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Preparation of a Mixed N-Bonded–S-Bonded *trans*-Dithiocyanato Complex. The Three Isomers of Tetraphenylarsonium *trans*-(Dithiocyanato)bis(dimethylglyoximato)cobaltate(III)

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Three complexes having the formulation of the title complex have been isolated. Spectral data (ir and pmr) were interpreted as being consistent with the three tetraphenylarsonium salts differing only in the mode of attachment of the SCN group. The mixed N-bonded–S-bonded isomer is believed to be the first isolated octahedral complex of this type. It is also the first such complex of any geometry in which the SCN groups are mutually trans to each other. The implications of this geometry with regard to current theories of bonding of thiocyanate are discussed. It is concluded that metal–SCN π back-bonding is unimportant in these complexes. The most stable linkage isomer is not the S,S-bonded material as is commonly accepted. In dimethylformamide the ratio of isomers was found to be approximately 2:2:1 for N,N:N,S:S,S.

Introduction

Thiocyanate occupies a special place among small anionic ligands because an understanding of the two modes of bonding (S or N bonding) holds the potential for a more exact evaluation of the importance of π bonding in coordination compounds. A considerable number of complexes containing the thiocyanate ligand have been prepared.[1,2] but relatively few complexes containing both N- and S-bonded thiocyanate have been isolated.[3] Synthesis of mixed N,S-bonded complexes has been stimulated by the recognition that other ligands in the coordination sphere may influence the bonding mode.[4] The primary argument advanced for such influences is based on the π-bonding potential of the "soft" S donor and the relatively "hard" ionic bonding of the N donor of the SCN$^-$ ligand. It has been argued that a good π-acceptor ligand trans to the thiocyanate ligand will favor N bonding and that a weak π acceptor would favor S bonding. Using this concept, Meek and his coworkers have succeeded in synthesizing a variety of mixed-bonded dithiocyanato complexes of Pd(II).[5] An ingenious approach was utilized in that a bidentate mixed donor atom ligand, containing only one π-acceptor ligating atom, would promote N bonding of only one of the necessarily cis thiocyanate ligands. A logical extension of this argument is that *trans*-dithiocyanato complexes of borderline class a–class b metal centers should be preferentially either mixed bonded or N bonded since each of the thiocyanate ligands in the S,S isomer would be competing for the π electrons on the metal. However, no trans N,S-bonded complexes have been reported, although examples of trans N,N and trans S,S isomeric pairs exist.[4c]

These types of arguments hold well primarily in describing the chemistry of square-planar complexes of the 4d and 5d transition metals.[6] By contrast, octahedral complexes, particularly those involving 3d transition metals, follow the opposite pattern in that π-acceptor (usually "soft") ligands favor S bonding. Jorgensen has termed this behavior "symbiotic" and has ascribed it to a general softening of the metal ion favoring bonding to soft ligands.[7] More recently, Norbury[8] has attempted to describe the contrasting phenomenological behavior between square-planar and octahedral complexes. His approach was to utilize the perturbation theory developed by Klopman[9] in conjunction with a MO calculation on SCN$^-$.[10] The proposed M to ligand bonding scheme utilized does not involve any π bonding but rather uses the σ_3 and σ_4 orbitals of SCN$^-$. This scheme seems to be unrealistic in that the bent M–SCN bond requires that a π orbital on SCN$^-$ be involved in the bonding.

Gutterman and Gray[11] have suggested that the π_2 orbital on SCN$^-$ can account for the bent M–SCN bond and have presented a more appropriate description of metal–thiocyanate bonding in an MO scheme for $M(CN)_5(CNS)^{3-}$ (M = Co(III),[11] Fe(III);[12] CNS does not imply bonding mode). Their assessment of the MO energies of SCN$^-$ led to the conclusion that the lowest unoccupied orbital of SCN$^-$ (π_3) is approximately 15,000 cm^{-1} higher in energy than the π* orbital in CN$^-$. Therefore, it was suggested that the π_3 orbital was too high in energy to act as an acceptor in the Co(III) complex.

In contrast to the several reports of mixed-bonded dithiocyanato square-planar complexes, only one report of a study of an octahedral complex has appeared.[3] A complicating feature of some previous studies on mixed *N*- and *S*-dithiocyanato square-planar complexes[5,6] arises from the difference in steric requirements[13] of the bent M–SCN group as compared to the linear M–NCS compound. It may well be that steric hindrance rather than π bonding is determining coordination mode.[5,6] Therefore, it seemed highly desirable to prepare octahedral complexes in which steric interactions were invariant.

