Proton Transfer and Base Hydrolysis Reactions of Some *trans*-Bis(dimethylglyoximato)cobalt(III) Complexes[1]

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Abstract: The equilibria and kinetics of the reversible deprotonation of *trans*-$Co(DH)_2(NO_2)Br^-$ (where $DH^- = HON{=}C(CH_3)C(CH_3){=}NO^-$) and of several other *trans*-bis(dimethylglyoximato)cobalt(III) complexes, exemplified by the reaction, $Co(DH)_2(NO_2)Br^- + OH^- \rightleftarrows Co(D_2H)(NO_2)Br^{2-} + H_2O$, have been examined. Equilibrium constants, determined spectrophotometrically, ranged from 31 M^{-1} for $Co(DH)_2(NO_2)Br^-$ to 1.8×10^2 M^{-1} for $Co(DH)_2(NO_2)_2^-$. The rate of approach to equilibrium, determined by the temperature-jump or stopped-flow method, obeyed first-order kinetics with the apparent first-order rate constant given by $k_{obsd} = k_{-1} + k_1[OH^-]$, where k_1 and k_{-1} are the rate constants of the forward and reverse reactions, respectively. Values of k_1 ranged from 1.2×10^5 M^{-1} sec^{-1} for $Co(DH)_2(NO_2)_2^-$ to 1.3×10^6 M^{-1} sec^{-1} for $Co(DH)_2(NH_3)_2^+$. The hydrolysis of $Co(DH)_2(NO_2)Br^-$ to $Co(DH)_2(NO_2)OH_2$ was found to be accelerated by OH^-, according to a rate law which can be expressed as $-d([Co(DH)_2(NO_2)Br^-] + [Co(D_2H)(NO_2)Br^{2-}])/dt = k_a[Co(DH)_2(NO_2)Br^-] + k_b[Co(D_2H)(NO_2)Br^{2-}]$, where $k_a = 3.5 \times 10^{-5}$ sec^{-1} and $k_b = 1.1 \times 10^{-3}$ sec^{-1}. Neither the kinetic behavior nor the results of hydrolysis experiments in the presence of added NO_2^- serve to distinguish between SN2, SN2CB, and SN1CB mechanisms for the base hydrolysis path.

The addition of OH^- to solutions of *trans*-bis(dimethylglyoximato)cobalt(III) complexes results in two distinct spectral changes. The first, which is reversible and very rapid, is attributable to the deprotonation reaction

$$Co^{III}(DH)_2XY + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Co^{III}(D_2H)XY + H_2O \qquad (1)$$

where DH is the dimethylglyoximate anion, $HON{=}C(CH_3)C(CH_3){=}NO^-$, and $Co^{III}(DH)_2XY$ = $Co(DH)_2(NO_2)_2^-$, $Co(DH)_2(CN)_2^-$, $Co(DH)_2(NO_2)Br^-$, or $Co(DH)_2(NH_3)_2^+$. Spectrophotometric equilibrium measurements on these reactions, along with kinetic measurements made by the temperature-jump method, are described. These studies have relevance to the effect of internal hydrogen bonding on the rates of proton-transfer reactions.

The second, much slower, absorbance change corresponds to the base hydrolysis of the cobalt(III) complex, exemplified by the reaction

$$Co(DH)_2(NO_2)Br^- + OH^- \longrightarrow Co(DH)_2(NO_2)OH^- + Br^- \qquad (2a)$$

or

$$Co(D_2H)(NO_2)Br^{2-} + H_2O \longrightarrow Co(DH)_2(NO_2)OH^- + Br^- \qquad (2b)$$

A kinetic study of this reaction is described.

Experimental Section

Materials. The following cobalt(III) complexes were prepared[2] by published procedures: $Na[Co(DH_2)(NO_2)_2]$,[3] $H[Co(DH)_2(NO_2)Br] \cdot H_2O$,[4] $[Co(DH)_2(NO_2)(H_2O)]$,[4] $K[Co(DH)_2(CN)_2] \cdot 1.5H_2O$,[5] $[Co(DH)_2(NH_3)_2]Cl \cdot 5H_2O$,[6] $[Co(DH)_2(py)Br]$,[7] $[Co(DH)_2(py)Cl]$,[7] and $[Co(DH)_2(P(C_6H_5)_3)Br]$.[7]

Stock solutions of sodium perchlorate, used to maintain constant ionic strength, were prepared from the triply recrystallized product of the reaction of sodium carbonate and perchloric acid. The solutions were analyzed by ion-exchange titration. Sodium hydroxide solutions were Fisher Analyzed 1.00 or 0.10 *M* NaOH. All other materials were of reagent grade. Distilled water was used in the preparation of all solutions.

