$NC)_2(PhP(OEt)_2)_3]^+$ cation. Its pmr spectrum in deuteriochloroform exhibits a 1:4:5:2 quartet ($J = 7$ Hz) centered at τ 8.64, assigned to the methyl protons, which become two (1:2:1, 2:4:2) triplets in hexadeuterioacetone and in hexadeuteriodimethyl sulfoxide with a difference in the chemical shift of 0.10 and 0.13 ppm, respectively. This means that two magnetically equivalent phosphine ligands are different from the third. Although the structure with two equatorial and one apical phosphine cannot be excluded completely for this complex, we prefer structure IV because of the analogy with structure III.

The pmr spectra of all the isocyanide-phosphine derivatives show no changes in the +30 to −80° temperature range except minor, but significant, changes in the spectrum of the $[Co(p\text{-}NO_2C_6H_4NC)_2(PhP(OEt)_2)_3]^+$ complex. While two 1:1 doublets ($J = 9$ Hz) at τ 1.61 and 2.18 assignable to the phenyl ring protons (AA′BB′ spectrum which approximates to AB) can be observed for the free *p*-nitrophenyl isocyanide (Figure 2), a set of four 1:1 doublets ($J = 9$ Hz) at τ 1.48, 1.67, 2.09, and 3.17 due to the corresponding protons is present in the spectrum of the bis(*p*-nitrophenyl isocyanide)tris(diethyl phenylphosphonite)cobalt(I) cation at −91° in acetone-Freon (1:1) solution. The downfield doublets can be assigned to the protons in the ortho positions with respect to the nitro group (bb′ and dd′) and the two upfield doublets to the other protons (aa′ and cc′). As shown in Figure 2 an increase in temperature causes a decrease in Δf_1 and Δf_2[26] and at +47° the two downfield doublets collapse in a 1:2:1 pseudotriplet. These facts can be rationalized in terms of an increase of the internal rotation of the two isocyanide ligands. There are two rotational modes which will tend to make these pairs of protons equivalent. One is rotation about the Co-CN axis and the other is rotation about the CN-Ph axis. Presumably at sufficiently high temperatures total equivalence of the protons ortho to the nitro group and those ortho to the isocyanide function will be observed and two 1:1 doublets, as for the free ligand, should be observed. Two 1:1 doublets at τ 1.63 and 2.38 are in fact observed in the pmr spectrum of the $[Co(p\text{-}NO_2C_6H_4NC)_3(P(OMe)_3)_2]^+$ cation at 25°. In this case the apical trimethyl phosphite ligands, whose steric influence is minor relative to that of $PhP(OEt)_2$, allows a complete rotation of the isocyanide ligands even at room temperature.

Acknowledgments. This research was supported by the Consiglio Nazionale delle Ricerche. We thank Dr. Gyorgy Bor and Professor Peter R. Welles for valuable suggestions and discussions on infrared and pmr spectra. Thanks are also due to Mr. Adriano Berton and to Mrs. Adriana Lucchiari for elemental analysis.

Registry No. $[Co(CO)_2L_3]BPh_4$, 42294-95-1; $[CoI(CO)_2L_2]$, 42294-96-2; $[Co(C_6H_5NC)_3L_2]BPh_4$, 42294-97-3; $[Co(p\text{-}NO_2C_6H_4NC)_2L_3]ClO_4$, 42422-51-5; $[Co(C_6H_5NC)_3L_2]ClO_4$, 42294-98-4; $[Co(p\text{-}CH_3C_6H_4NC)_3L_2]ClO_4$, 42294-99-5; $[Co(p\text{-}CH_3OC_6H_4NC)_3L_2]ClO_4$, 42295-00-1; $[Co(o\text{-}CH_3C_6H_4NC)_3L_2]ClO_4$, 42295-01-2; $[Co(o\text{-}(CH_3)_2C_6H_3NC)_3L_2]ClO_4$, 42295-02-3; $[Co(C_6H_{11}NC)_3L_2]ClO_4$, 42295-03-4; $[Co(p\text{-}NO_2C_6H_4NC)_3L'_2]ClO_4$, 42295-04-5; $[Co(C_6H_5NC)_3L'_2]ClO_4$, 42295-05-6; $[Co(o\text{-}(CH_3)_2C_6H_3NC)_3L'_2]ClO_4$, 42388-31-8; $[CoI(PhP(OEt)_2)_4]BPh_4$, 38798-28-6. ($L = PhP(OEt)_2$; $L' = P(OMe)_3$.)