This report contains evidence for the preparation and isolation of the first octahedral complex as well as the first ionic complex containing both N- and S-bonded thiocyanate. It is to our knowledge the first complex in which the SCN- ligands are trans. In addition, the N,N and S,S isomers have been prepared. The three compounds (Figure 1) are isomers of

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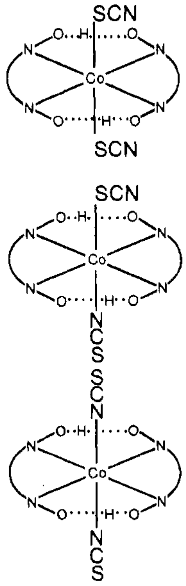

Figure 1. The three possible isomers of $[Co(DH)_2(CNS)_2]^-$. Note the proposed bent M-SCN bonds.

the anion *trans*-$[Co(DH)_2(CNS)_2]^-$ (where DH = monoanion of dimethylglyoxime). Our examination of this system was prompted by our recent findings that the two isomers of (4-*t*-Bu(py))Co$(DH)_2$CNS were of approximately equal stability.[14] Work on related systems has also demonstrated linkage isomerism for other cobaloxime(III)-thiocyanate complexes.[15] Several other studies have revealed that the $(DH)_2$ ligand system modifies the typical class a or "hard" cobalt(III) center such that class b or "soft" behavior is often observed.[16-18]

Experimental Section

Instrumentation. The pmr spectra were obtained on a Varian A-60 instrument and chemical shifts referenced to internal tetramethylsilane. Infrared spectra were measured using a Perkin-Elmer 337 spectrometer (KBr disks) or a Perkin-Elmer 521 spectrometer (DMF solutions, 0.5-mm Irtran cells). Analyses were performed as described previously.[18]

Materials. All chemicals were of reagent grade or higher purity.

Preparations. $K[Co(DH)_2(SCN)_2]\cdot H_2O$. Cobalt acetate tetrahydrate (16.8 g, 0.06 mol) and potassium thiocyanate (12.0 g, 0.12 mol) were dissolved in 50% aqueous ethanol (100 ml). Dimethylglyoxime (15.4 g, Baker Analyzed reagent) was partially dissolved in 95% ethanol (300 ml) by boiling and this mixture added to the cobalt solution. The resulting mixture was filtered to remove undissolved residues (primarily from the dimethylglyoxime) and the solution was aerated for 3 hr. A difficultly soluble yellow-brown material which deposited after the solution had been standing overnight was collected and washed three times with 2-propanol (25 ml); yield 8.1 g. The filtrate and washings were combined and allowed to stand overnight in a hood. The resulting reddish brown crystals were washed as above; yield 7.4 g. The filtrate and washings were combined and allowed to evaporate slowly (48 hr). The large black-green crystals which formed were collected and washed with ether and allowed to air-dry; yield 6.0 g.

Unlike the first two fractions which are poorly soluble in most solvents, this last fraction was found to be soluble in water, methanol, acetone, ethanol, etc. In addition, the first two fractions are most probably acid salts whereas the last fraction gave evidence of being a potassium salt (tetraphenylborate test). The ir spectrum clearly indicated that the material was hydrated (a very strong peak at 3490 cm^{-1}). The pmr spectrum of this material dissolved in water contains a single methyl resonance at τ 7.6. *Anal.* Calcd for $C_{10}H_{16}CoKN_6O_5S_2$: C, 25.97; H, 3.47; Co, 12.75. Found: C, 26.10; H, 3.41; Co, 12.50.

$As(C_6H_5)_4[Co(DH)_2(NCS)(SCN)]$. The complex $As(C_6H_5)_4$[Co-in 10 ml of H_2O) was added quickly to a *freshly* prepared solution of $K[Co(DH)_2(SCN)_2]$ (0.47 g in 10 ml of H_2O). The yellow-brown product formed was removed on a filter, washed liberally with water, and air-dried. *Anal.* Calcd for $C_{34}H_{34}AsCoN_6O_4S_2$: C, 51.77; H, 4.32; Co, 7.49. Found: C, 51.30; H, 4.55; Co, 7.75.

