specificity. The barrier in $\mathrm{Co^{III}}$-CyDTA can only be larger, and thus we support the previously assigned stereochemistry for the deuteration of $\mathrm{Co^{III}}$-CyDTA.[5] The downfield shift of $\mathrm{H_A}$ and the upfield shift of $\mathrm{H_B}$ in $\mathrm{Co^{III}}$-CyDTA (as compared to, say, $\mathrm{Co^{III}}$-EDTA) can be understood in terms of steric compression, as reported by Winstein, *et al.*, for half-cage compounds,[11] with the same result as the electron orbital interaction suggested by Terrill and Reilley.[5] The cyclohexane ring proton $\mathrm{H_4}$ (see I) in $\mathrm{Co^{III}}$-CyDTA must strongly compress $\mathrm{H_B}$, producing a downfield shift in $\mathrm{H_B}$ and an upfield shift in $\mathrm{H_A}$. The compressed hydrogens in half-cage compounds essentially attempt to occupy the same space, and it appears that $\mathrm{H_B}$ and $\mathrm{H_4}$ in $\mathrm{Co^{III}}$-CyDTA are likewise extremely close in space. Therefore, in addition to C–N anisotropic shielding, at least one additional factor, that of steric compression, may be necessary in order to account for chemical shifts of α-hydrogen atoms in aminocarboxylate chelates.

The present studies should prove useful in the assignment of metal chelate nmr spectra, in the synthesis of deuterated ligands, and in further studies of stereospecific substitutions in metal chelates.

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(11) S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Am. Chem. Soc.*, **87**, 5247 (1965).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF NEVADA, RENO, NEVADA 89507

The Solid-Phase Dehydration of *trans*-$[\mathrm{Co}((\pm)\mathrm{pn})_2\mathrm{Cl}_2](\mathrm{H_5O_2})\mathrm{Cl}_2$ and *trans*-$[\mathrm{Co}(\mathrm{en})_2\mathrm{Cl}_2](\mathrm{H_5O_2})\mathrm{Cl}_2$

BY H. EUGENE LEMAY, JR.

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The dehydration of *trans*-$[\mathrm{Co}((\pm)\mathrm{pn})_2\mathrm{Cl}_2](\mathrm{H_5O_2})\mathrm{Cl}_2$ and *trans*-$[\mathrm{Co}(\mathrm{en})_2\mathrm{Cl}_2](\mathrm{H_5O_2})\mathrm{Cl}_2$ has been studied both in static air and *in vacuo*. The kinetics of the single-step loss of HCl and $\mathrm{H_2O}$ were investigated by measuring mass loss on a thermobalance and were correlated with changes in crystal structure and with microscopic observations of the solids. The ethylenediamine complex loses $\mathrm{H_2O}$ and HCl from all faces of the solid. The propylenediamine complex resists loss from the (100) faces, presumably because of the packing of the complex cations. The activation energy for dehydration of both compounds *in vacuo* was found to be 16 kcal $\mathrm{mol^{-1}}$ and independent of particle size. A suggestion is made as to the activation process.

Introduction

Many years ago Werner[1] reported that *trans*-$[\mathrm{Co}((\pm)\mathrm{pn})_2\mathrm{Cl}_2](\mathrm{H_5O_2})\mathrm{Cl}_2$[2] loses HCl and $\mathrm{H_2O}$ and isomerizes to *cis*-$[\mathrm{Co}((\pm)\mathrm{pn})_2\mathrm{Cl}_2]\mathrm{Cl}$ when heated to about 100° in the solid phase. Recent preliminary studies[3] of this reaction have indicated that isomerization occurs only while HCl and $\mathrm{H_2O}$ are being evolved from the solid. As a first stage in an attempt to determine the mechanism of this *trans* to *cis* isomerization, a detailed study of the dehydration process was carried out.