[26] Δf_1 and Δf_2 are the differences in chemical shifts of the two downfield and the two upfield doublets, respectively, as shown in Figure 2.

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Stereochemical Studies of the Radiocobalt Exchange in Solids Containing the $Co(pn)_2Cl_2^+$ Ion[1]

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The solid-phase radiocobalt exchange reactions between labeled $CoCl_2$ and the complexes *trans*-$[Co(pn)_2Cl_2]Cl$, *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$, and *cis*-$[Co(pn)_2Cl_2]Cl\cdot H_2O$ (pn = 1,2-diaminopropane) were studied in static air at 100, 120, and 150°. Although isomerization occurs during dehydration, cobalt exchange takes place mainly after dehydration and occurs with complete retention of configuration. In some cases, however, $Co(pn)_3^{3+}$ forms. The results are compared with those obtained in transfer annealing and postradiation annealing studies of related complexes.

Introduction

When complexes of cobalt(III) and chromium(III) are irradiated with neutrons in the solid state, Szilard-Chalmers recoil occurs causing bond rupture. If the solid is subsequently heated, the recoil fragments recombine, a process known as thermal annealing. A striking feature of this postradiation annealing of cobalt(III) and chromium(III) complexes is that it generally occurs with retention of configuration. This has been reported in studies of *d*-$[Co(en)_3](NO_3)_3$[2] and *cis*- and *trans*-$[M(en)_2Cl_2]X$, where M = Cr[3,4] or Co[5,6] and X = Cl or NO_3. The only cases where significant stereochemical changes have been reported are *cis*- and *trans*-$[Co(NH_3)_4(NO_2)_2]NO_3$.[7]

Stereochemical retention is also observed in the solid-phase isotopic metal exchange reactions of *cis*- and *trans*-$[M(en)_2$-

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$Cl_2]Cl$.[3,6] This exchange, known as transfer annealing, takes place when the complex is doped with radioactively labeled $CoCl_2$ or $CrCl_3$ and subsequently heated. Considerable similarity exists between postradiation annealing and transfer annealing leading several investigators to propose that the same mechanism is involved in both processes. Thus, Nath and his coworkers[8] and Venkateswarlu[9] have proposed that the annealing of Szilard-Chalmers recoils consists of isotopic exchange between interstitial recoiled atoms and atoms occupying normal lattice sites. The picture, however, is somewhat confusing, and experimental evidence has been presented which suggests that transfer annealing alone may not account for the annealing of recoil effects.[10] Indeed, it has been claimed that the observed stereospecificity in the postradiation annealing of *cis*- and *trans*-$[Cr(en)_2Cl_2]Cl$ cannot be explained on the basis of the isotopic exchange mechanism.[3,11]

In contrast to the general stereospecificity reported for annealing processes, an increasing number of cases of thermally induced stereochemical changes have been reported to occur within solids. Thus, for example, *l-cis*-$[Cr(en)_2Cl_2]\text{-}Cl\cdot H_2O$,[12] *d-cis*-$[Co(en)_2Cl_2]Cl$,[12] and a number of salts of *d*-$[Co(en)_3]^{3+}$ [13] have been found to undergo racemization. Similarly, trans-to-cis isomerization has been found for $[Co(NH_3)_4Cl_2]IO_3\cdot 2H_2O$,[14–16] $[Cr(NH_3)_4Cl_2]Cl$,[17] $[Cr(en)_2Cl_2]Cl$,[18] and $[Co(pn)_2Cl_2](H_5O_2)Cl_2$,[19,20] and stereochemical changes have also been reported for *cis*- and *trans*-$[Co(NH_3)_2enCl_2]X$ ($X = Br$ or ClO_4).[21,22] The ease with which many of these reactions occur raises some question about the generality of stereochemical retention occurring during annealing.

We therefore became interested in investigating the transfer annealing of *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$, a compound which undergoes isomerization but otherwise resembles previously studied systems. The present paper reports the annealing studies on this compound and on two related complexes, *trans*-$[Co(pn)_2Cl_2]Cl$ and *cis*-$[Co(pn)_2Cl_2]Cl\cdot H_2O$.

Experimental Section

The compound *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$ was prepared as described elsewhere.[23] This was dissolved in methanol and precipitated as *trans*-$[Co(pn)_2Cl_2]Cl$ (containing 1–4% H_2O) upon addition of ether. The anhydrous complex was obtained by dissolving this substance in absolute methanol, adding 2,2-dimethoxypropane, waiting 3–4 min, and then precipitating the complex with anhydrous ether. The compound was then stored in a vacuum desiccator over P_2O_5. The preparation of *cis*-$[Co(pn)_2Cl_2]Cl$ is described elsewhere.[24] Upon standing open in the laboratory, this compound picks up approximately a molecule of lattice water from the atmosphere.