$As(C_6H_5)_4[Co(DH)_2(NCS)(SCN)]$. The complex $As(C_6H_5)_4[Co(DH)_2(SCN)_2]$ prepared as above, but not collected, was extracted into methylene chloride (50 ml). Pmr study of such methylene chloride solutions revealed that, on standing at room temperature even for short periods, the ion $[Co(DH)_2(SCN)_2]^-$ isomerized to greater than 50% $[Co(DH)_2(NCS)(SCN)]^-$. Since the tetraphenylarsonium salt of the latter ion was less soluble, the N,S-bonded material could be obtained in high isomeric purity (>90%) by adding hexane (50 ml) and letting the solution evaporate until crystals formed. The resulting pale brown product was collected, washed three times with 95% ethanol (30 ml) and then ether, and air-dried. *Anal.* Calcd for $C_{34}H_{34}AsCoN_6O_4S_2$: C, 51.77; H, 4.32; Co, 7.49. Found: C, 51.52; H, 4.26; Co, 7.62.

$As(C_6H_5)_4[Co(DH)_2(NCS)_2]$. The complex $As(C_6H_5)_4[Co(DH)_2(SCN)_2]$ prepared as above was extracted into methylene chloride (50 ml) and 95% ethanol (100 ml) added. The solution was warmed and the poorly soluble orange product $As(C_6H_5)_4[Co(DH)_2(NCS)_2]$ crystallized. The solution was cooled in ice. The crystals were collected, washed three times with 95% ethanol (30 ml) and then ether, and air-dried. *Anal.* Calcd for $C_{34}H_{34}AsCoN_6O_4S_2$: C, 51.77; H, 4.32; Co, 7.49. Found: C, 51.59; H, 4.68; Co, 7.38.

Results

Preparation and Isomeric Separation. The salt $K[Co(DH)_2(SCN)_2]$ was the most soluble product obtained from the air oxidation of a solution of cobalt(II) acetate, dimethylglyoxime, and KSCN in the ratio of 1:2:2. The pmr spectrum of this material in DMF or water contains a single methyl resonance. On standing, the spectrum of the DMF solution gradually changes giving first one and later a second additional peak in the methyl region (Figure 2). The pmr spectrum was unaffected by addition of KSCN and this result indicated that none of the three peaks was that of a solvate.

A preparative scheme combined with fractional crystallization was developed based on the rapid conversion of the $[Co(DH)_2(SCN)_2]^-$ ion to the $[Co(DH)_2(NCS)(SCN)]^-$ ion and the relative solubility of the isomers $[Co(DH)_2(NCS)_2]^- < [Co(DH)_2(NCS)(SCN)]^- < [Co(DH)_2(SCN)_2]^-$. The N,N and S,S isomers are believed to be isomerically pure within experimental error and the N,S isomer is believed to be at least 85% isomerically pure (pmr spectral evidence).

Structural Assignment. Of all the spectral methods of structural characterization of linkage isomers of thiocyanate, the use of infrared appears to be the most reliable. Two approaches have been used relying principally either on the energy of the ir bands or on the intensity of the band. It is now generally accepted that the intensity of the ν(CN) band at *ca.* 2100 cm^{-1} is most diagnostic since, in some cases, the intensity of this band in the M-SCN isomer is *ca.* 10 times less than that in the M-NCS isomer.[19] The intensity of the ν(CN) band of the most soluble salt $As(C_6H_5)_4[Co(DH)_2(SCN)_2]$ in DMF solution (10 mg of complex/ml of DMF) was found to be $^1/_{3.8}$th that of the least soluble $As(C_6H_5)_4[Co(DH)_2(NCS)_2]$ and $^1/_{2.3}$ times that of $As(C_6H_5)_4[Co(DH)_2(NCS)(SCN)]$. The ir spectra of the two most soluble arsonium salts (KBr disks) were almost identical, but the least soluble salt had a moderate-to-weak band at 835 cm^{-1}. The ir spectrum of the complex (py)Co$(DH)_2$NCS also differs from the S-bonded isomer in having a band at 837 cm^{-1},

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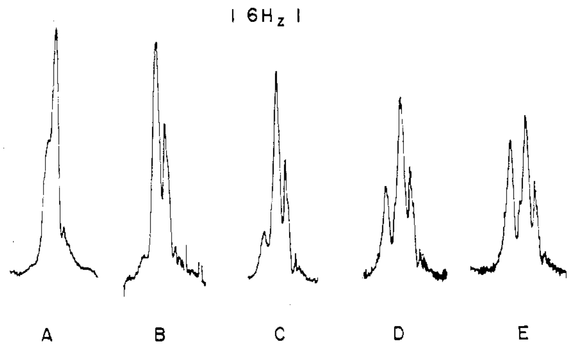