Kinetic Measurements. The deprotonation reactions were studied in aqueous solution at 15.0° and 0.10 *M* ionic strength using a temperature-jump apparatus manufactured by Messanlagen Studiengesellschaft, Göttingen, Germany. In this apparatus, a 0.05-μF capacitor was charged to 41 kV and then discharged through a solution previously equilibrated at 10.0°, causing the temperature to rise by 5.0° in 2 μsec or less. The relaxation to the new equilibrium position was then observed spectrophotometrically, at wavelengths in the range 400–500 mμ, on a Tektronix-type 564 storage oscilloscope. A typical temperature-jump oscillogram is reproduced in Figure 1.

Some deprotonation reactions were also studied in 80 vol. % methanol at 25.0°, in an attempt to extend observations to complexes which are only slightly soluble in water. Because of complications associated with the nonaqueous solvent, measurements on these solutions were made with a Durrum stopped-flow spectrophotometer rather than with the temperature-jump apparatus.

The kinetics of the base hydrolysis of $Co(DH)_2(NO_2)Br^-$ (reaction 2) were determined spectrophotometrically (at 360–400 mμ) at 15.0° and 0.10 *M* ionic strength using a Beckman DB spectrophotometer equipped with a recorder.

Equilibrium Measurements. Equilibrium quotients for the proton-transfer reactions (eq 1) were determined spectrophotometrically, by measuring the absorbancies of solutions containing a given total concentration of the $Co^{III}(DH)_2XY$ complexes and various concentrations of added OH^-. To minimize effects due to hydrolysis of the complex, the sodium hydroxide was added immediately before the spectra were recorded with a Cary 14 spectrophotometer. Equilibrium quotients, *K*, defined by

$$K = [Co^{III}(D_2H)XY][Co^{III}(DH)_2XY]^{-1}[OH^-]^{-1} \qquad (3)$$

were determined from the linear plots of $(A/[Co]_{tot} - \epsilon_{DH})^{-1}$ *vs.* $[OH^-]^{-1}$, shown in Figure 2, fitted to the relation

$$(A/[Co]_{tot} - \epsilon_{DH})^{-1} = (\epsilon_D - \epsilon_{DH})^{-1}(1 + K^{-1}[OH^-]_{eq}^{-1}) \qquad (4)$$

where *A* is the absorbance of the solution, ϵ_D and ϵ_{DH} are the measured extinction coefficients of $Co^{III}(D_2H)XY$ and $Co^{III}(DH)_2XY$, respectively, $[Co]_{tot}$ = $([Co^{III}(DH)_2XY] + [Co^{III}(D_2H)XY])$, and $[OH^-]_{eq}$ is the equilibrium OH^- concentration (*i.e.*, the concentration of added OH^-, less that consumed by reaction with $Co^{III}(DH)_2XY$), calculated by an iterative procedure.

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[1] This research was supported by grants from the National Science Foundation and the Advanced Research Projects Agency.

[2] We are grateful to Drs. P. W. Schneider and D. N. Hague for preparation of some of these complexes.

[3] L. Tschugaeff, *Chem. Ber.*, **41**, 2230 (1908).

[4] A. V. Ablov, *Dokl. Akad. Nauk SSSR*, **97**, 1019 (1954).

[5] N. Maki, *Bull. Chem. Soc. Japan*, **38**, 2013 (1965).

[6] L. Tschugaeff, *Z. Anorg. Allgem. Chem.*, **46**, 160 (1905).

[7] L. Tschugaeff, *Chem. Ber.*, **40**, 3498 (1907).

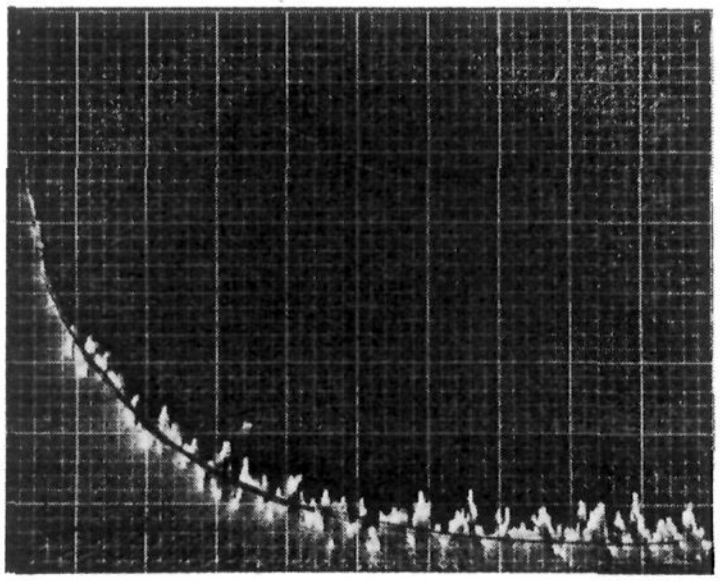


Figure 1. Sample temperature-jump oscillogram for the reaction $Co(DH)_2(CN)_2^- + OH^- \leftrightarrows Co(D_2H)(CN)_2^{2-} + H_2O$: 7.2×10^{-4} M $Co(DH)_2(CN)_2^-$; 0.05 M OH^-; 15°; 0.10 M ionic strength. Time scale: 100-μ sec/division.