It is of interest in this regard that the dehydration of *trans*-$[\mathrm{Co}(\mathrm{en})_2\mathrm{Cl}_2](\mathrm{H_5O_2})\mathrm{Cl}_2$ proceeds without formation of the *cis* isomer. In solution, ethylenediamine complexes normally behave in very much the same fashion as their propylenediamine analogs. Furthermore, *trans*-$[\mathrm{Co}((\pm)\mathrm{pn})_2\mathrm{Cl}_2](\mathrm{H_5O_2})\mathrm{Cl}_2$ and *trans*-$[\mathrm{Co}(\mathrm{en})_2\mathrm{Cl}_2](\mathrm{H_5O_2})\mathrm{Cl}_2$ have very similar crystal structures.[4–6] Therefore a study was also made of the dehydration of this ethylenediamine complex. Although several studies of complexes containing the $\mathrm{H_5O_2^+}$ ion have been reported recently, no detailed studies of the dehydration of these compounds have appeared in the literature.

Experimental Section

Both *trans*-$[\mathrm{Co}((\pm)\mathrm{pn})_2\mathrm{Cl}_2](\mathrm{H_5O_2})\mathrm{Cl}_2$[7] and *trans*-$[\mathrm{Co}(\mathrm{en})_2\mathrm{Cl}_2](\mathrm{H_5O_2})\mathrm{Cl}_2$[8] were prepared as described elsewhere except racemic propylenediamine was used in place of the resolved amine in the first preparation.[9] Both compounds were analyzed for chloride by titration with $\mathrm{AgNO_3}$ and for total HCl and $\mathrm{H_2O}$ by weight loss accompanying heating to 110–120° on a thermobalance. *Anal.* Calcd for $[\mathrm{Co}((\pm)\mathrm{pn})_2\mathrm{Cl}_2](\mathrm{H_5O_2})\mathrm{Cl}_2$: Cl, 36.76; HCl + $\mathrm{H_2O}$, 18.80. Found: Cl, 36.9; HCl + $\mathrm{H_2O}$, 18.56. Calcd for $[\mathrm{Co}(\mathrm{en})_2\mathrm{Cl}_2](\mathrm{H_5O_2})\mathrm{Cl}_2$: Cl, 39.64; HCl + $\mathrm{H_2O}$, 20.27. Found: Cl, 39.9; HCl + $\mathrm{H_2O}$, 20.35.

Mass loss studies were conducted in static air and under reduced pressure (0.1–0.3 torr) using a Cahn Model RG recording electrobalance mounted in a Cahn vacuum bottle. Samples ranged from 15 to 20 mg in mass. Temperature control was maintained (to within ±0.5° during isothermal studies) by use of an F & M Scientific Model 240 power proportioning temperature programmer. The temperature immediately above the sample was measured with a calibrated iron–constantan thermocouple with a 0° cold junction. The rate of dehydration of both compounds studied appeared to be affected by the thickness of

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(1) A. Werner and A. Frohlich, *Chem. Ber.*, **40**, 2228 (1907).

(2) This compound is frequently formulated as *trans*-$[\mathrm{Co}((\pm)\mathrm{pn})_2\mathrm{Cl}_2]\mathrm{Cl}\cdot\mathrm{HCl}\cdot2\mathrm{H_2O}$. However, recent studies indicate that it contains $\mathrm{H_5O_2^+}$ and $\mathrm{Cl^-}$ ions. The same is true of *trans*-$[\mathrm{Co}(\mathrm{en})_2\mathrm{Cl}_2](\mathrm{H_5O_2})\mathrm{Cl}_2$.

(3) H. E. LeMay, Jr., unpublished results.

(4) A. Nakahara, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, **35**, 331 (1952).

(5) J. M. Williams, *Inorg. Nucl. Chem. Letters*, **3**, 297 (1967).

(6) Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Japan*, **35**, 1131 (1962).

(7) J. C. Bailar, Jr., C. A. Stiegman, J. H. Balthis, Jr., and E. H. Huffman, *J. Am. Chem. Soc.*, **61**, 2402 (1939).

(8) J. C. Bailar, Jr., *Inorg. Syn.*, **2**, 222 (1946).

(9) A later preparation was carried out using *l*-propylenediamine. Preliminary dehydration studies on this compound have shown it to behave in the same fashion as the compound prepared from the racemic amine.

the sample bed. The results reported in this article were obtained on a loosely packed, shallow bed of sample (sample holder was about 1.5 cm in diameter).