Figure 2. Pmr spectral changes of a DMF solution initially containing $As(C_6H_5)_4[Co(DH)_2(SCN)_2]$. Spectra were taken at the following times after dissolution: A, 3 min; B, 11 min; C, 25 min; D, 50 min; E, 185 min. Spectrum A contains primarily the methyl resonance of the S,S isomer with a shoulder resulting from a small amount of the N,S isomer formed before the spectrum was recorded. The peak of N,S isomer reaches maximum intensity at 11 min (B). Eventually, a third peak attributable to the N,N isomer appears (C). Spectrum E is identical with one recorded at 120 min (not shown) and thus is believed to be that of the equilibrium mixture. Note that after 11 min (B), the predominant isomer is the N,S species and that the subsequent isomerization N,S → N,N has not occurred significantly. Such a rate differential was exploited in the preparation of the N,S isomer. The potassium salt exhibited similar changes in spectrum.

which was assigned to the C–S stretch.[15a] The reason for the absence of a band at *ca.* 835 cm^{-1} in the spectrum of $As(C_6H_5)_4[Co(DH)_2(NCS)(SCN)]$ is not understood, but this band may be weakened or shifted by the trans sulfur donor. The absence of the band at 835 cm^{-1} in the mixed-bonded isomer is evidence that the material of intermediate solubility is not a mixture of the N,N- and S,S-bonded isomers. In DMF the ν(CN) band occurred at 2110 cm^{-1} for all three isomers, differing only in intensity. However, the sharpness of the bands followed the order S,S > S,N > N,N.

Other physical properties such as color and solubility are those expected by analogy to complexes of the type $LCo(DH)_2CNS$. Furthermore, for this latter type of complex, we have found[18] that in pmr spectra in most solvents (DMF, acetone, methylene chloride, etc.) the methyl resonance of the S-bonded isomer is upfield to that of the N-bonded isomer; but in aromatic solvents (benzene, nitrobenzene,) the resonance of the N-bonded isomer is upfield. We are currently investigating a large number of complexes of the type $(4\text{-}t\text{-Bu(py)})Co(DH)_2X$ ($X = Cl, Br, I, N_3, NO_2$, NCS, SCN, CH_3) and find that aromatic solvents are exerting solvent-induced shifts.[20] These shifts arise from dipole–solvent interactions. The charge separation in the complexes is expected to be greatest for the N,N isomer (which contains linear Co–NCS bonds) and least for the S,S isomer (which contains bent M–SCN bonds). On the basis of these findings, it can be predicted that the N,N isomer would be furthest downfield in nonaromatic solvents and furthest upfield in aromatic solvents. The positions of the methyl resonances of the $[Co(DH)_2(CNS)_2]^-$ isomers are as follows: (A) (DMF) S,S, τ 7.61; S,N, τ 7.58; N,N, τ 7.55; (B) (nitrobenzene) S,S, τ 7.44; S,N, τ 7.58; N,N, τ 7.72.

Solution Studies. In DMF solutions containing bromotrichloromethane, the pmr spectrum of $As(C_6H_5)_4[Co(DH)_2(SCN)_2]$ remains unchanged for several days. We have found[18] that many reactions of cobaloximes(III) are catalyzed by trace amounts of cobalt(II) impurities usually contained in such products prepared by the accepted route of aerial oxidation. Addition of oxidizing agents such as bromotrichloromethane inhibits these reactions. Therefore, we propose that the isomerization reactions we have observed are cobalt(II)-catalyzed processes, reaction 1. The low abundance of such

$$[Co(DH)_2(SCN)_2] \xrightleftharpoons{Co(II)} [Co(DH)_2(NCS)(SCN)]^- \xrightleftharpoons{Co(II)} [Co(DH)_2(NCS)_2]^- \tag{1}$$

catalysts (<0.1%) precludes characterization, but we have speculated as to their nature.[18] Addition of cobaloxime(II) complexes resulted in immediate equilibrium.

