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Kinetics of the Reduction of Nitro to Hydroxylamine Groups by Dithionite in a Cobalt(II) Cryptand Complex. X-ray Analysis of [1,8-Bis(hydroxyamino)-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane]cobalt(III) Chloride Tetrahydrate

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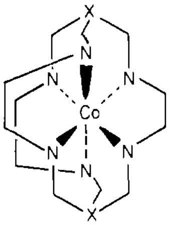
The cobalt(III) complex of a dinitrohexaazacryptand, (1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane)cobalt(III), Co(dinosar)$^{3+}$, is reduced quantitatively by dithionite to the cobalt(III) complex of the corresponding bis(hydroxyamino)hexaaza cryptand through an intermediate cobalt(II) complex. The overall reaction occurs in two kinetically distinguishable steps that both follow the rate law $k_{obsd} = k_2K_1^{1/2}[S_2O_4^{2-}]^{1/2}$, where k_{obsd} is the first-order rate constant with excess dithionite, K_1 is the equilibrium constant for the reaction $S_2O_4^{2-} \rightleftarrows 2SO_2^-$, and k_2 refers to attack of SO_2^- on the complex. At 25 °C $k_2 = 3.5 \times 10^5$ M^{-1} s^{-1} for production of the cobalt(II) complex and 1.6×10^4 M^{-1} s^{-1} for production of the cobalt(III) product (pH 6.3, MES buffer, $I = 0.50$ M (Na_2SO_4)). An X-ray crystal structure determination of the cobalt(III) product confirms that both nitro groups from the starting material have been converted to hydroxyamino groups. The crystals of [1,8-bis(hydroxyamino)-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane]cobalt(III) chloride tetrahydrate are monoclinic, space group $P2_1/n$, $a = 11.212$ (1) Å, $b = 18.327$ (4) Å, $c = 13.713$ (3) Å, $\beta = 103.24$ (2)°, and $Z = 4$. The structure was determined by the heavy-atom method, and refined by block-diagonal least-squares calculations, $R = 0.034$, $R_w = 0.037$, for 1717 observed reflections. If the terminal NH_2OH moieties are excluded, the cation has very close to D_3 symmetry, with Co–N 1.966–1.979 (6) Å, mean 1.973 (5) Å.

Introduction

A series of complexes of type I, first synthesized by Sargeson and co-workers,[1,2] have several interesting and unique properties the most important of which is the inertness of the cobalt(II) forms. Since a large variation in redox potential for different X values can be achieved, these complexes are potentially useful as outer-sphere redox reagents in kinetic studies. For example, with X = N (Co(sepulchrate)$^{3+}$) $\epsilon°$, the reduction potential, is = –0.30 V,[2] whereas for X = CNO_2 (Co(dinosar)$^{3+}$) $\epsilon° = 0.0$ V.[3a] The cobalt(II) form of the complexes can be easily generated by reduction over zinc dust. Interestingly, Co(sepulchrate)$^{3+}$ is not reduced by dithionite (pH 6–12) despite the favorable driving force, indicating some measure of kinetic control.[3a] However, Co(dinosar)$^{3+}$ does react readily with dithionite (pH 6.3) in two stages, producing finally a cobalt(III) cryptand with X = CNHOH.[3b] This paper is concerned with the kinetics of this reaction. Furthermore, since the product of the reaction was unexpected, and its characterization depended mainly on the stoichiometry of the reaction, a single-crystal X-ray structure analysis was carried out.



I

Experimental Section

Preparation of (1,8-Dinitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane)cobalt(III) Chloride Dihydrate, [Co($C_{14}H_{30}N_8O_4$)]Cl_3·$2H_2O$ (I, X = CNO_2). To a solution of 25 g of Li_2CO_3 and 9.1 g of [Co(en)$_3$]Cl_3 in 125 mL of H_2O was added 592 mL of 36% formaldehyde. To this solution 135 mL of nitromethane was added dropwise over a period of 2 h. The solution was made acidic with concentrated HCl and concentrated $HClO_4$, and solid $NaClO_4$ was added to precipitate the complex. The complex was submitted to cation-exchange chromatography on CM-Sephadex resin. Elution with 0.2 to 0.7 M NaCl removed several minor products and moved the major orange band slowly down the column. This band was removed physically from the column and the complex removed from the resin by addition of concentrated HCl until the solution was just acidic. After filtration the desired complex was isolated by adding an equal volume of acetone to the solution and cooling. Anal. Calcd for [Co($C_{14}H_{30}N_8O_4$)]Cl_3·$2H_2O$: C, 29.2; H, 5.90; N, 19.4. Found: C, 29.0; H, 5.71; N, 19.4. Electronic spectrum: γ_{max} (ϵ_{max}) 474 (158), 345 nm (131 M^{-1} cm^{-1}). IR: 1560 (s), 1455 (m, br), 1350 (s), 1080 (s), 805 cm^{-1} (s).

