al.*,[7] and recrystallized as the bromide from water. Conversion of this complex to *cis*-$Co(en)_2Br_2^+$, *cis*-$Co(en)_2OH_2Br^{2+}$, and *trans*-$Co(en)_2Br_2^+$ salts was effected by minor modifications of the methods of Werner.[8]

cis-$[Co(en)_2Br_2]BrH_2O$ was recrystallized from water as the bromide. *trans*-$[Co(en)_2Br_2]Br$ was recrystallized from water and then from well-dried methanol to remove traces of tris(ethylenediamine)cobalt(III). *cis*-$[Co(en)_2OH_2Br]Br_2H_2O$ was purified by recrystallization from very dilute acid as the bromide.

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