Discussion

A complicating feature and criticism often leveled[6] at studies of ambidendate isomers is the uncertainty associated with the structure assignment. We feel that the combined evidence presented in the Results provides the strongest evidence for an N,S-bonded isomeric species for any system reported thus far, except for those substantiated by X-ray structural analysis. For no other system have all the following types of studies been done: (1) pmr spectra in several solvents, (2) equilibrium measurements, (3) isolation of all possible linkage isomers, (4) ir spectra of all isomers in solution, and (5) ir spectra of all isomers in solid phase. In most previous studies, it was not possible definitely to rule out bridged species (since the complexes were coordinatively unsaturated) or mixtures of N,N and S,S isomers. In our system we can rule out both of these possibilities since a bridged species would necessitate the presence of the ν(CN) band of free SCN^- in the ir spectrum and two equal methyl resonances in the pmr spectrum. Both the pmr and ir spectra of the N,S-bonded isomer are also inconsistent with a mixture of N,N and S,S isomers because the methyl resonance occurs at different chemical shifts for all three species and because no band was observed at *ca.* 835 cm^{-1} in the ir spectrum of the N,S isomer. Similar arguments can be used to rule out the possibility of cis complexes which are highly unfavored in the $(DH)_2$ ligand system and which would give more complex pmr spectra than were in fact observed.

From statistical considerations, the distribution of isomers should be N,N:S,N:S,S = 1:2:1. In DMF, we find 2:2:1. Therefore, there is no special instability associated with the S,S isomer, as might be expected if the two ligating S atoms were competing for π-bonding electrons in the metal. In complexes of the type $LCo(DH)_2CNS$ when L is a good π-acceptor ligand (PPh_3) the S-bonded isomer is favored over the N-bonded isomer, but when L is an exclusively σ-donor ligand (benzylamine) both isomers are of approximately equal stability.[21] Allowing for the statistical factor of 2, the N,S and S,S isomers are of comparable stability. If we equate one S-bonded SCN to L, this result can be interpreted as indicating that -SCN is a good σ donor but a poor π acceptor.

The above evaluation of the σ and π properties of -SCN is supported by some spectroscopic and MO studies on $Co(CN)_5NCS^{3-}$ and $Co(CN)_5SCN^{3-}$.[11] Gray found no evidence to indicate that -SCN was a π acceptor and instead suggested that the ligand might be a good π *donor.* This evaluation of π bonding in SCN complexes of trivalent first-row transition metal complexes leads to the prediction that good π-acceptor ligands trans to SCN would promote S bonding. This conclusion is consistent with results we have obtained in our studies of dimethylglyoximate complexes.

If it is accepted that (1) the π_3 orbital on thiocyanate is too high in energy to act as a π acceptor with 3d transition metal ions, (2) 4d and 5d transition metals have orbitals higher in energy and more suitable to π bonding, and (3) the

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(20) R. Stewart and L. G. Marzilli, unpublished data.

(21) L. A. Epps and L. G. Marzilli, unpublished data.

square-planar arrangement is more suitable than an octahedral arrangement for π bonding, then the contrasting behavior of octahedral systems and square-planar systems can be understood. Evidence in the form of MO calculations,[11] spectroscopic studies,[11,12] and the results presented here support point (1) above; the second and third points are well established.[22] There does not seem to be a need for two theories (symbiosis and MO) to account for the contrasting behavior discussed above. It seems unlikely that any theory will adequately explain in detail every case of linkage isomerism since the energy differences found must be quite small (~1 kcal/mol) for isomers to coexist in detectable amounts.

Registry No. $K[Co(DH)_2(SCN)_2]$, 38625-16-0; $As(C_6H_5)_4[Co(DH)_2(SCN)_2]$, 39494-93-4; $As(C_6H_5)_4[Co(DH)_2(NCS)(SCN)]$, 39494-94-5; $As(C_6H_5)_4[Co(DH)_2(NCS)_2]$, 39494-95-6.

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Acidopentaaminecobalt(III) Complexes with Polyamine Ligands. VIII. Kinetics of Hydrolysis of π-, κ-, and ω-Chloro(ethylenediamine)(diethylenetriamine)cobalt(III) and α- and β-Chloro(ethylenediamine)(dipropylenetriamine)cobalt(III) Cations in Aqueous Acidic Solution