In order to dope *trans*-$[Co(pn)_2Cl_2]Cl$ with $^{60}CoCl_2$, 0.5 g of this complex was dissolved in 5 ml of methanol, and $^{60}CoCl_2$ which was dissolved in a minimum amount of water (0.1 ml containing 5 μCi) was added. After mixing, 20 ml of 2,2-dimethoxypropane was added followed by sufficient dry ether to precipitate the complex from solution. The product was collected by vacuum filtration and stored *in vacuo* over P_2O_5 for 24 hr prior to use.

In order to obtain doped *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$, 0.4 g of this compound was dissolved in 1 ml of cold water, 0.1 ml (5 μCi) of $^{60}CoCl_2$ was added, and the complex was precipitated from solution upon addition of 2 ml of concentrated HCl. The mixture was then frozen to a slush using a Dry Ice–acetone bath and finally lyophilized for 1 hr. The resulting residue was ground to ensure uniformity of the mixture and analyzed by measuring mass loss at 100°. *Anal.* Calcd for $[Co(pn)_2Cl_2](H_5O_2)Cl_2$: $HCl + H_2O$, 18.80. Found: $HCl + H_2O$, 18.50.

The doped *cis*-$[Co(pn)_2Cl_2]Cl\cdot H_2O$ was obtained by adding $^{60}CoCl_2$ to a methanolic solution of the complex after which 2,2-dimethoxypropane and then ether were added. The resulting product was stored *in vacuo* over P_2O_5 for 24 hr prior to use.

On a mole basis, the quantity of cobalt used to dope each complex was five to six orders of magnitude less than that available in the complex. The $^{60}CoCl_2$ used in each case had a specific activity of 13.7 Ci/g Co; thus, 5 μCi contained 6×10^{-9} mol of cobalt of which 1% was ^{60}Co.

Samples were heated in thin sample beds in static air in *ca.* 50-mg lots in an oven controlled to ±2°. Separation of products was achieved using ion-exchange chromatography. Each sample was dissolved in 1 ml of 0.3 *M* methanolic HCl (made by adding sufficient concentrated HCl to absolute methanol to make a solution 0.3 *M* in HCl) and placed on a 1 × 7 cm column of Dowex 1X8 anion-exchange resin (100–200 mesh; in the chloride form) which had been previously washed with absolute methanol. Samples were then eluted with 10 ml of 0.3 *M* methanolic HCl followed by 10 ml of absolute methanol. This left cobalt(II) on the column as $CoCl_4^{2-}$, and *ca.* 20 ml of solution containing the cationic species was collected. This procedure completely removed radioactivity from unheated samples doped with $^{60}CoCl_2$.

The solution removed from the anionic-exchange column was diluted to *ca.* 30 ml with absolute methanol and placed on a 1 × 3 cm column of Dowex 50X2 cation-exchange resin (100–200 mesh; in the hydrogen form). The *trans*-$Co(pn)_2Cl_2^+$ was eluted first and collected in a 50-ml volumetric flask. The eluent was then changed to 0.6 *M* methanolic HCl to speed removal of *cis*-$Co(pn)_2Cl_2^+$ which was likewise collected in a 50-ml volumetric flask. Finally, remaining complexes, $Co(pn)_3^{3+}$ and $Co(pn)_2(H_2O)_2^{3+}$, were removed using 1 *M* methanolic HCl and collected in a 50-ml volumetric flask. Each solution was diluted to 50 ml, and the amount of complex in solution was determined spectrophotometrically using the following wavelengths and extinction coefficients: *trans*-$Co(pn)_2Cl_2^+$, 610 mμ (ϵ 37); *cis*-$Co(pn)_2Cl_2^+$, 540 mμ (ϵ 88); $Co(pn)_3^{3+}$ and $Co(pn)_2(H_2O)_2^{3+}$, 465 mμ (ϵ 64). These wavelengths and extinction coefficients were obtained using authentic samples handled in the same fashion as the samples used in the annealing experiments. Some extinction coefficients are therefore low[20,24] owing presumably to aquation which takes place during the operations. All spectra were recorded with a Cary 14 spectrophotometer using 10-cm quartz cells.