Differential thermal analysis (dta) was carried out in static air using a Stone Model 12AC dta apparatus (150–200-mg samples were employed).

X-Ray powder patterns were obtained on a Norelco diffractometer using copper Kα radiation. The prominent d spacings for *trans*-$[Co((\pm)pn)_2Cl_2](H_5O_2)Cl_2$ are 10.68 (s), 6.08 (m), 5.78 (m), 5.40 (m), 3.89 (m), and 3.60 Å (m). The prominent d spacings for *trans*-$[Co(en)_2Cl_2](H_5O_2)Cl_2$ are 9.89 (s), 5.75 (s), 5.59 (m), 4.98 (m), 4.53 (m), 3.94 (m), and 2.81 Å (m), while those for *trans*-$[Co(en)_2Cl_2]Cl$ are 6.29 (s), 5.87 (m), 4.98 (m), 4.48 (m), 4.39 (m), 3.07 (m), and 2.49 Å (m).[10]

Microscopic studies were made with an American Optical polarizing microscope equipped with a Kofler–Thomas micro hot stage.

By carrying out recrystallizations from concentrated HCl solution, three different ranges of particle sizes of *trans*-$[Co((\pm)pn)_2Cl_2](H_5O_2)Cl_2$ and two different ranges of particle sizes of *trans*-$[Co(en)_2Cl_2](H_5O_2)Cl_2$ were obtained. The approximate range of particle sizes in each case was determined by microscopy. The "small" particles of the propylenediamine complex contained a large proportion of crystals 0.01–0.05 mm in length, the "medium" ones were mainly in the 0.04–0.12-mm range, and the "large" ones ranged mainly from 0.10 to 0.30 mm. The "small" particles of the ethylenediamine compound were mainly 0.01–0.02 mm in length, while the "medium" ones were 0.02–0.05 mm.

Results and Discussion

The Dehydration of *trans*-$[Co(en)_2Cl_2](H_5O_2)Cl_2$.—Both tga and dta results indicate that HCl and H_2O are lost in a single step. At a heating rate of 4° min^{-1}, a single endothermic dta peak was found centered at about 120°. No further transitions were observed until endothermic decomposition began at about 220°. Tga curves, obtained at a heating rate of 5° min^{-1} on smaller, much more loosely packed samples, indicated simultaneous loss of HCl and H_2O in both static air and *in vacuo*.[11] In static air the mass loss began at about 60° and was complete at about 120°. The single-step loss of HCl and H_2O is in keeping with the known crystal structure of this substance which has been shown to contain $H_5O_2^+$ and Cl^- rather than discrete HCl and H_2O molecules.[4,5] Dollimore, Gillard, and McKenzie[12] previously reported the single-step mass loss, although their dta results, contrary to ours, indicated two endothermic peaks in the temperature range in which HCl and H_2O are lost. It is possible that the two peaks resulted from dissociation followed by the formation of a saturated solution and subsequent evaporation of H_2O and HCl.[13]

When studied under a microscope, the dehydration reaction was found to begin at the corners and edges of the tabular crystals. Within a short time, small, diffuse, approximately circular nuclei developed on all of the surfaces. The hydrated phase was translucent emerald green, whereas the dehydrated areas were an opaque pale green which appeared dark in the microscope field. Therefore, the reaction was easily followed visually. Once nucleation reached the visual stage, the reaction proceeded rapidly across the surfaces of the crystals. The reaction then proceeded toward the interior of the crystals at a slower rate.