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The kinetics of hydrolysis of π-, κ-, and ω-$Co(en)(dien)Cl^{2+}$ and α- and β-$Co(en)(dpt)Cl^{2+}$ have been investigated in aqueous $HClO_4$, by spectrophotometry and by chloride release. Over the range 0.01–1.0 F H^+, with $C_0 \approx 1$ mF and $\mu = 1.0$, the hydrolysis of the π isomer follows the rate law: $-d[Co(en)(dien)Cl^{2+}]/dt = k[Co(en)(dien)Cl^{2+}]$ at 70°, independent of $[H^+]$. The hydrolysis of the other cations was investigated in 1.0 F $HClO_4$ only, over the 65–85° (π, κ, ω), 50–70° (α), or 35–55° (β) temperature ranges. For the π, κ, ω, α, and β cations respectively at 65.0°, 10^5k (sec^{-1}) = 5.22 ± 0.31, 2.58 ± 0.11, 2.22 ± 0.12, 26.07 ± 0.96, and 169.4 ± 2.5 (extrapolated); E_a (kcal mol^{-1}) = 27.0 ± 1.1, 26.2 ± 1.1, 26.7 ± 0.5, 25.2 ± 0.7, and 22.6 ± 0.4; $\Delta S^{\ddagger}{}_{298}$ (cal deg^{-1} mol^{-1}) = −0.4 ± 3.6, −4.2 ± 3.6, −2.8 ± 1.7, −2.5 ± 2.3, and −6.1 ± 1.0. Under the conditions studied, isomerization between these chloro isomers is negligibly slow relative to the hydrolysis, and only in the case of the κ isomer is any isomerization of the aquo product observed. The κ-$Co(en)(dien)(OH_2)^{3+} \rightarrow \pi$-$Co(en)(dien)(OH_2)^{3+}$ isomerization was followed spectrophotometrically over the 65–85° temperature range in 1.0 F $HClO_4$. At 65.0°, the first-order rate constant for this reaction is 10^5k (sec^{-1}) = 4.75 ± 0.19; E_a (kcal mol^{-1}) = 29.7 ± 1.1 and $\Delta S^{\ddagger}{}_{298}$ (cal deg^{-1} mol^{-1}) = +7.4 ± 3.6. The Hg^{2+}-catalyzed aquation of the π-, κ-, and ω-$[Co(en)(dien)Cl]ZnCl_4$ isomers has also been investigated spectrophotometrically. In the 15–35° temperature range at $\mu = 1.0$ ($HClO_4$) with $[Hg^{2+}] \approx 0.155$ F and $C_0 \approx 0.01$ F, the observed rate law is $-d[Co(en)(dien)Cl^{2+}]/dt = k_{obsd}[Co(en)(dien)Cl^{2+}]$ where $k_{obsd} = k[Hg^{2+}]$. At 25.0° ($\mu = 1.0$), for the π, κ, and ω isomers respectively, 10^3k (M^{-1} sec^{-1}) = 14.7 ± 0.5, 5.11 ± 0.09, and 4.86 ± 0.1; E_a (kcal mol^{-1}) = 13.9 ± 0.4, 19.5 ± 0.3, and 18.0 ± 0.3; $\Delta S^{\ddagger}{}_{298}$ (cal deg^{-1} mol^{-1}) = −22.3 ± 1.4, −5.6 ± 1.1, and −10.7 ± 1.1. Evidence is also presented for the $HgCl^+$-catalyzed hydrolysis of the π isomer.

Introduction

The effect of chelation on the rate of acid hydrolysis of Co(III) complexes has been investigated by several workers.[1-3] The classic paper of Pearson, Boston, and Basolo[1] gives data for several chloropentaaminecobalt(III) complexes with polyamine ligands but, in most cases, the configuration (or even the isomeric purity) of the particular chloropentaamine complex was not established. The $Co(en)(dien)Cl^{2+}$ system[4] was further investigated by Bosnich and Dwyer,[2] who separated two isomers (ω and ϵ) and measured their rates of acid hydrolysis, but, again, the geometric configurations were not known with certainty. Following the successful synthesis of the α- and β-$Co(tetren)Cl^{2+}$ isomers,[5,6] Ni and Garner[3] measured the rates of acid hydrolysis. At the time of the kinetic study, the geometric configurations were unknown, but later, single-crystal X-ray analysis showed that the α and β cations contained a similar polyamine skeleton and were related by alternate positions available to the secondary NH proton in the peripheral polyamine configuration (Figure 1).[7]

Three (π, κ, ω) $Co(en)(dien)Cl^{2+}$ and two (α, β) $Co(en)(dpt)Cl^{2+}$ isomers have recently been isolated[8-10] and their structures have been established by single-crystal X-ray analysis[11-14] (Figure 1). In this present paper we report

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