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A Monodentate Ethylenediamine Complex of Cobalt(III)[1]

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The first complex of cobalt(III) in which ethylenediamine functions as a monodentate ligand is reported. The mode of preparation, elemental analysis, visible absorption spectrum, pmr spectrum, and the acid strength of the complex are all in accord with the formulation *cis*-$[Co(en)_2(enH)Cl]Cl_3 \cdot H_2O$. In basic aqueous solution the predominant reaction of the complex is base hydrolysis of the chloro group yielding $Co(en)_2(mono\text{-}en)OH^{2+}$. However, in basic dimethyl sulfoxide chelate ring closure occurs to yield $Co(en)_3^{3+}$.

Introduction

There have been mechanisms proposed for several reactions of coordination compounds utilizing reactive intermediates in which ethylenediamine functions as a monodentate ligand.[2-7] However, to our knowledge, only three complexes containing monodentate ethylenediamine have been isolated all of which are complexes of chromium(III): $[(NH_3)_5Cr(OH)Cr(enH)(NH_3)_4]Cl_6$,[8] $Cr(enH)(OH_2)_5^{4+}$,[9] and $Cr(en)(enH)(OH_2)_3^{4+}$.[10] Herein are described the synthesis and characterization of the first cobalt(III) complex known to us in which ethylenediamine assumes the role of a monodentate ligand. Also reported are some significant reactions of this complex.

Experimental Section

Preparation of *cis*-$[Co(en)_2(enH)Cl]Cl_3 \cdot H_2O$.—To a suspension of finely ground *trans*-$[Co(en)_2Cl_2]Cl$ (8.55 g) in 100 ml of absolute methanol was added a solution of 1.60 g of ethylenediamine in 60 ml of methanol. The reaction mixture was stirred for 30 min at which time it was filtered to remove unreacted *trans*-$[Co(en)_2Cl_2]Cl$. Concentrated hydrochloric acid (5 ml) was immediately added to the filtrate and the resulting solution was cooled in an ice bath causing the desired compound to precipitate. After standing for 3 hr the precipitate was filtered, washed with ethanol, and air dried. One gram of this material was dissolved in 20 ml of water and the solution was placed on a Dowex 50W-X8 (100–200 mesh) cation-exchange column (19 mm × 800 mm) in the acid form. On elution with 2 *N* hydrochloric acid three principal bands separated; the fastest moving band (red) consisted of the desired complex, the next faster band (yellow) consisted of $Co(en)_3^{3+}$, and the third band (red), which eluted only with difficulty, consisted of binuclear cobalt(III) complexes containing ethylenediamine bridges.[11] The eluent containing the desired compound was evaporated on a rotary evaporator, dissolved in water, reevaporated, and finally dried *in vacuo* overnight; yield 0.5 g. *Anal.* Calcd for $CoC_6H_{27}ON_6Cl_4$: C, 17.98; H, 6.74; Cl, 35.4. Found: C, 18.26; H, 6.98; Cl, 35.2.

Elemental Analysis.—Carbon and hydrogen analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tenn.

The total chloride content of the complex was determined by potentiometric titration using standard silver nitrate solution. A weighed sample dissolved in 50 ml of water with 3 ml of 3 *M* NaOH was boiled for 5 min. After the sample had cooled to room temperature 3 ml of 3 *M* HNO_3 was added and the solution was checked to ensure that it was acid to litmus. Then 0.1 g of $Ba(NO_3)_2$ was added and the solution was titrated to the end point. The electrodes employed were a silver wire and a standard calomel electrode. The change in millivolts *vs.* volume of titrant was plotted and the point of greatest $\Delta mV/\Delta V$ taken as the end point.

Visible Absorption Spectra.—Visible absorption spectra were obtained using a Cary Model 14 recording spectrophotometer using 1-cm standard silica cells. A 0.01 *M* aqueous solution of *cis*-$Co(en)_2(NH_3)(OH_2)^{3+}$ was prepared for spectral measurement by allowing 10 ml of a 0.02 *M* solution of *cis*-$[Co(en)_2(NH_3)Cl]Cl_2$ to react with 10 ml of 0.16 *M* mercury(II) perchlorate solution in 0.1 *M* perchloric acid generating the desired complex. A solution of *cis*-$Co(en)_2(NH_3)(OH)^{2+}$ was prepared for measurement from the above solution by raising the pH of the solution to approximately 9 by addition of tris(hydroxymethyl)aminomethane. Mercury(II) does not precipitate under these conditions probably because of the chelating ability of Tris.