The results of isothermal mass loss studies conducted in static air were found to fit the kinetic expression

$$(1 - \alpha)^{1/3} = 1 - kt$$

over a range of α (fraction of dehydration) from about 0.2 to 1.0 (k is a rate constant and t is time). This expression has been derived[14] using the assumptions that nucleation occurs extremely rapidly on and near the surface of the crystals forming a spherical or cubic interface and that the resulting reactant–product interface then grows toward the center of the crystal. The rate constant, k, equals k'/a where k' is a rate constant which is independent of particle size and a is the radius of the sphere or half of the edge of the cube. The "contracting-cube" model is in agreement with the visual observations noted in the previous paragraph. The well-formed crystals used here were parallelepipeds with approximately rectangular faces and heights usually only about half of their lengths and widths. However, since mass loss measurements were made on an aggregation of crystals consisting of many which were fractured or broken, the "contracting-sphere" model is probably equally valid for mass loss. The deviations from this rate law which occurred for values of α below 0.1–0.2 could be due to the occurrence of a slow two-dimensional surface growth rather than the instantaneous surface growth assumed in the theory. It could also be due, in part, to thermal lag of the sample.

The results of isothermal studies of mass loss *in vacuo* were described reasonably well by the same law found in static air studies within the range of 0.2–0.8 for α. However, plots of $(1 - \alpha)^{1/3}$ *vs.* time showed large deviations from linearity at values of α above about 0.8. The results were described better (and over a slightly larger range, for α = 0.2–0.9) by the expression

$$-\log (1 - \alpha) = kt + c$$

The rate law shown above can be derived by assuming random nucleation with the formation of a spherical reactant–product interface which then moves rapidly toward the center of the particle.[14] However, the rate constant, k, in the expression derived in this fashion is the rate of nucleation (the over-all reaction rate is controlled by the nucleation process). It might be expected that the rate of nucleation would not change significantly with particle size. However, the rate of dehydration of *trans*-$[Co(en)_2Cl_2](H_5O_2)Cl_2$ showed a very noticeable dependence on particle size

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(10) Only the strong (s) and medium (m) intensity reflections are given.

(11) Both this compound and its propylenediamine analog also exhibited simultaneous loss of HCl and H_2O at a heating rate of 1° min^{-1}. The temperature range over which mass loss occurs in static air increases if a larger, more densely packed sample is used.

(12) D. Dollimore, R. G. Gillard, and E. D. McKenzie, *J. Chem. Soc.*, 4479 (1965).

(13) See H. J. Borchardt and E. Daniels, *J. Phys. Chem.*, **61**, 917 (1957).

(14) P. W. M. Jacobs and F. C. Tompkins in "Chemistry of the Solid State," W. E. Garner, Ed., Academic Press, New York, N. Y., 1955, pp 198–207; A. K. Galwey, "Chemistry of Solids," Chapman and Hall Ltd., London, 1967, Chapter 5.

(see Figure 1). For example, at 65°, $k = 1.4 \times 10^{-3}$ sec^{-1} for the "small" particles and 7.0×10^{-4} sec^{-1} for "medium" ones (these values are taken from Figure 1). The relative magnitude of these rate constants is roughly inversely proportional to the relative particle sizes of the samples.

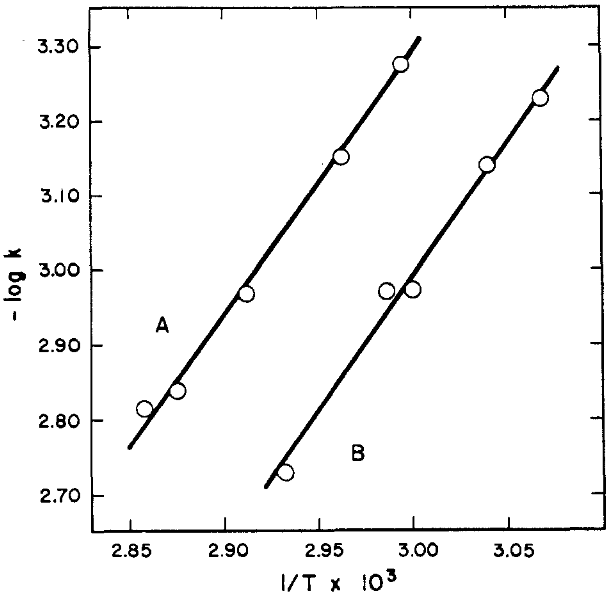

Figure 1.—Arrhenius plot of the rate data for the dehydration of "small" crystals (B) and "medium" crystals (A) of *trans*-$[Co(en)_2Cl_2](H_5O_2)Cl_2$.

