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The Acid Dissociation Constant of the Tris(ethylenediamine)cobalt(III) Ion

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Evidence is given for an acid-base dissociation reaction of tris (ethylenediamine) cobalt (III) ion in basic aqueous solutions.
The evidence is based on the nmr chemical shifts of the methylene protons and on the u.v. absorption spectra of $Co(en)_3^{3+}$ ion in basic solution. The equilibrium constant of the deprotonation reaction is estimated by each of the two methods.

Introduction

The base catalyzed hydrogen exchange between many metal amino complexes and water, as well as the basic hydrolysis of these complexes are commonly attributed to the equilibrium:[1]

$$M(NH_3)_6^{3+} + OH^- \rightleftarrows M(NH_3)_5NH_2^{2+} + H_2O \qquad (1)$$

It was suggested that both exchange and hydrolysis proceed via the basic form of the complexes. However, though the participation of the basic form has been postulated in many kinetic studies of Cobalt III complexes, the equilibrium constant for its formation has not been determined for any of them. For the $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$ complexes (en = ethylenediamine) it was estimated[2] that their pK's lie above pH = 14. On the other hand, it has been argued that the kinetic as well as the spectroscopic data could be explained by assuming that ion pairs between the complexes and the hydroxide ion are formed.[2,3] It has been recently suggested for $Co(NH_3)_6^{3+}$ that an acid-base dissociation occurs in this pH region.[4] We have decided to attempt to resolve this question by measuring the effect of base on the optical absorption spectrum, as well as on the nmr spectrum of the methylene protons of $Co(en)_3^{3+}$.

Experimental Section

$Co(en)_3Cl_3 \cdot 3H_2O$ (Alfa Inorganics) was twice recrystallized from water. $Co(en)_3(ClO_4)_3$ was prepared from the chloro salt by crystallization from 4 *M* $NaClO_4$ solution. All solutions which contained base were freshly prepared before use and were kept in tightly sealed vessels throughout the experiment to avoid CO_2 absorption. All solutions of $Co(en)_3Cl_3$ were completely stable as judged from their optical absorption spectra, which remained unchanged during time periods exceeding the time of the experiments.

All spectrophotometric measurements were performed using a Cary 14 spectrophotometer. A Varian HA 100 spectrometer was used for the nmr measurements. Solutions for the nmr measurements were prepared in D_2O and contained 0.01 *M* dioxane which was used as an internal reference. The signal due to residual HDO molecules was utilized as a locking signal. The solutions temperature was 24±C° for the spectrophotometric measurements and 30±1°C for the nmr measurements.

Results

The nmr spectrum of the methylene protons of $Co(en)_3Cl_3$ in aqueous solution consists of a broad symmetrical line which only partially narrows upon dissolving the complex in D_2O, where the N–H protons are substituted by deuterons.[5,6] This broad line has been shown recently to consist of an AA'BB' multiplet which is broadened by an unresolved spin-spin interaction with the ^{59}Co nucleus.[7] The multiplet corresponds to a weighted averaged spectrum of the different non-equivalent protons, over the various conformations of the chelate rings.[8,10] The line shape has been shown to be almost unaffected by ion pair formation with monovalent anions[10] while it is considerably narrowed by ion pair formation with more highly charged anions like SeO_3^{2-} and PO_4^{3-},[7-10] due to an enhanced quadropolar relaxation of the ^{59}Co nucleus.

When hydroxide ion was added either as KOH or NaOH, the signal due to the methylene protons of $Co(en)_3^{3+}$ was shifted to a higher field and its shape changed and became asymmetrical (see Figure 1).

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[*] To whom correspondance should be addressed.
[1] F. Basolo and R.G. Pearson, « Mechanism of Inorganic Reactions », 2nd edition, Wiley, New York, N.Y. 1967.
[2] R.G. Pearson and F. Basolo, *J. Am. Chem. Soc.*, *78*, 4878 (1956).
[3] S.C. Chan, *J. Chem. Soc. (A)*, 2103 (1967).
[4] L. Heck, *Inorg. Nucl. Chem. Letters*, *6*, 657 (1970).
[5] D.B. Powell and N. Sheppard, *J. Chem. Soc.*, 791 (1959).
[6] S.T. Spees, Jr., L.J. Durham, and A.M. Sargeson, *Inorg. Chem.*, *5*, 2103 (1966).
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[9] I.R. Collogly, C.J. Hawkins, and J.K. Beattie, *Inorg. Chem.*, *10*, 317 (1971).
[10] L.R. Froebe and B.E. Douglas, *Inorg. Chem.*, *9*, 1513 (1970).