Proton Magnetic Resonance Measurements.—Proton magnetic resonance (pmr) data were obtained at ambient temperatures using a Varian A-60A nmr spectrometer equipped with an integration accessory. Solutions employed were 5–15% by weight of complex dissolved in 99.77% D_2O containing about 1% sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal reference standard.

Determination of the pK_a of *cis*-$Co(en)_2(enH)Cl^{3+}$.—A solution of 0.100 g (0.25 mmol) of complex in 5.0 ml of water was mixed rapidly with 10.0 ml of 0.0125 *N* sodium hydroxide solution and the pH of the resulting solution was measured using a Beckman expanded-scale pH meter equipped with standard glass and saturated calomel electrodes. The visible spectrum of the solution was indistinguishable from that of the untreated complex indicating no detectable base hydrolysis of the complex had occurred.

Reaction of *cis*-$Co(en)_2(enH)Cl^{3+}$ in Basic Aqueous and Dimethyl Sulfoxide Media.—A tris(hydroxymethyl)aminomethane–cacodylate aqueous buffer solution (pH 8.5) was prepared by adding cacodylic acid to a 0.1 *M* Tris solution until the desired pH was obtained. Enough complex was added to 15 ml of this solution to give a concentration of 0.01 *M* with respect to complex. After 1 hr the spectrum of this solution was measured. No further spectral change occurred after standing for an additional 24 hr. Following this period the solution was acidified by adding 0.30 ml of 72% perchloric acid and the spectrum was measured. This solution was then placed upon a Dowex 50W-X8 (100–200 mesh) cation-exchange column in the acid form and

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[11] These complexes are the subject of a paper to be published subsequently by M. D. Alexander and D. H. Busch.

the adsorbed complexes were eluted with 2 *M* hydrochloric acid. Two bands separated, the faster being very faint and yellow and the slower being very intense and orange.

For the reaction in dimethyl sulfoxide the following procedure was employed. Twenty milliliters of a 0.02 *M* solution of the complex in dimethyl sulfoxide was mixed with 20 ml of a 0.2 *M* solution of dry distilled piperidine in dimethyl sulfoxide. Spectra of the solution were obtained until no further spectral change occurred (approximately 24 hr). The product solution was absorbed on a cation-exchange column as in the aqueous case and eluted with 2 *M* hydrochloric acid. Only a single band (yellow) was obtained.

Results and Discussion

It has been known for many years that primary amines will react with *trans*-$Co(en)_2Cl_2^+$ in water and other solvents to yield *cis*-chloro(amine)bis(ethylenediamine)cobalt(III) products.[12-15] Similarly, we have found that ethylenediamine will react with *trans*-$Co(en)_2Cl_2^+$ in methanol to yield a complex of the *cis*-chloro(amine) type, *cis*-$[Co(en)_2(enH)Cl]Cl_3 \cdot H_2O$, in which an ethylenediamine molecule has one amine function coordinated and the other protonated. The visible absorption spectrum of the complex is very nearly superimposable upon that of the well-known complex *cis*-$Co(en)_2(NH_3)Cl^{2+}$ (ϵ_{367}^{max} 77, ϵ_{525}^{max} 74 for *cis*-$Co(en)_2(enH)Cl^{3+}$; ϵ_{367}^{max} 77, ϵ_{525}^{max} 72 for *cis*-$Co(en)_2NH_3Cl^{2+}$) confirming chloropentamine coordination and the *cis* topology.[15]

The pmr spectrum of *cis*-$Co(en)_2(enH)Cl^{3+}$ in D_2O is shown in Figure 1. Since the broad band centered at 2.9 ppm downfield from DSS is in the same position as the single broad CH_2 band in the spectrum of $Co(en)_3^{3+}$,[16] we assign this band to the CH_2 groups adjacent to the coordinated amines. Therefore, the remainder of the peaks centered downfield at 3.3 ppm are attributed to the CH_2 adjacent to the ammonium group. If the two groups of peaks are integrated according to the dashed lines, the intensity ratio of 1:5 is obtained supporting these assignments. The greater deshielding of the CH_2 next to the ammonium group could likely reflect the relative electronegatives of the coordinated amine and ammonium functions.