The samples were counted both before and after separation using a multichannel γ-ray spectrometer with a 4 × 8 in. NaI(Tl) scintillation counter. Samples were counted for 5 min and the total counts of the initial samples were approximately 150,000 when summed over five channels.

Results and Discussion

Radiocobalt Exchange in *trans*-$[Co(pn)_2Cl_2]Cl$. Radiocobalt exchange in anhydrous *trans*-$[Co(pn)_2Cl_2]Cl$ produced

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no detectable amount of *cis*-$Co(pn)_2Cl_2^+$.[25] Furthermore, negligible radioactivity accompanied carrier *cis*-$Co(pn)_2Cl_2^+$ during chromatographic separation of products.[26] Hence radiocobalt exchange in anhydrous *trans*-$[Co(pn)_2Cl_2]Cl$ occurs with complete retention of steric configuration. A yellow-orange compound was observed among the reaction products, however, after samples had been heated for an extended time. Although too little was formed to permit a definitive identification, this compound was found to have the same retention time as $Co(pn)_3^{3+}$ and hence was eluted with $Co(pn)_3^{3+}$ when this ion was added to the reaction products as a carrier. Furthermore, apparently the same compound forms during the transfer annealing of *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$. In that case sufficient quantities were obtained to analyze the compound spectrophotometrically and identify it as $Co(pn)_3^{3+}$.[27] Since there was not enough $Co(pn)_3^{3+}$ produced in the transfer annealing of *trans*-$[Co(pn)_2Cl_2]Cl$ to obtain its visible spectrum, it is significant that a high proportion of the radiocobalt appears in this form. Thus 2.5, 4.5, and 29.5% of the radiocobalt was in this form after 265 hr at 100, 120, and 150°, respectively. By comparison, the corresponding percentages of radiocobalt in *trans*-$Co(pn)_2Cl_2^+$ were 21.8, 40.7, and 33.1%, respectively. The remainder of the radiocobalt was in the form of the dopant, cobaltous chloride. The small quantity of $Co(pn)_3^{3+}$ produced compared to its high incorporation of radiocobalt suggests that metal exchange occurs predominantly during the formation of this ion rather than subsequently.

The rate and extent of radiocobalt exchange in *trans*-$[Co(pn)_2Cl_2]Cl$ was found to increase with increasing temperature (Figure 1). The exchange data were reduced using the rate equation $-\log(1-\alpha) = kt^n$, where α represents the fraction of infinite-time annealing at any time, t, and n has values of ${}^1/_2$, ${}^2/_3$, or 1. The cases where $n = {}^1/_2$ and ${}^2/_3$ have been discussed by Veljkovic[28] and interpreted as indicating that the reactions are dominated by dislocations and limited diffusion of reacting species using these dislocations; when $n = 1$ the rate expression is the usual first-order equation for homogeneous radioactive exchange. No single value of n best fit the data for all three temperatures, although a reasonably good data fit was obtained in each case for $n = {}^2/_3$. The 150° data clearly fit the $n = {}^2/_3$ equation best, but for 100 and 120° the better fits were obtained with $n = 1$. Plots of $-\log(1-\alpha)$ *vs.* t for the data at 150° produced a smooth curve which appeared to be composed of two straight-line portions. Several reasonable models may be cited to show how such curvature can result if several species compete for the radioisotope,[5,29] and similar curves have been reported for the annealing of *trans*-$[Co(en)_2Cl_2]NO_3$. The rate constants at 100 and 120° together with the constant for the initial, rapid portion of the 150° data yields an Arrhenius activation energy of 17 ± 3 kcal/mol for total radiocobalt exchange when $n = 1$. When $n = {}^2/_3$, the corresponding activation energy was found to be 11 ± 3 kcal/mol.

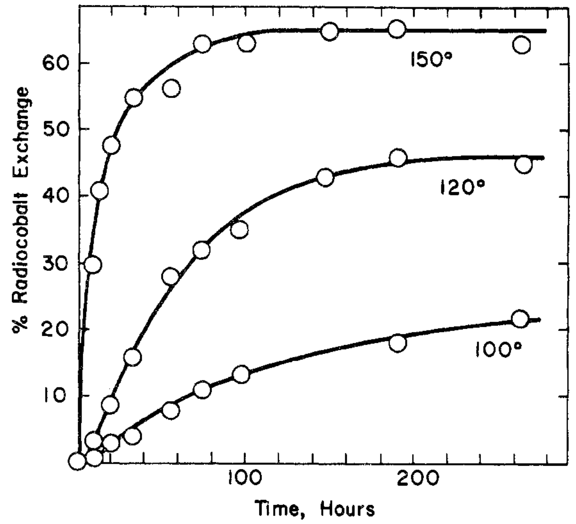

Figure 1. The total radiocobalt exchange in *trans*-$[Co(pn)_2Cl_2]Cl$ as a function of time at 100, 120, and 150°.