This is in contrast to other monovalent anions like chloride and perchlorate ions which were found to cause a smaller shift and in the opposite direction.

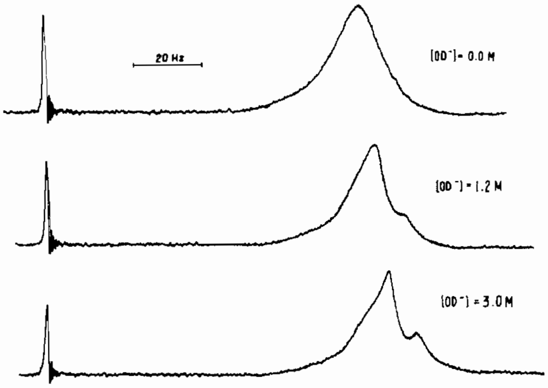

Figure 1. 100 MHz nmr spectra of 0.1 M $Co(en)_3Cl_3$ in D_2O with various base concentrations. The signal on the left is due to about 0.01 M dioxane which serves as an internal reference.

In order to make a quantitative estimation of the shifts of the frequently asymmetric lines, the average shift, which is the point for which the areas on its two sides are equal, was measured for each spectrum. The average chemical shift for 0.1 M $Co(en)_3(ClO_4)_3$ in D_2O was found to shift by 0.07±0.01 ppm to a higher field upon the addition of 3 M NaOD. For comparision, both NaCl and $NaClO_4$ in concentrations of 3 M induced a shift of −0.03±0.01 ppm. The shift caused by the trivalent phosphate ion, on the other hand, was similar in sign and in magnitude to that caused by the hydrovide ion. The marked difference in the effect of hydroxide ion and other monovalent anions may lead to the conclusion that a deprotonation reaction takes place in strongly basic solutions.

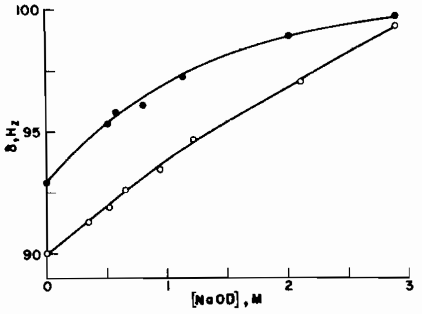

Figure 2. Chemical shifts of $Co(en)_3^{3+}$ methylene protons from internal dioxane standard as a function of NaOD concentration. (●) 0.1 M $Co(en)_3Cl_3$. (○) 0.1 M $Co(en)_3(ClO_4)_3$. $NaClO_4$ was added to keep a constant ionic strength of 3.0 M.

For the purpose of estimating the equilibrium constant of the deprotonation reaction the average shift was recorded as a function of OH^- concentration. The same set of measurements was repeated also with an added $NaClO_4$ to give a constant ionic strength of 3.0 M. The results are given in Figure 2.

The equilibrium constant K is estimated from the intercept on the abscissa in a double reciprocal plot of $1/\Delta\delta$ *vs.* $1/[OH^-]$ according to Equation (2).

$$\frac{1}{\Delta\delta}=\frac{1}{\Delta_o}\left(1+\frac{1}{K[OH^-]}\right) \qquad (2)$$

$\Delta\delta$ is the average chemical shift relative to a solution without added NaOD and Δ_o is the chemical shift difference between the deprotonated and the protonated $Co(en)_3^{3+}$ ions.