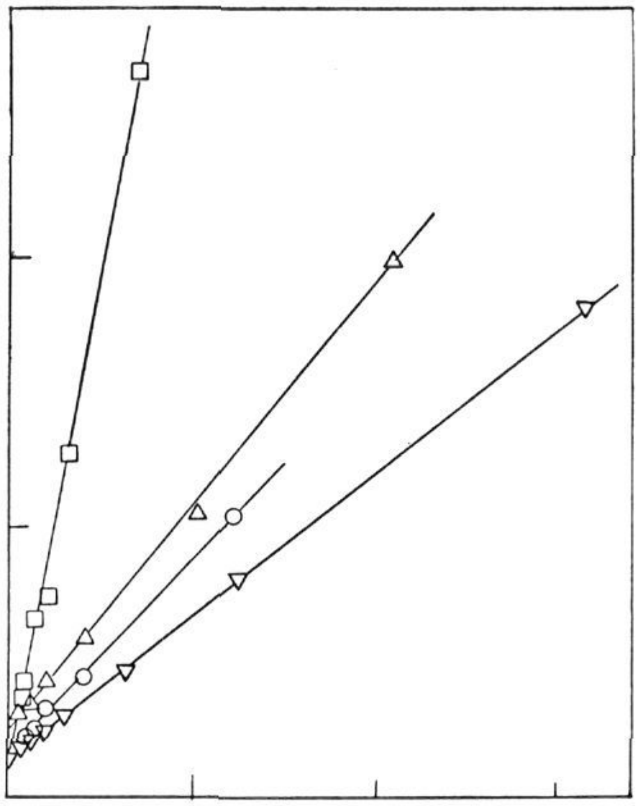
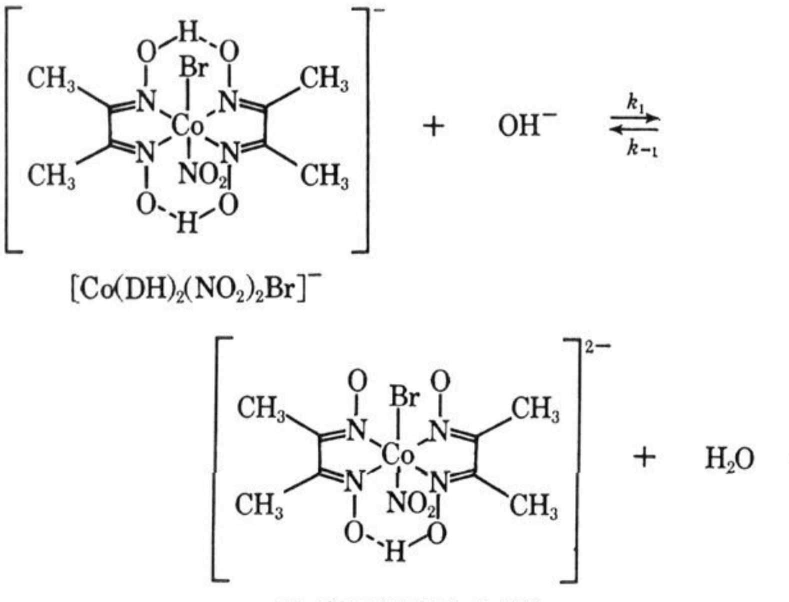


Figure 2. Plots of $(A/[Co]_{tot} - \epsilon_{DH})^{-1}$ *vs.* $[OH^-]_{eq}^{-1}$ according to eq 4: ▽, $Co(DH)_2(CN)_2^-$; □, $Co(DH)_2(NO_2)Br^-$; ○, $Co(DH)_2(NO_2)_2^-$; △, $Co(DH)_2(NO_2)_2^-$ in 80 vol. % methanol.