A least-squares analysis of kinetic results gave an Arrhenius activation energy of 20 ± 2 kcal mol^{-1} in static air ("small" particles) and values of 16.6 ± 1.3 kcal mol^{-1} ("small" particles) and 16.0 ± 0.7 kcal mol^{-1} ("medium" particles) *in vacuo*.[15,16] The error limits are one standard deviation. In the case of the studies conducted at reduced pressure, the same activation energies were obtained using both the $-\log(1 - \alpha) = kt + c$ and the $(1 - \alpha)^{1/3} = 1 - kt$ rate laws. Figure 1 shows the Arrhenius activation energy plots for the dehydration where the rate constants are those for the first of these rate laws.

Comparison of the crystal structures of *trans*-$[Co(en)_2Cl_2](H_5O_2)Cl_2$ and *trans*-$[Co(en)_2Cl_2]Cl$ suggests that the dehydration is a topotactic reaction—definite orientation relations appear to exist between reactant and product phases.[17] The crystal structure of *trans*-$[Co(en)_2Cl_2](H_5O_2)Cl_2$ has been determined by X-ray analysis.[4] In addition, a preliminary neutron diffraction study of this compound has been reported recently.[5] A single-crystal X-ray study of *trans*-$[Co(en)_2Cl_2]Cl$ has also been conducted.[18] The hydrated complex used in the present study and the dehydrated material obtained from it by heating in the solid phase have X-ray powder patterns in agreement with the unit cell dimensions of the structures reported in the literature.

These crystal structure studies have shown that in *trans*-$[Co(en)_2Cl_2](H_5O_2)Cl_2$ the complex cations are arranged in layers, separated from each other by layers of $H_5O_2^+$ and Cl^- ions (in the (100) plane of the monoclinic C_{2h}^{5}-$P2_1/c$ class crystals). The complex cations lie in such a fashion that the Cl–Co–Cl portions of the ions are oriented principally along the *c* axis. The $H_5O_2^+$ group appears to have a hydrogen equidistant from two water molecules.[5] The oxygen–oxygen distance has been reported as 2.50 Å[5] and as 2.66 Å.[6] This diaquohydrogen ion has a *trans* configuration and the terminal hydrogens are hydrogen bonded to the ionic chlorides.

In *trans*-$[Co(en)_2Cl_2]Cl$, the ionic chlorides take positions in the same plane as the complex cations, and the cations are located so that the Cl–Co–Cl portion of the ion lies principally along the *a* axis. The changes in the unit cell dimensions as one goes from *trans*-$[Co(en)_2Cl_2](H_5O_2)Cl_2$ to *trans*-$[Co(en)_2Cl_2]Cl$ reflect the loss of HCl and H_2O and the accompanying movement of complex cations and chloride ions. While the angle β changes only slightly, from 110.43 to 109.27°, *a* changes from 10.68 to 6.26 Å, *b* changes from 7.89 to 8.96 Å, and *c* changes from 9.09 to 9.49 Å.[19] The shrinkage along *a* occurs because of the loss of H_2O and HCl and the movement of the remaining chloride ions into the same plane as the complex cations. The increase in *b* and *c* distances reflects the movement of the chlorides into the same plane (100) as the complex cations.

The Dehydration of ***trans*-$[Co((\pm)pn)_2Cl_2](H_5O_2)Cl_2$.**—The dta of this complex, obtained in static air at a heating rate of 4° min^{-1}, exhibited a single endothermic transition centered at about 170° and an exothermic transition beginning at about 220°. The first peak corresponds to the simultaneous loss of HCl and H_2O, while the second is due to decomposition of the complex cation. The tga obtained both in static air and *in vacuo* also indicated loss of H_2O and HCl in a single step. A small, loosely packed sample heated in static air at a rate of 5° min^{-1} began to lose mass at 85° and reached a constant weight at about 120°. This simultaneous evolution of HCl and H_2O is in keeping with the crystal structure of this substance which has been shown to contain $H_5O_2^+$ and Cl^- ions.[6] It is also consistent with the behavior of *trans*-$[Co(en)_2Cl_2](H_5O_2)Cl_2$.