Such a plot gives a straight line for the results without added $NaClO_4$ (see the lower part of Figure 3), with an apparent equilibrium constant of K = 0.6±0.2 M^{-1}. The results with a constant ionic strength do not conform to the above treatment as can be seen from the absence of a straight line in the double reciprocal plot (see lower part of Figure 4). This may be due to the appreciable shift caused by the perchlorate ion. The reciprocal of the intercept on the ordinate in the double reciprocal plot (Figure 4) gives the chemical shift Δ_o of the basic form of the complex relative to the acidic form. This shift, which amounts to Δ_o = 0.11±0.02 ppm, is the average chemical shift of all methylene protons of the complex. Per one ethylenediamine molecule, the average shift is 0.22 ppm. By analogy to chemical shift values obtained upon protonation of free amines and amino acids, Erickson[11] predicted an average shift of 0.35 ppm between the methylene protons of deprotonated and neutral ethylenediamine molecules. This value is in excellent agreement with our experimental result and the agreement further substantiates our proposition that the origin of the shift is indeed a deprotonation reaction.

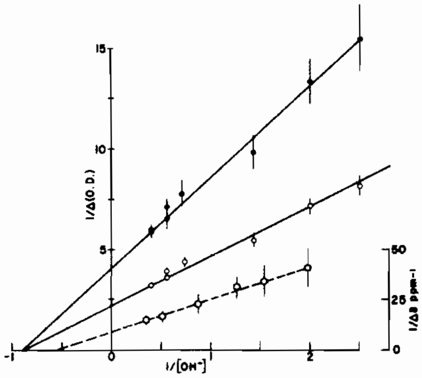

Figure 3. A double reciprocal plot used for the determination of the deprotonation elquilibrium constant. Solid lines: Optical absorption data (left scale): $[Co(en)_3Cl_3)=3.1\times10^{-4}$ M. Wavelengths 265 mμ (●) and 255 mμ (○). Dashed line: Nmr chemical shifts data (right scale): $[Co(en)_3Cl_3]=0.1$ M (○).

The u.v. optical absorption spectrum of $Co(en)_3^{3+}$ is red shifted in strongly basic solutions relative to neutral solutions, while no shift is observed in the two *d-d* bands in the visible an dthe near u.v. regions.[2] The absence of a shift in the two *d-d* transition has led previous authors to the conclusion that the spec-

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[11] L.E. Erickson, *J. Am. Chem. Soc.*, *91*, 6284 (1969).

tral change in the u.v. region is due to a hydroxide ion pair formation rather than an acid-base dissociation reaction.[2]

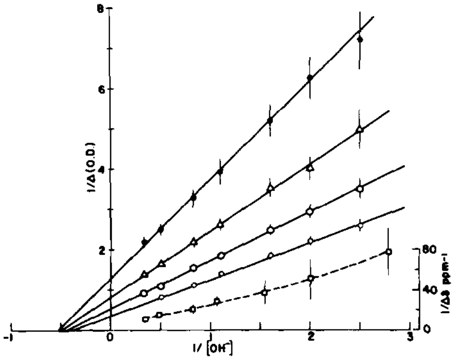

Figure 4. A double reciprocal plot used for the determination of the deprotonation equilibrium constant at a constant ionic strength. Solid lines: Optical absorption data (left scale): $[Co(en)_3ClO_4)_3]=2.4\times10^{-3}$ *M*. Wavelength: 280 mμ (●), 275 mμ (△), 270 mμ (○) and 265 mu (◊). Dashed line: nmr chemical shifts data (right scale): $[Co(en)_3(ClO_4)_3]$ $=0.1$ *M*.

In a careful examination of the spectral changes of the $Co(en)_3^{3+}$ ion in basic solutions we observed a significant increase of the absorption coefficients of the two *d-d* bands. The increase amounted to 6 and 14 percent for the bands centered at 465 and 338 mμ, respectively (see Figure 5).

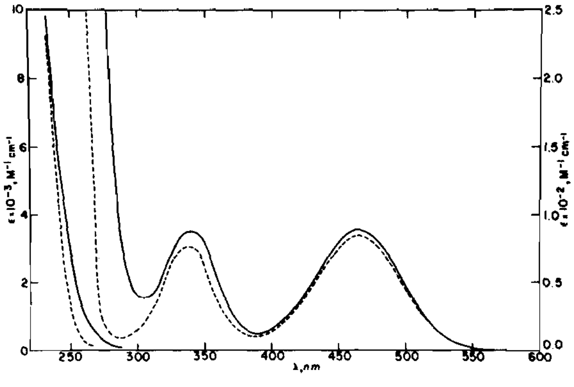

Figure 5. Optical absorption spectra of $Co(en)_3Cl_3$ ion in neutral (dashed line) and in 3 *M* NaOH(solid line) in aqueous solutions.