Results and Discussion

Deprotonation Reactions. Addition of sodium hydroxide to aqueous (or aqueous methanolic) solutions of various bis(dimethylglyoximato)cobalt(III) complexes, *i.e.*, $Co(DH)_2(NO_2)_2^-$, $Co(DH)_2(NO_2)Br^-$, $Co(DH)_2(CN)_2^-$, $Co(DH)_2(NH_3)_2^+$, $Co(DH)_2(py)Br$ (py = pyridine), $Co(DH)_2(py)Cl$, and $Co(DH)_2(PPh_3)Br$, resulted in rapid reversible changes in the visible and near-ultraviolet spectra. This effect had been previously observed for a number of such complexes, *e.g.*, $Co(DH)_2(NO_2)_2^-$, $Co(DH)_2(NO)_2NH_3$, and $Co(DH)_2(NH_3)_2^+$, by Ablov and Fillipov,[8,9] and attributed by them to the reversible loss of a bridging proton by the dimethylglyoxime ligands. This process is exemplified for $Co(DH)_2(NO)_2Br^-$ by eq 5 or, more generally, by eq 1.



$[Co(DH)_2(NO_2)_2Br]^-$ + OH^- $\underset{k_{-1}}{\overset{k_1}{\rightleftarrows}}$ $[Co(D_2H)(NO_2)_2Br]^{2-}$ + H_2O (5)

This conclusion is supported by our observations that (i) the spectral changes for complexes such as $Co(DH)_2(NO_2)_2^-$ and $Co(DH)_2(CN)_2^-$ are quantitatively reversible (reacidification of a solution to which OH^- has been added restores the spectrum of the original solution); (ii) spectra of solutions of $Co(DH)_2(NO_2)_2^-$, containing different concentrations of OH^-, exhibit two isosbestic points at 345 and 363 mμ, in agreement with Ablov and Fillipov[8] (342 and 365 mμ), indicating the presence of only two absorbing species; and (iii) plots of $(A/[Co]_{tot} - \epsilon_{DH})^{-1}$ *vs.* $[OH^-]^{-1}$ (Figure 2) are linear in accord with eq 4 derived for an equilibrium involving the loss of a single proton from the cobalt complex.

Kinetic data, obtained by the temperature-jump technique, for $Co(DH)_2(NO_2)_2^-$, $Co(DH)_2(NO_2)Br^-$, $Co(DH)_2(CN)_2^-$, and $Co(DH)_2(NH_3)_2^+$, are summarized in Table I, which also includes some data for $Co(DH)_2(NO_2)_2^-$ in 80 vol. % methanol, obtained by the stopped-flow method. In each case, the approach to equilibrium obeyed the pseudo-first-order rate law, derived for the reversible reaction described by eq 1, *i.e.*

$$-\mathrm{d}\ln(A_t - A_{eq})/\mathrm{d}t = k_{obsd} = k_{-1} + k_1[OH^-] \quad (6)$$

where A is the absorbance at the indicated time.

Values of k_1 and k_{-1}, determined from the slopes and intercepts of linear plots of k_{obsd} *vs.* $[OH^-]$, are listed in Table II, along with values of K, determined both from the kinetic data ($K = k_1/k_{-1}$) and spectrophotometrically, as described earlier. The discrepancy between the two values of K for $Co(DH)_2(NO_2)_2^-$ in 80% methanol is probably not unreasonable, since the reaction was so rapid ($t_{1/2}$ = 1–7 msec) as to be barely within the range accessible to the stopped-flow technique used, resulting in a rather low signal-to-noise ratio. For $Co(DH)_2(NO_2)Br^-$, the best value of K yielded by the kinetic data was 61 M^{-1}; however, the data could also be accommodated reasonably well by the spectrophotometrically determined value of 31 M^{-1}, which is considered more accurate. Attempts to determine K spectrophotometrically for $Co(DH)_2(NH_3)_2^+$ were thwarted by irreversible absorbance changes of undetermined source. However, this equilibrium quotient has been determined at 25° by Ablov and Fillipov to be 1.6×10^3 M^{-1}; the discrepancy from our kinetic value of 9.0×10^2 M^{-1} is in the direction expected for the difference in temperature.

A possible complication in the study of the deprotonation of $Co(DH)_2(NO_2)Br^-$ arises from the irreversible

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(8) A. V. Ablov and M. P. Fillipov, *Russ. J. Inorg. Chem.*, 5, 1311 (1960).

(9) A. V. Ablov and M. P. Fillipov, *ibid.*, 7, 525 (1962).