In the absence of a detailed kinetic model, these activation energies must be considered to be purely empirical parameters.[30]

Attempts were made to obtain doped *trans*-$[Co(pn)_2Cl_2]Cl\cdot H_2O$ by hydration of doped *trans*-$[Co(pn)_2Cl_2]Cl$ in a hydrator over a saturated solution of $(NH_4)(H_2PO_4)$ for 24 hr. Although a substance having the correct water content was obtained, it had undergone significant metal exchange during the hydration procedure (*ca.* 30%, totally in the form of *trans*-$Co(pn)_2Cl_2^+$). After 229 hr at 100°, total exchange increased to 38% with 21% in the trans form, 9% in *cis*-$Co(pn)_2Cl_2^+$, and 8% in $Co(pn)_3^{3+}$. The amount of $Co(pn)_3^{3+}$ formed was much larger than from the anhydrous *trans*-$[Co(pn)_2Cl_2]Cl$, amounting to about 12% of the total products after 229 hr at 100°. Doped samples which had picked up approximately 1 mol of lattice water when crystallized from alcohol upon addition of ether also formed larger amounts of $Co(pn)_3^{3+}$ than the anhydrous complex when heated. In each of these hydrated complexes, *cis*-$Co(pn)_2Cl_2^+$ was found among the products.

Radiocobalt Exchange in *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$. Samples of this complex doped with $^{60}CoCl_2$ produced both $Co(pn)_3^{3+}$ and *cis*-$Co(pn)_2Cl_2^+$ upon heating. For example, after 192 hr at 120°, the reaction mixture consisted of 70% *trans*-$Co(pn)_2Cl_2^+$, 15% *cis*-$Co(pn)_2Cl_2^+$, and 15% $Co(pn)_3^{3+}$. The corresponding amounts of radiocobalt exchange normalized to the quantity of each form present were 0.14, 0.38, and 1.2, respectively.[31] After 72 hr at 150°, the reaction mixture consisted of 53% *trans*-$Co(pn)_2Cl_2^+$, 30% *cis*-$Co(pn)_2Cl_2^+$, and 17% $Co(pn)_3^{3+}$, and the enrichment ratios were 0.26, 0.37, and 0.87, respectively.

The enrichment ratios cited above for $Co(pn)_3^{3+}$ may actually be low while those for *cis*- and *trans*-$Co(pn)_2Cl_2^+$ may be high. The reason for this is hydrolysis of the chloro complexes during the separation procedure. The $Co(pn)_2(H_2O)_2^{3+}$ formed in this way is generally eluted from the ion-exchange column with $Co(pn)_3^{3+}$. When these two tripositive ions were separated, exchange in $Co(pn)_2(H_2O)_2^{3+}$

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[25] Earlier studies[20] have led to the conclusion that isomerization occurs only in the presence of lattice water. The present results agree with this.

[26] A mixture of *cis*- and *trans*-$[Co(pn)_2Cl_2]Cl$, prepared by heating *trans*-$[Co(pn)_2Cl](H_5O_2)Cl_2$ at 110°, was added to the reaction mixture to provide the carrier because of the difficulty in preparing the pure cis isomer.[24]

[27] In studies of similar compounds, *trans*-$[Co(en)_2Cl_2]Cl$[6] and *trans*-$[Co(en)_2Cl_2]NO_3$,[5] some radioactivity was reported to occur in unidentified products. In analogy to our studies, we feel that this might be due to the formation of a small quantity of $Co(en)_3^{3+}$.

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[31] The amount of exchange normalized to the quantity of each chemical form present (*i.e.*, the ratio of the percentage of ^{60}Co retention in a particular chemical form to the percentage of that chemical form present in the reaction mixture) is hereafter referred to as the enrichment ratio.