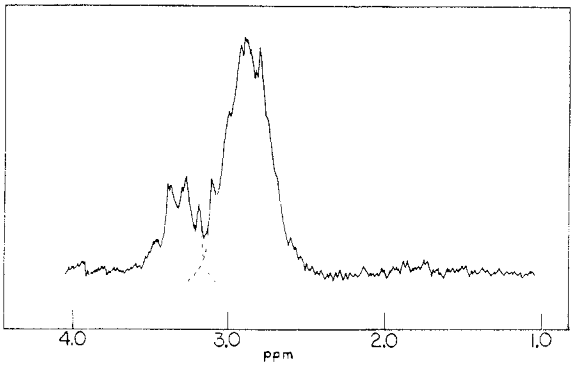

Figure 1.—Pmr spectrum of $Co(en)_2(enH)Cl^{3+}$.

The pH of a solution containing equimolar amounts of *cis*-$Co(en)_2(enH)Cl^{3+}$ and *cis*-$Co(en)_2$(mono-en)Cl^{2+} is 7.1 indicating this to be the approximate pK_a of the ammonium function. This is very nearly the same as pK_{a1} of enH_2^{2+}. A similar relationship has been found between the acid strengths of *cis*-$Co(en)_2(NH_2CH_2CO_2H)Cl^{2+}$, in which complex glycine is monodentate, and $^+NH_3CH_2CO_2H$.[17] Thus, additional evidence for the monodentate role is provided.

In basic aqueous solution at pH 8.5 (Tris–cacodylate buffer) the uncoordinated amine function of the complex is nearly completely deprotonated. At this pH, reaction occurs to yield, after approximately 1 hr, a solution exhibiting a visible absorption spectrum with a band at 498 nm (ϵ 89) and a shoulder at 350 nm. The spectrum is quite similar to that of *cis*-$Co(en)_2(NH_3)OH^{3+}$ (ϵ_{495}^{max} 90; ϵ_{360}^{max} 90). On acidification of the reaction product solution the spectrum changes to exhibit bands at 480 nm (ϵ 72) and 347 nm (ϵ 70) which are nearly at the same position and of nearly the same intensity as those in the spectrum of *cis*-$Co(en)_2(NH_3)(OH_2)^{3+}$ (ϵ_{484}^{max} 68; ϵ_{347}^{max} 62). Thus, the predominant product of the reaction is apparently $Co(en)_2$(mono-en)$(OH)^{2+}$. However, on separation of the reaction products on a Dowex 50W-X8 cation-exchange column, a small amount of $Co(en)_3^{3+}$ was obtained in addition to the major product (<5% of total). The hydroxo complex itself does not undergo any detectable ring closure to yield $Co(en)_3^{3+}$ on standing for several hours under the same conditions as those under which the base hydrolysis occurs. This suggests that the small amount of $Co(en)_3^{3+}$ produced in the reaction of $Co(en)_2$(mono-en)Cl^{2+} was not formed *via* a hydroxo intermediate.

It is generally accepted that base hydrolyses of chloropentaminecobalt(III) complexes proceed *via* SN1CB mechanisms.[18-22] If this type of mechanism is operative in the present case, then apparently the free amine function does not compete favorably with water for the vacant coordination site in the five-coordinate intermediate. This seems rather alarming particularly when a closely related system is examined. In the case of the base hydrolysis of *cis*-$Co(en)_2(NH_2CH_2CO_2CH_3)Cl^{2+}$, in which the ester is coordinated through the amine group, it has been found that water and the carbonyl function compete nearly equally for the vacant coordination site.[22] The conditions under which this reaction was examined are similar to those for the reaction of the monodentate en complex. Thus it would appear that in these systems an ester carbonyl group is a better nucleophile than a primary amine function.