Table I. Kinetic Data[a] for the Reactions of Various Bis(dimethylglyoximato)cobalt(III) Complexes with OH^- (eq 1)

$Co^{III}(DH)_2XY$ complex	$10^4[Co^{III}(DH)_2XY]_{tot}$, M	$10^2[OH^-]_{added}$, M	$10^2[OH^-]_{eq}$, M	$10^{-3}k_{obsd}$,[b] sec^{-1}	$(10^{-3}k_{obsd})_{calcd}$,[c] sec^{-1}
$Co(DH)_2(CN)_2^-$	9.5	4.00	3.92	8.56 ± 0.10	8.8
	9.0	2.00	1.94	5.35 ± 0.57	5.0
	5.6	1.00	0.97	3.28 ± 0.14	3.2
	7.2	0.500	0.474	2.42 ± 0.12	2.3
	5.1	0.200	0.191	1.56 ± 0.05	1.7
	8.7	0.100	0.092	1.52 ± 0.02	1.5
$Co(DH)_2(NO_2)Br^-$	9.0	5.91	5.85	9.9	9.2
	5.1	4.95	4.92	9.26 ± 0.36	8.1
	7.2	4.93	4.89	6.50 ± 0.36	8.0
	4.6	3.95	3.93	7.11 ± 0.18	6.8
	4.8	3.95	3.93	7.30 ± 0.08	6.8
	4.3	2.96	2.94	5.18 ± 0.06	5.6
	3.9	1.96	1.95	4.14 ± 0.06	4.4
	3.7	0.963	0.96	2.82 ± 0.05	3.2
	4.4	0.456	0.45	2.87 ± 0.04	2.6
$Co(DH)_2(NO_2)_2^-$	5.3	3.89	3.84	5.56 ± 0.31	5.3
	8.4	3.00	2.93	4.78 ± 0.16	4.3
	5.2	2.00	1.96	2.84 ± 0.17	3.1
	6.5	2.00	1.95	2.66	3.1
	3.5	1.00	0.98	1.76 ± 0.06	2.0
	5.5	1.00	0.97	1.54 ± 0.06	2.0
	3.5	0.50	0.49	1.56 ± 0.05	1.4
	5.2	0.20	0.19	1.02 ± 0.03	1.0
	2.5	0.10	0.097	0.62 ± 0.05	0.91
$Co(DH)_2(NO_2)_2^-$ [d]	2.0	2.00	...	0.64 ± 0.03[d]	0.63
	0.7	1.00	...	0.35 ± 0.03[d]	0.36
	2.0	0.50	...	0.23 ± 0.01[d]	0.23
	0.7	0.50	...	0.18 ± 0.01[d]	0.23
	2.0	0.20	...	0.15 ± 0.01[d]	0.14
	0.7	0.20	...	0.14 ± 0.01[d]	0.14
	0.7	0.10	...	0.11 ± 0.01[d]	0.12
$Co(DH)_2(NH_3)_2^+$	5.6	0.50	0.453	8.11 ± 1.03	7.5
	8.9	0.35	0.283	4.99	5.3
	10.7	0.25	0.179	3.50 ± 0.37	3.9
	4.9	0.10	0.0774	2.33 ± 0.10	2.5
	4.7	0.05	0.0366	2.12 ± 0.10	2.0

[a] Ionic strength maintained at 0.10 M with $NaClO_4$; 15°. [b] Uncertainties cited are the average deviations of duplicate determinations on the same solution. [c] Calculated from eq 6 using the values of k_1 and k_{-1} in Table II. [d] 25°; in 80 vol. % methanol.

Table II. Rate Constants and Equilibrium Quotients for the Reactions of Various Bis(dimethylglyoximato)cobalt(III) Complexes with OH^- [a]

Complex	$10^{-5}k_1$, M^{-1} sec^{-1}	$10^{-3}k_{-1}$, sec^{-1}	$10^{-2}K$,[b] M^{-1}	$10^{-2}K$,[c] M^{-1}
$Co(DH)_2(CN)_2^-$	1.90 ± 0.07	1.35 ± 0.13	1.4 ± 0.2	1.18
$Co(DH)_2(NO_2)Br^-$	1.23 ± 0.04	2.0 ± 0.4	0.61 ± 0.15	0.31
$Co(DH)_2(NO_2)_2^-$	1.18 ± 0.07	0.80 ± 0.13	1.5 ± 0.3	1.29
$Co(DH)_2(NO_2)_2^-$ [d]	0.27 ± 0.09[d]	0.09 ± 0.01[d]	2.9 ± 0.4[d]	1.80[d]
$Co(DH)_2(NH_3)_2^+$	13.3 ± 1.5	1.5 ± 0.4	9.0 ± 3.0	(15.8)[e]

[a] Ionic strength maintained at 0.10 M with $NaClO_4$; 15°. [b] $K = (k_1/k_{-1})$. [c] Determined spectrophotometrically using eq 4 from data in Figure 2. [d] At 25° in 80 vol. % methanol. [e] At 25°, from ref 9.

hydrolysis reaction of this complex (eq 2), the kinetics of which are described below. Although much faster than the hydrolysis of the other complexes studied, this reaction was nevertheless slow enough to permit the temperature-jump measurements on the proton-transfer reaction to be performed. Successive temperature-jump experiments on the same solution at various stages of hydrolysis were characterized by a decreasing total absorbance change but by an essentially constant relaxation time (k_{obsd}^{-1}), yielding constant values of k_1 and k_{-1}. This is consistent with our observations that the absorbance change accompanying the deprotonation of $Co(DH)_2(NO_2)OH_2$ in the wavelength range of these measurements (400–500 mμ) is negligible.