The equilibrium constant for the formation of the basic form $Co(en)_3^{3+}$ was estimated by recording the optical density in the U.V. region at various NaOH concentrations. The difference in the optical densities of the basic and neutral solutions, Δ(OD) obeys the folowing relation:

$$\frac{1}{\Delta(OD)}=\frac{1}{\Delta\varepsilon C_o}(1+\frac{1}{K[OH^-]})$$

where C_o is the total concentration of the complex, Δε is the difference in the absorption coefficients of the basic and the neutral forms of the complex, and K is the formation equilibrium constant of the basic form of the complex. Δ(OD) was corrected for the slight absorption due to $[OH^-]$. Plots of $1/\Delta(OD)$ *vs.* $1/[OH^-]$ at various wavelengths in the u.v. region are given in Figures 3 and 4. The data for Figure 4 was collected at a constant ionic strength of 3.0 *M* adjusted with added $NaClO_4$, while in Figure 3 no $NaClO_4$ was added. The values of K obtained from the intercepts of the straight lines on the abscissa are 0.9 ± 0.2 and $0.5\pm0.2\ M^{-1}$ for the sets of experiments without added $NaClO_4$ and with added $NaClO_4$ to a constant ionic strength, respectively. These values are in a reasonable agreement with the nmr result measured at slightly different conditions (see Experimental Section). The considerable experimental error does not allow a more detailed comparison. It should be mentioned that the slight variation in K for the different wavelength in Figure 4 was reproducable when this experiment was repeated. It might be due to a slight contribution to the absorption by hydroxide ion pairs which are present in the solutions as is discussed below.

Let us consider now the possibility mentioned in the literature[2,3] that the u.v. absorption is due to ion pairs. The equilibrium constant measured above is much smaller than the ion pair stability constants which were measured both potentiometrically[2] and folowing the u.v. absorption spectra[3] as 31 and 27 M^{-1} respectively. This means that the acid-base dissociation process occurs only at high base concentrations, where the ion pairing process has been completed. Furthermore the u.v. absorption of the basic form of the complex is much stronger than that expected for an absorption due to an ion pair of the complex with OH^-. It has been shown[12] that the onset of the u.v. absorption bands of $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$ are shifted to the red by the formation of ion pairs with halides. The shifts are due to charge transfer transitions from the anions to the complex and they were shown to be linearly correlated to the sum of the electronegativity and the energy of hydration of the radicals corresponding to the anions. An identical correlation holds also for the $Fe^{3+}X^-$ charge transfer bands. In the later series the energy of the charge transfer band of the OH^- complex is very close to that of Cl^{-}[13]. This is true also for the series of $[Co(NH_3)_5X]^{2+}$ complex ions. [14,15] A comparison of the spectrum of the basic form of $Co(en)_3^{3+}$ (see Figure 5) with those of the ion pairs of this complex with halide ions[12] indicates that its u.v. onset of absorption is red shifted even relative to the $Co(en)_3^{3+}\ Br^-$ ion pair. Therefore, it is very unlikely to be due to an ion pair with OH^-, but to a basic deprotonation product.

The absence of the shift in the two *d-d* bands is quite unexpected, but may be a result of several opposing effects and require further consideration. The increase in the intensity of these bands, on the other hand, can be accounted for in a straightforward man-

(12) M.G. Evans and G.H. Nancollas, *Trans. Faraday Soc.*, *49*, 363 (1953).

(13) M.G. Evans, N.S. Hush, and N. Uri, *Quart. Rev.*, *6*, 186 (1952).

(14) M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, *266*, 49 (1951).

(15) H. Siebert and H. Feuerhake, *Chem. Ber.*, *102*, 2951 (1969).

ner by the deprotonation reaction, in terms of reduction of the local symmetry around the cobalt (III) ion and thus increasing the probability of these transitions which are partially symmetry forbidden.

We can, therefore conclude that both nmr and optical spectral data strongly indicate that the $Co(en)_3^{3+}$ complex ion undergoes an acid dissociation reaction in basic solutions with a formation equilibrium constant of its deprotonated form of the order of 0.6 M^{-1}. This supports the possible role of the deprotonated species in base catalyzed proton exchange and substitution reactions.