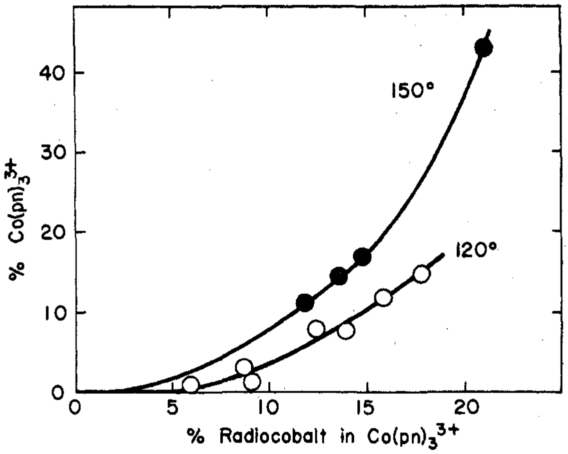

Figure 2. The percentage of $Co(pn)_3{}^{3+}$ in the reaction mixture as a function of the percentage of radiocobalt incorporated into $Co(pn)_3{}^{3+}$ (starting with *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$).

was found to be negligible by comparison with that in $Co(pn)_3{}^{3+}$. Duplicate experiments revealed that hydrolysis did not affect the total measured radiocobalt exchange but did introduce errors in the amount of isomerization and extent of radiocobalt incorporated into the various reaction products rendering them (and hence also enrichment ratios) less reproducible. It should also be noted that formation of $Co(pn)_3{}^{3+}$ is probably accompanied by the formation of Co^{2+} which would affect enrichment ratios.

It is nonetheless evident from these enrichment ratios that $Co(pn)_3{}^{3+}$ is the most effective scavenger of radiocobalt. Figure 2 shows the relationship between the extent of radiocobalt capture in $Co(pn)_3{}^{3+}$ and the amount of this ion found in the reaction mixture. Radiocobalt incorporation into $Co(pn)_3{}^{3+}$ seems to be the most efficient at the initial stages of the reaction; the enrichment ratio decreases with increasing time. This is due mainly to the decreasing quantity of $^{60}CoCl_2$ available during the course of the annealing. It is also, in smaller part, due to increasing amounts of *cis*-$Co(pn)_2Cl_2{}^+$ and hence hydrolysis products which give spuriously high values for the percentage of $Co(pn)_3{}^{3+}$.

In contrast, incorporation of radiocobalt into *cis*-$Co(pn)_2Cl_2{}^+$ appears to occur primarily subsequent to the formation of this compound rather than during the isomerization reaction by which it is formed. This is seen most clearly at 100° where detectable amounts of $Co(pn)_3{}^{3+}$ are not formed and data interpretation is consequently simpler. Figure 3 shows that isomerization occurs more readily than radiocobalt exchange, ceasing long before the metal exchange ceases. Indeed, no correlation between isomerization and radiocobalt exchange could be found. Furthermore, once isomerization has stopped, the enrichment ratios of *cis*- and *trans*-$Co(pn)_2Cl_2{}^+$ are linearly related (Figure 4). A similar linear correlation has been found in the postradiation annealing of *cis*-$[Co(en)_2(NO_2)_2][CoEDTA]$ where two different sites are available for exchange.[32] The results of the present study are therefore consistent with annealing in two already available sites with no indication of isomerization accompanying the exchange reaction.

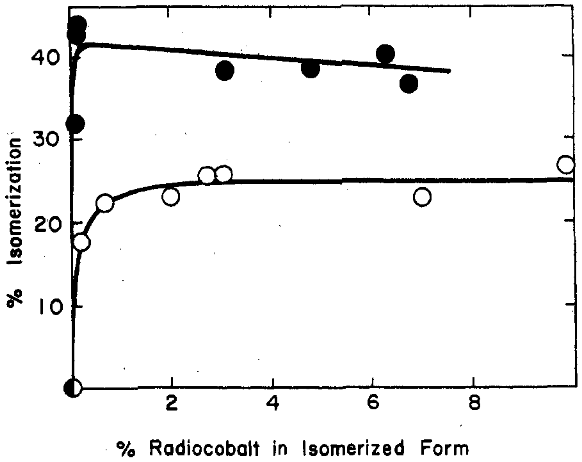

Figure 3. The relationship between isomerization and radiocobalt exchange: The percentage of *cis*-$Co(pn)_2Cl_2{}^+$ formed from *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$ at 100° as a function of the percentage of radiocobalt incorporated into *cis*-$Co(pn)_2Cl_2{}^+$ (○); corresponding data for *trans*-$Co(pn)_2Cl_2{}^+$ formed from *cis*-$[Co(pn)_2Cl_2]Cl \cdot H_2O$ (●).