$Co(DH)_2(py)Br$, $Co(DH)_2(py)Cl$, and $Co(DH)_2(PPh_3)Br$ also exhibited reversible absorbance changes on addition of OH^-. However, because of limited solubility in water, studies on these complexes could not be made by the temperature-jump method, and the reactions in 80% methanol proved too fast for stopped-flow measurement.

Influence of Internal Hydrogen Bonding on the Rates of Proton Transfer. Eigen[10] has discussed in some detail the influence of internal hydrogen bonding on the rates of proton-transfer reactions. The formation of a chelating internal hydrogen bond (such as that present in bis(dimethylglyoximato)cobalt(III) complexes) apparently interferes with hydrogen bonding between the donor proton and the acceptor (OH^- or solvent), thereby decreasing the rate of proton transfer. Thus, whereas thermodynamically favorable proton-transfer

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[10] M. Eigen, W. Kruse, G. Maass, and L. D. Maeyer, *Progr. Reaction Kinetics*, 2, 285 (1964).

reactions between –NH or –OH donors and OH^- normally proceed with rates close to diffusion-controlled ($k \sim 10^9$–10^{11} M^{-1} sec^{-1}), the transfer of a proton protected by internal H-bonding is generally appreciably slower. Rate constants reported for such proton-transfer reactions to OH^- are typically in the range 4 × 10^5 to 4 × 10^6 M^{-1} sec^{-1} for O—H···N donors and 2 × 10^7 to 7 × 10^8 M^{-1} sec^{-1} for O—H···O donors. Secondary influences, causing variations within these ranges, include charge and steric effects.

Our results are generally consistent with this pattern and interpretation. The values of the rate constants (k_1) for proton transfer to OH^- found by us for various $Co^{III}(DH)_2XY$ complexes, which lie in the range 1.2 × 10^5 to 1.3 × 10^6 M^{-1} sec^{-1} (corresponding to 6 × 10^4 to 6 × 10^5 M^{-1} sec^{-1} *per proton* in $Co^{III}(DH)_2XY$), are among the lowest yet reported for such proton-transfer reactions and are well below the previously observed values for proton transfer from O—H···O donors to OH^-. This is consistent with the generally accepted presence of very strong H bonds in bis(dimethylglyoximato)cobalt(III) complexes, and with the view that the energy required to "liberate" the proton from the internal H bond (*i.e.*, to break the internal H bond) makes an important contribution to the barrier for proton transfer.

The principal factor responsible for the variation of k_1, within the range of observed values, appears to be the charge of the cobalt(III) complex. Thus, in aqueous solution, the value of k_1 for $Co(DH)_2(NH_3)_2^+$ (1.3 × 10^6 M^{-1} sec^{-1}) is appreciably higher than the values for the three anionic complexes $Co(DH)_2(NO_2)_2^-$, $Co(DH)_2(NO_2)Br^-$, and $Co(DH)_2(CN)_2^-$, all of which lie within the relatively narrow range, 1.2 × 10^5 to 1.9 × 10^5 M^{-1} sec^{-1}. The decrease in k_1 for $Co(DH)_2(NO_2)_2^-$ from 1.2 × 10^5 to 2.7 × 10^4 M^{-1} sec^{-1} in going from water to 80% methanol as solvent may reflect the reduced effectiveness of methanol (possibly because of its lower acidity), as compared with water, as a bridging medium for proton transfer.

Base Hydrolysis of $Co(DH)_2(NO_2)Br^-$. The kinetics of the hydrolysis reaction of $Co(DH)_2(NO_2)Br^-$, *i.e.*

$$Co(DH)_2(NO_2)Br^- + H_2O \longrightarrow Co(DH)_2(NO_2)OH_2 + Br^- \quad (7)$$

have previously been examined in acid solutions by Hague and Halpern.[11] We have extended this investigation to the region of higher pH (up to 0.1 M OH^-) and found the rate of hydrolysis to increase with the OH^- concentration according to the rate law

$$-d[Co(DH)_2(NO_2)Br^-]_{tot}/dt = -d([Co(DH)_2(NO_2)Br^-] + [Co(D_2H)(NO_2)Br^{2-}]) = k_a[Co(DH)_2(NO_2)Br^-] + k_b[Co(D_2H)(NO_2)Br^{2-}] = (k_a + k_bK[OH^-])[Co(DH)_2(NO_2)Br^-]_{tot}/(1 + K[OH^-]) \quad (8)$$

Hence

$$-d \ln [Co(DH)_2(NO_2)Br^-]_{tot}/dt = k_{hyd} = (k_a + k_bK[OH^-])/(1 + K(OH^-]) \quad (9)$$

where K is the equilibrium quotient of reaction 5, defined by eq 3.