In static air the ethylenediamine complex loses HCl and H_2O more readily than the propylenediamine complex. This can be seen from the dta and tga data and is also evident at room temperature where the ethylenediamine complex undergoes much more rapid efflorescence. However, under vacuum tga both compounds commenced mass loss at about the same tem-

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[15] These activation energies are in agreement with those calculated from the appropriate 5° min^{-1} tga curves by the method of Fuoss, Salyer, and Wilson.[16] However, the values obtained from 1° min^{-1} tga curves were high by as much as 5–10 kcal mol^{-1}.

[16] R. M. Fuoss, I. O. Salyer, and H. S. Wilson, *J. Polymer Sci.*, **A2**, 3147 (1964).

[17] See L. S. Glasser, F. P. Glasser, and H. F. W. Taylor, *Quart. Rev.* (London), **16**, 343 (1962).

[18] K. A. Becker, G. Grosse, and K. Plieth, *Z. Krist.*, **112**, 375 (1959).

[19] This comparison has been made by redefining the *a* and *c* axes of the dehydrated crystal (which belongs to the monoclinic C_{2h}^{5}-$P2_1/a$ class) to correspond to the *c* and *a* axes, respectively, of the hydrated crystal.

perature ("small" particles of both compounds began to lose mass at 40–45°).

When viewed under a microscope, the dehydration of *trans*-[Co((±)pn)$_2$Cl$_2$](H$_5$O$_2$)Cl$_2$ was found to begin at the corners and edges of the parallelepiped crystals. In contrast to the ethylenediamine complex, however, rapid surface nucleation was not observed on the predominant (100) faces. When viewed perpendicular to the (100) plane, the reaction appears to proceed like a contracting square, although the interphase boundaries are somewhat irregular. During dehydration, fissures develop principally along the crystallographic axes, and further reaction also begins and spreads from these defects.

In static air as well as *in vacuo*, the results of isothermal mass loss studies were best described (for α = 0.1–0.9) by the rate law

$$(1 - \alpha)^{1/2} = 1 - kt$$

This expression has been derived by assuming extremely rapid nucleation of a parallelepiped particle on all but two parallel square faces followed by movement of interphase boundaries by a "contracting-square" model.[14] Hence the kinetic results are consistent with microscopic observations. It should be noted, however, that the rate law

$$(1 - \alpha)^{1/3} = 1 - kt$$

also fits the data reasonably well although over a somewhat shorter range (α = 0.3–0.9). The isomerization accompanying the dehydration of *trans*-[Co((±)pn)$_2$Cl$_2$](H$_5$O$_2$)Cl$_2$ *in vacuo* (less than about 30–40%) may add some uncertainty to these kinetic studies. The isomerization was greater in static air partly because of the higher temperatures used and partly because the evolved water had greater opportunity to interact with the complex cation.

The rate constant k in the contracting-square law equals k'/a where k' is the particle-size-independent rate constant, and a is half the length of the particle. Using particle lengths of 0.04, 0.08, and 0.20 mm for the "small," "medium," and "large" particle samples, respectively (roughly the sizes of the "average" particles in each sample) we obtain from Figure 2 rate constants, k', of 2.9 × 10^{-5}, 3.5 × 10^{-5}, and 2.6 × 10^{-5} mm sec^{-1} for each particle size at 59° (T^{-1} = 3.01 × 10^{-3}). Thus the rate of dehydration varies with particle size in the expected manner.

The Arrhenius activation energies, obtained by least-squares analysis of the isothermal mass loss studies, are 31 ± 2 kcal mol^{-1} in static air ("small" particles) and 16.3 ± 0.5, 15.5 ± 0.5, and 16.6 ± 0.6 kcal mol^{-1} *in vacuo* for the "small," "medium," and "large" particles, respectively. The error limits are one standard deviation. The activation energy is thus independent of particle size and has the same value *in vacuo* as that obtained for the ethylenediamine complex. Figure 2 shows the Arrhenius activation energy plots for the dehydration of *trans*-[Co((±)pn)$_2$Cl$_2$](H$_5$O$_2$)Cl$_2$ *in vacuo*.