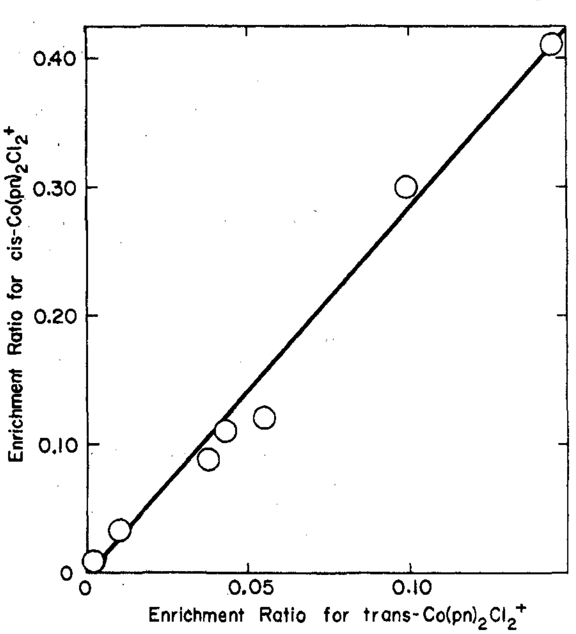

Figure 4. Enrichment ratios for *cis*-$Co(pn)_2Cl_2{}^+$ as a function of the corresponding enrichment ratios for *trans*-$Co(pn)_2Cl_2{}^+$ (starting with *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$ heated at 100°).

The difference between the radiocobalt exchange behavior of *cis*-$Co(pn)_2Cl_2{}^+$ and $Co(pn)_3{}^{3+}$ discussed above is not surprising since metal exchange involves ligand transfer. More bond breaking and re-forming is required to form the second compound. Hence there is greater opportunity for radiocobalt incorporation in $Co(pn)_3{}^{3+}$.

Water of hydration has been found to accelerate postradiation annealing as well as cobalt-exchange reactions. Presumably, the higher dielectric constant of the hydrate telescopes the electron-trapping levels, and hence release of electrons requires less energy (Nath's model).[33] Hydration may also influence the behavior of excitons and/or electron transfer from a cobaltous complex to an unfilled electron trap (Venkateswarlu's model).[9] One might wonder whether salts containing $H_5O_2{}^+$ would behave similarly. The initial rate of annealing of the $H_5O_2{}^+$-containing substance does indeed appear to be greater than the anhydrous complex, although the final extent of exchange was found to be less. However, since most annealing takes place after dehydration is complete, differences between radiocobalt exchange in

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trans-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$ and *trans*-$[Co(pn)_2Cl_2]Cl$ may be due to differences in crystal lattices or particle size.

As in the case of *trans*-$[Co(pn)_2Cl_2]Cl$, the equation $-\log (1 - \alpha) = kt^n$ was used to reduce the data for total radiocobalt exchange. Again no single value of n fit the data at every temperature, but $n = {}^2/_3$ gave the most satisfactory results over the entire temperature range. When $n = 1$, plots of $-\log (1 - \alpha)$ *vs.* t could be separated into two straight-line portions; the initial, rapid portion at each temperature was used to calculate activation energy. Resultant activation energies were 22 ± 4 and 16 ± 3 for $n = 1$ and ${}^2/_3$, respectively. Although these values are higher than the corresponding values for the anhydrous complex, the activation energies are equal within the relatively large experimental errors involved.

Radiocobalt Exchange in *cis*-$[Co(pn)_2Cl_2]Cl\cdot H_2O$. This compound was found to undergo isomerization forming *trans*-$Co(pn)_2Cl_2^+$ when heated. Thus, after 93 hr at 150° the reaction mixture contained nearly equal amounts of *cis*- and *trans*-$Co(pn)_2Cl_2^+$. As in the case of *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$, isomerization ceases before it is complete and $Co(pn)_3^{3+}$ is found among the reaction products. Indeed, *cis*-$[Co(pn)_2Cl_2]Cl\cdot H_2O$ is basically analogous in behavior to *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$. Thus, increasing temperature increases the amount of exchange; exchange does not appear to be correlated with isomerization and plots such as that shown in Figure 3 are obtained. Since exchange takes place mainly after isomerization, a cis-trans mixture is involved in annealing whether starting with *cis*-$[Co(pn)_2Cl_2]Cl\cdot H_2O$ or *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$. This provides the basis for explaining the similarities in the two systems as far as the annealing process is concerned. Thus, the cis isomer gives a higher enrichment ratio than the trans isomer irrespective of whether the starting material is of cis or trans geometry. Once isomerization ceases, the enrichment ratios of the cis and trans isomers are linearly correlated in the same way as was previously found for *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$. Indeed, the slopes of plots such as that in Figure 4 are essentially equal regardless of whether the starting material is of cis or trans geometry.[34] The difference in enrichment ratios for the cis and trans isomers presumably results from an inherently greater ease of ligand dissociation for the cis isomer. Hydrolysis of $[CoA_4Cl_2]^+$ ions in solution shows this same pattern.[35] In contrast, halide exchange in $[Co(en)_2X_2]X$ (X = Cl or Br) in the solid phase is largely independent of the halide and of geometric configuration and appears to depend on the availability of anion vacancies in the crystal lattice.[6,36]