In accord with eq 9, the hydrolysis reactions, examined at 15° and 0.10 M ionic strength, exhibited pseudo-first-order kinetic behavior, yielding the values of k_{hyd} listed in Table III. Using K = 31 M^{-1}, these data yielded linear plots of $k_{hyd}(1 + K[OH^-])$ *vs.* $[OH^-]$ which were fitted to eq 9 to yield the values k_a = 3.5 × 10^{-5} sec^{-1} and k_b = 1.1 × 10^{-3} sec^{-1}. The above value of k_a agrees with that (4.0 × 10^{-5} sec^{-1}) determined by Hague and Halpern[11] at 1.0 M ionic strength.

Table III. Kinetic Data for the Base Hydrolysis of $Co(DH)_2(NO_2)Br^-$ [a]

$10^3[Co(DH)_2(NO_2)Br^-]_{tot}$, M	$10^2[OH^-]_{eq}$, M	10^4k_{hyd}, sec^{-1}	$(10^4k_{hyd})_{calcd}$,[b] sec^{-1}
1.22	9.88	8.64	8.4
1.06	4.90	6.90	6.8
1.16	2.38	4.07	4.9
1.37	1.11	2.86	3.1
1.37	0.488	1.95	1.8
1.30	0.183	0.96	0.92

[a] Ionic strength maintained at 0.10 M with $NaClO_4$; 15°. [b] Computed from eq 9 using the values of k_a, k_b, and K given in the text.

The kinetic behavior of the OH^--dependent path for the hydrolysis of $Co(DH)_2(NO_2)Br^-$ is consistent with, and fails to distinguish between, three alternative mechanisms, analogous to those that have been proposed for the corresponding base hydrolysis reactions of acidopentaamminecobalt(III) complexes, which exhibit similar rate laws.[12] These are (i) an SN2 mechanism, corresponding to eq 2a, (ii) an SN2CB mechanism, corresponding to the rapid preequilibrium 5, followed by the SN2 hydrolysis of the conjugate base according to eq 2b, and (iii) an SN1CB mechanism, corresponding to the rapid preequilibrium 5, followed by the hydrolysis of the conjugate base according to the SN1 mechanism

$$Co(D_2H)(NO_2)Br^{2-} \longrightarrow Co(D_2H)(NO_2)^- + Br^- \text{ (rate determining)} \quad (10)$$

$$Co(D_2H)(NO_2)^- + H_2O \longrightarrow Co(DH)_2(NO_2)OH^- \quad (11)$$

In the case of the base hydrolysis of pentaamminecobalt(III) complexes, evidence for an SN1CB mechanism has been provided by the observation[12] of competition between water and a variety of anions (NO_2^-, NCS^-, etc.) for the proposed five-coordinate intermediate, $Co(NH_3)_4(NH_2)^+$. Thus, the base hydrolysis of $Co(NH_3)_5X^{2+}$ (X^- = Cl^-, Br^-, I^-) in the presence of 1 M NO_2^- yields about 4–5% $Co(NH_3)_5(NO_2)^{2+}$, this yield being nearly independent of the identity of X, and proportional to the NO_2^- concentration. A similar experiment, attempted by us for $Co(DH)_2(NO_2)Br^-$, yielded negative results. Thus, no $Co(DH)_2(NO_2)_2^-$ product could be detected spectrophotometrically when the hydrolysis of $Co(DH)_2(NO_2)Br^-$ was effected in a solution containing 0.2 M OH^- and 1.0 to 4.0 M NO_2^-. In connection with the interpretation of this result, it should be noted that NO_2^- does not react appreciably with $Co(DH)_2(NO_2)OH_2$, nor does $Co(DH)_2(NO_2)_2^-$ undergo appreciable hydrolysis, under the conditions and during the duration of these

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[11] D. N. Hague and J. Halpern, *Inorg. Chem.*, **6**, 2059 (1967). The basis for the assignment of *trans* configurations to $Co(DH)_2(NO_2)Br^-$ and related complexes is discussed in this reference.

[12] D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, **88**, 5443 (1966).

experiments. It should further be noted that, from the standpoint of the charge of the proposed SN1CB intermediate, the competition of NO_2^- with water might be expected to be less favorable for $Co(D_2H)(NO_2)^-$ than for $Co(NH_3)_4(NH_2)^{2+}$. In any case, the mechanistic ambiguity relating to possible contributions from SN2, SN2CB, and SN1CB paths to the base hydrolysis of $Co(DH)_2(NO_2)Br^-$ remains to be resolved.