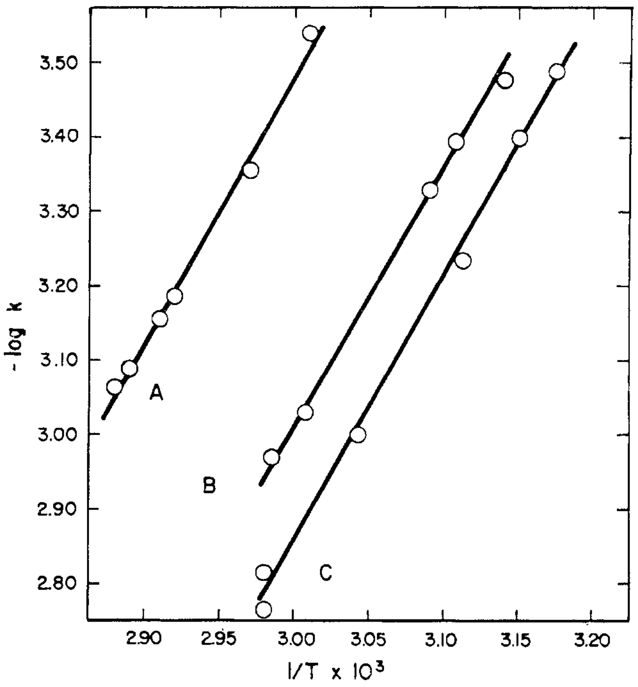

Figure 2.—Arrhenius plot of the rate data for the dehydration of "small" crystals (C), "medium" crystals (B), and "large" crystals (A) of *trans*-[Co((±)pn)$_2$Cl$_2$](H$_5$O$_2$)Cl$_2$.

X-Ray powder patterns 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$_2$ were virtually identical and agreed with reflections calculated from the unit cell dimensions reported for *trans*-[Co((−)pn)$_2$Cl$_2$](H$_5$O$_2$)Cl$_2$.[6] This compound is reported to have a crystal structure based on the monoclinic C2 space group. As in the case of the ethylenediamine compound, the complex cations are arranged in layers parallel to the (100) plane with H$_5$O$_2$$^+$ and Cl$^-$ ions located between the layers of complex cations. The Cl–Co–Cl portion of the complex cation lies principally along the c axis and the methyl group of the propylenediamine ligand lies principally along the a axis.

Upon loss of H$_2$O and HCl, the lattice undergoes rearrangement to give a structure possessing an X-ray powder pattern exhibiting a single strong reflection with a d spacing of 8.06 Å. In addition, weak, broad reflections were found corresponding to spacings of 6.51, 5.91, 4.78, 3.69, 3.65, and 3.03 Å. Quite possibly the lattice simply collapses along the a axis as the layers of H$_5$O$_2$$^+$ and Cl$^-$ are removed from the crystal. The single strong reflection would then be the distance between layers of complex cations, and the weaker reflections would be due to some slight amount of ordering of these layers relative to one another.

The powder pattern of the isomerized complex, *cis*-[Co((±)pn)$_2$Cl$_2$]Cl, exhibits a single strong reflection at 8.98 Å suggesting the same type of collapse as in the formation of *trans*-[Co((±)pn)$_2$Cl$_2$]Cl. The absence of additional, even very weak, reflections suggests accompanying disorganization within what was the (100) layers of the hydrated complex.

Comparison of the Dehydrations of the Ethylenediamine and Propylenediamine Complexes.—Although *trans*-$[Co(en)_2Cl_2](H_5O_2)Cl_2$ and *trans*-$[Co((\pm)pn)_2Cl_2](H_5O_2)Cl_2$ exhibit different rate laws for dehydration *in vacuo*, they appear to possess virtually identical activation energies for this process. This seems to indicate that the same activation process occurs in both compounds. One possible means of activation would be through vibration of the $H_5O_2^+$ ion. The infrared spectra of these compounds have been reported in the literature.[20] The high-frequency vibration (the so-called "band I" in ref 20) occurs at 2850 cm^{-1} (8.16 kcal mol^{-1}) for the ethylenediamine complex and at 2920 cm^{-1} (8.36 kcal mol^{-1}) for the propylenediamine complex. The first overtone of this band would be of the same energy (16.3–16.7 kcal mol^{-1}) as the activation energy for dehydration.