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This apparent anomaly could likely be due to several factors among which are strong hydrogen bonding between the free amine and coordinated amines, greater solvation of the amine relative to the ester carbonyl function, steric considerations, etc.

In other solvent systems *cis*-$Co(en)_2(enH)Cl^{3+}$ behaves differently under basic conditions. For example in dimethyl sulfoxide, using piperidine to deprotonate the ammonium function, $Co(en)_3^{3+}$ is the sole product identified *via* its visible adsorption spectrum (ϵ_{469}^{max} 86 for product; ϵ_{469}^{max} 87 for $[Co(en)_3]Cl_3$[23]).

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On the Rates of Complex Formation Reactions of Hexa(dimethyl sulfoxide)nickel(II). The Five-Coordinate Intermediate Problem

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Rates of complex formation reactions of $Ni(DMSO)_6^{2+}$ ion with SCN^- and the murexide anion in DMSO are reported and compared with the rate of the corresponding reaction with bipyridine. All three complex formation rates appear to be significantly less than might be predicted from the solvent exchange rate. The rates are not related as are complex formation and solvent exchange rates of $Ni(OH_2)_6^{2+}$. It is suggested that the discrepancy could be explained by postulation of $Ni(DMSO)_5^{2+}$ as a kinetically detectable intermediate. Complex formation rates are related to other evidence for this intermediate. In support of the attempt to understand the mechanisms in DMSO, some complex formation rates in CH_3NO_2–DMSO mixtures are reported and the reaction of $Ni(OH_2)_6^{2+}$ with the murexide anion in water is described.

Introduction

There have been several studies of the rate at which solvent molecules exchange between the bulk solvent and the coordination sphere of hexa(dimethyl sulfoxide)nickel(II) ion in dimethyl sulfoxide (DMSO) as solvent.[1,2] Recently, Frankel[3] has reported a study in the mixed-solvent system DMSO–CH_3NO_2. The system has the simplifying feature that CH_3NO_2 fails to compete with DMSO for coordination sites (within the sensitivity of the nmr integration method for determining solvation numbers).[3] The surprising feature of Frankel's result is that the first-order experimental rate constant for solvent exchange is *not* a function of the bulk concentration of CH_3NO_2 (the inert solvent) in the solvent mixtures. There are only two straightforward interpretations of Frankel's observation. Either there is an intermediate formed in the substitution process so that the overall rate of exchange is independent of the probability of encounter between the $Ni(DMSO)_6^{2+}$ ion and DMSO, or the probability of encounter is independent of the bulk composition (the complex is strongly preferentially solvated by DMSO). Frankel preferred the first interpretation and the second is subject to test using the nmr relaxation time method for the study of preferential solvation recently proposed.[4-6]

If a labile intermediate is formed in the mixed solvent which reacts rapidly with DMSO to complete the exchange, there are two possible structures which deserve careful consideration since they imply quite distinct forms of behavior for Ni (II). One would be a labile CH_3NO_2-containing complex, $Ni(DMSO)_5(CH_3NO_2)^{2+}$, and the other, the elusive five-coordinate intermediate of octahedral substitution, $Ni(DMSO)_5^{2+}$. The decision between these two cannot be made on the basis of data obtained in mixed solvents unless the species $Ni(DMSO)_5(CH_3NO)^{2+}$ can be prepared and shown to be insufficiently labile for the requirements of the exchange kinetics. However, careful analysis of the details of the kinetics of complex formation reactions of $Ni(DMSO)_6^{2+}$ in DMSO with nonsolvent ligands can shed light on the problem.

In particular, it is of interest to explore the possibility of imperfect fitting of the complex formation data to the dissociative interchange model (discussed by Eigen[7])

$$Ni(DMSO)_6^{2+} + L \overset{K_E}{\rightleftharpoons} Ni(DMSO)_6^{2+},L$$

$$Ni(DMSO)_6^{2+},L \xrightarrow{k} Ni(DMSO)_5L^{n+} + DMSO \qquad (1)$$

In eq 1, $Ni(DMSO)_6^{2+}$,L represents the encounter complex or outer-sphere complex which is formed

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