Mechanism for the Proton-Transfer Reactions of a Peptide Hydrogen in Copper(II) Triglycine

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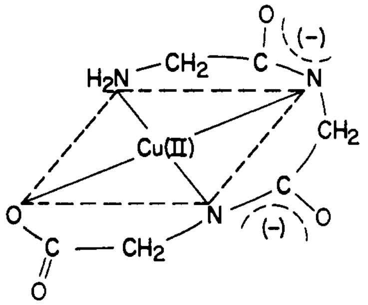
Abstract: The rate of interconversion of $CuH_{-2}L^-$ and $CuH_{-1}L$ (where L is triglycine and the protons are ionized from the peptide linkages) is much slower than normal acid–base reactions. The rate constant for the reaction of H_3O^+ with $CuH_{-2}L^-$ is $4.9 \times 10^6\ M^{-1}\ sec^{-1}$, and the value for the reaction of OH^- with $CuH_{-1}L$ is $2.5 \times 10^4\ M^{-1}\ sec^{-1}$. The reason proposed for the slower rates is the necessity to break and rearrange coordinate bonds to copper. The proton addition is general acid catalyzed and proton removal is subject to base catalysis. Two reaction paths are proposed. The copper–imide bond in $CuH_{-2}L^-$ is not easily broken and tends to dissociate after the addition of a proton to the peptide nitrogen.

Copper(II) complexes of short-chain polypeptides promote the ionization of the peptide hydrogens.[3–9] In the present work the speed and mechanism of this type of proton-transfer reaction is examined for copper(II) triglycine which forms $CuH_{-1}L$ (or CuA) and $CuH_{-2}L^-$ (or CuB^-) with the loss of one and two protons, respectively, from triglycine (L^-). The pK_a values for these ionizations are 5.4 and 6.6, and from infrared studies in D_2O it was concluded that the structure of $CuH_{-2}L^-$ can be represented by I.[9] The crystal structures of disodium tetraglycinocuprate(II) and of sodium triglycinocuprate(II) ($NaCuH_{-2}L \cdot H_2O$) have the peptide nitrogens coordinated to copper.[5,6,10] When copper triglycine is crystallized from acid solutions to give $CuLCl \cdot 1.5H_2O$, the peptide chain is attached to two copper atoms and each copper atom is bonded to two different peptide molecules. The copper is coordinated to the carbonyl oxygen of the peptide link.[5] Structures have been suggested for CuL^+ and for $CuH_{-1}L$ in solution where the -NH- group of the peptide link is coordinated.[9] Our kinetic evidence suggests that the proton-transfer reactions between $CuH_{-2}L^-$ and $CuH_{-1}L$ involve copper–nitrogen dissociation and that $CuH_{-1}L$ has carbonyl oxygen coordination.



I ($CuH_{-2}L^-$)

The reaction of H_3O^+ with $CuH_{-2}L^-$ to form $CuH_{-1}L$ is much less than the diffusion-controlled rate.[11] This proton-transfer reaction is general acid catalyzed and can be studied in the presence of ethylenediaminetetraacetate ion (EDTA) which does not react as a nucleophile with $CuH_{-2}L^-$ but does react with $CuH_{-1}L$. The reactions of $CuH_{-1}L$ with bases were studied directly using a pH-jump method.

Experimental Section

Kinetic runs were followed using stopped-flow spectrophotometers. One instrument was described earlier[12] and the other was a Durrum–Gibson stopped-flow, Durrum Instrument Corp., Palo Alto, Calif. Both instruments were thermostated at 25.0 ± 0.1°.

The reaction between copper triglycine and EDTA was followed by the disappearance of $CuH_{-2}L^-$ which has a much higher molar absorptivity than $CuH_{-1}L$ or $CuEDTA^{2-}$ at 555 mμ. This wavelength was used for reactions at pH 6.0–7.5 where a significant percentage of the copper triglycine is present as $CuH_{-1}L$. Above pH 7.5 the reactions were followed at 235 mμ.

Triglycine was obtained (chromatographically homogeneous) from Mann Research Laboratories (New York, N. Y.) and was used without further purification. A $9.85 \times 10^{-2}\ M$ stock solution of $Cu(ClO_4)_2$ was prepared from the twice-recrystallized salt and standardized against EDTA. The copper(II)–triglycine complex was prepared for each series of reactions by mixing copper(II) and triglycine using a 2% molar excess of triglycine. The concentration of copper(II) triglycine used for a kinetic run ranged from 2 ×

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