Although the activation energies for the dehydration *in vacuo* of both the ethylenediamine and the propylenediamine complexes are the same (or nearly the same), these two compounds clearly differ in their ease of dehydration in static air. This difference can be traced to the fact that the ethylenediamine complex can lose HCl and H_2O from all faces while the propylenediamine complex resists dehydration from the (100) face. The rate of dehydration depends in part on the rate of diffusion of water from the solid. This is a temperature-dependent process which will be of greater importance in static air than *in vacuo*. Consequently, it is logical that the rate of dehydration of the propylenediamine complex is lower than that of the ethylenediamine complex where diffusion is apparently freer and not restricted in direction. The different activation energies exhibited by these two compounds in static air seem to reflect this difference in ease of diffusion.

The fact that the ethylenediamine complex undergoes dehydration from all faces while the propylenediamine complex resists dehydration from the (100) face may be due to some subtle difference in the manner in which the complex cations are packed within the (100) layers. Loss of HCl and H_2O from all faces of the ethylenediamine complex may provide an opportunity for recrystallization which is lacking in the propylenediamine complex where the (100) layers of complex cations are apparently not penetrated by the evolved HCl and H_2O.

Acknowledgment.—The author wishes to thank the Desert Research Institute of the University of Nevada for financial assistance.

[20] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1640 (1964).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES, CALIFORNIA 90007

Rate and Equilibrium Studies of the Displacement of Water in *trans*-Sulfitoaquobis(dimethylglyoximato)cobalt(III) by Various Nucleophiles[1]

BY HON GEE TSIANG AND W. K. WILMARTH

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Ligation studies have been made of the rate of displacement of H_2O in $Co(DH)_2(SO_3)OH_2^-$, the symbol DH being used to represent the dimethylglyoxime anion. At 25° and unit ionic strength numerical values of the second-order rate constants (M^{-1} sec^{-1}) for the various nucleophiles are: thiourea (tu), 8.34; N_3^-, 7.30; HSO_3^-, 6.06; I^-, 5.50; py, 5.00; $S_2O_3^{2-}$, 1.45. Ligation by SO_3^{2-}, in contrast to the behavior of the other nucleophiles, appears to react in a limiting SN1 mechanism with maximum value of the rate constant of 0.56 sec^{-1}, independent of the SO_3^{2-} concentration above 0.10 *M*. Ligation by SCN^-, which is about as reactive as N_3^-, seems to occur by parallel reaction paths. The equilibrium quotient for formation of $Co(DH)_2(SO_3)I^{2-}$ is 2.56, a value larger than that for formation of $Co(DH)_2(SO)_3Br^{2-}$ (class b behavior). The equilibrium quotient for formation of $Co(DH)_2(SO_3)SCN^{2-}$ is 227. The acidity quotient of $Co(DH)_2(SO_3)OH_2$ at unit ionic strength is approximately 5.8×10^{-11}. The conjugate base $Co(DH)_2(SO_3)OH^{2-}$ does not react at an appreciable rate with SCN^- and probably not with the other nucleophiles listed above.

Introduction

It has recently been shown that the substitution reactions of Co(III) complexes may be markedly influenced by the presence of an SO_3^{2-} ligand.[2,3] Two aspects of the kinetic behavior of these sulfito complexes are of interest. First, the substitution reactions are remarkably rapid, the half-life at 25° being of the order of seconds or less. Since the available evidence indicates that substitution occurs in the *trans* position, this rapidity of reaction will be referred to below as *trans* activation. Second, the reactions which have been studied thus far proceed by a limiting type of SN1 mechanism with strong evidence for the generation of a five-coordinate reactive intermediate with a lifetime long enough to discriminate between the various nucleophiles present in the system.

Although only two studies[2,3] of the sort described above have been reported, the work involved complexes as dissimilar in structure as $Co(CN)_4(SO_3)OH_2^{3-}$ and

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