The primary difference noted between annealing in the *cis*-$[Co(pn)_2Cl_2]Cl\cdot H_2O$ system and in *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$ is the lower enrichment ratio for $Co(pn)_3^{3+}$ in the former system. Thus, after 306 hr at 150°, the reaction mixture consisted of 41% *trans*-$[Co(pn)_2Cl_2]^+$, 30% *cis*-$[Co(pn)_2Cl_2]^+$, and 29% $Co(pn)_3^{3+}$ with corresponding enrichment ratios of 0.35, 0.70, and 0.40, respectively. As previously noted, hydrolysis of $[Co(pn)_2Cl_2]^+$ leads to a low enrichment ratio for $Co(pn)_3^{3+}$. The cis isomer, which was present in greater amounts in these studies than in those of *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$, is especially susceptible to hydrolysis (*vide supra*), perhaps leading to the low values. Additionally, however, the activation energy for total radiocobalt exchange was lower than in the previous cases, amounting to 6 ± 2 kcal/mol for both $n = 1$ and ${}^2/_3$. The difference between this and previous values is puzzling, and we can only note experimental errors and the apparent complexity of the kinetic processes as possible sources of this difference.

Concluding Remarks. Both *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$ and *cis*-$[Co(pn)_2Cl_2]Cl\cdot H_2O$ isomerize during dehydration but not subsequently. In contrast, annealing occurs with retention of configuration mainly after dehydration. The involvement of water in the isomerization may be due to its attack of the metal center leading to aquation and subsequent anation as previously proposed for this and similar systems.[15,20] It is also possible that the water assists removal of the leaving group through hydrogen bonding or similar interactions. However, dehydration may also affect the rate of stereochemical change by disrupting the crystal lattice. Indeed, lattice water is not always necessary for stereochemical changes in the solid state although it generally accelerates such reactions.[13,21] In the case of *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$, dehydration might produce an open, metastable lattice at the reaction interface where chloride exchange could occur. The very openness of the lattice would decrease the probability of imposing a template effect on the exchange so that isomerization may occur. Metal exchange, however, would be hindered by the stability of the Co-N bond. The slower metal exchange may then take place primarily after the lattice has collapsed and the exchange site can act as a template. Unfortunately, dehydration-dehydrochlorination of *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$ leads to a product lattice which is amorphous to X-rays,[37] so detailed comparisons of the reactant and product lattices cannot be made in this system.

However, if the model outlined above is correct, changes in stereochemistry are expected to accompany annealing wherever the crystal lattice of the compound is sufficiently open to minimize the template effect. Thus, further examples of stereochemical changes accompanying annealing might be found. Studies of radiocobalt exchange in *d*-$[Co(en)_3]I_3$ would appear to be a possible test for this suggestion. This compound racemizes in the solid phase without an accompanying change in crystal structure. This suggests that the lattice does not impose a large template effect. Furthermore, the lack of stereochemical change accompanying postradiation annealing in $[Co(en)_3](NO_3)_3$[2] is not surprising in light of studies on other $[Co(en)_3]X_3$ compounds.[13] The sequence for the ease of racemization of these compounds has been found to be X = I > Br > NCS > Cl which follows the order expected for decreasing hydrogen bonding between the protons on the nitrogen atoms in ethylenediamine and the anions in the lattice (assuming N-H· · ·N bonding for NCS).[13] Thus, the compound with X = NO_3 would not be expected to undergo ready racemization.

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Registry No. *trans*-$[Co(pn)_2Cl_2](H_5O_2)Cl_2$, 50432-40-1; *trans*-$[Co(pn)_2Cl_2]Cl$, 29990-94-1; *cis*-$[Co(pn)_2Cl_2]Cl\cdot H_2O$, 50432-42-3; $Co(pn)_3^{3+}$, 16786-50-8; ^{60}Co, 10198-40-0.

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[34] These slopes are 0.34, 0.46, and 0.66 at 100, 120, and 150°, respectively.

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