Preparation of [1,8-Bis(hydroxyamino)-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane]cobalt(III) Chloride Tetrahydrate, [Co($C_{14}H_{36}N_8O_2$)]Cl_5·$4H_2O$ (I, X = CNH_2OH). An oxygen-free solution (20 mL) containing 0.25 g of [Co(dinosar)]Cl_3·$2H_2O$ in MES buffer at pH 6.3 was rapidly mixed under argon with an oxygen-free solution (20 mL) containing 0.83 g of sodium dithionite in MES buffer at pH 6.3. After approximately 5 min, the resulting solution was diluted with water and submitted to cation-exchange chromatography on CM-Sephadex resin. Elution with 0.3 M NaCl gave an orange band, which moved slowly down the column. There was a hint of a yellow band (<5%), which moved more rapidly down the column and was not isolated. The major complex was removed from the resin with concentrated HCl and the resulting solution allowed to evaporate slowly in a gentle stream of air until crystals were deposited. These crystals were used for the X-ray analysis. Anal. Calcd for [Co($C_{14}H_{36}N_8O_2$)Cl_5·$4H_2O$: C, 25.6; H, 6.70; N, 17.1. Found: C, 25.8; H, 6.69; N, 17.0.

Two recrystallizations from water gave **I**, X = CNHOH. Anal. Calcd for [Co($C_{14}H_{34}N_8O_2$)]Cl_3·H_2O: C, 31.7; H, 6.41; N, 21.1. Found: C, 31.3; H, 6.54; N, 21.1. Electronic spectrum: λ_{max} 471 nm (139 M^{-1} cm^{-1}). The infrared spectrum showed several bands in the 800–1600-cm^{-1} region which could be attributed to the –NH_2OH group. All NO_2 bands were absent.

Kinetic Studies. All kinetic measurements were obtained with a Durrum stopped-flow spectrophotometer. Reactions were monitored at 474 nm and rate constants were obtained by curve-fitting the exponential curves obtained by using an OLIS data collecting system. All reactions were carried out at pH 6.3 (MES buffer) at 25 °C and $I = 0.5$ M maintained with Na_2SO_4. Dithionite (2.5–124 mM) was

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(3) (a) Balahura, R. J.; Wilkins, R. G., unpublished observations (with respect to NHE). (b) In dilute HCl X = NH_2OH (crystal structure).

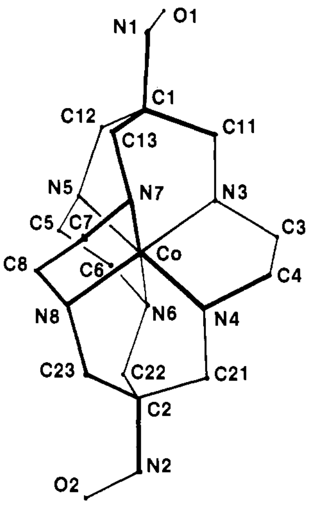

Figure 1. Structure of the $[C_{14}H_{36}CoN_8O_2]^{5+}$ cation with the crystallographic numbering scheme; hydrogen atoms are omitted for clarity.

used in excess over cobalt(III) complex (0.26–1.7 mM), and excellent pseudo-first-order kinetics were obtained. Solutions were handled anaerobically by use of standard syringe techniques. Spectral measurements employed a Beckman 24 spectrophotometer.

X-ray Analysis of I, X = CNH_2OH. Crystal data: $[C_{14}H_{36}CoN_8O_2]^{5+}$, $5Cl^-$, $4H_2O$; M_r 656.7, monoclinic, a = 11.212 (1) Å, b = 18.327 (4) Å, c = 13.713 (3) Å, β = 103.24 (2)°, Z = 4, D_c = 1.59 g cm^{-3}, $F(000)$ = 1376, Mo radiation, λ = 0.7107 Å, μ(Mo Kα) = 11.8 cm^{-1}, space group $P2_1/n$ (C_{2h}^5, No. 14) from systematic absences, $h0l$ absent if $h + l = 2n + 1$, $0k0$ absent if $k = 2n + 1$.

Accurate cell parameters were determined by a least-squares refinement of the setting angles of 25 reflections with $10° < \theta < 20°$ measured on an Enraf-Nonius CAD 4 diffractometer. Intensity data were collected by using monochromatized Mo Kα radiation to a maximal θ of 20° with a small crystal, and 2551 reflections were measured. Three well-separated reflections were monitored at regular intervals and showed no significant decay. After corrections for Lorentz and polarization factors, the data with $I > 3\sigma(I)$ (1717) were labeled observed and used in structure solution and refinement.

Structure Solution and Refinement. The coordinates of the Co atom were obtained from an analysis of a three-dimensional Patterson function, and the remaining non-hydrogen atoms were located in a subsequent heavy-atom-phased Fourier summation. Refinement was by block-diagonal least-squares calculations,[4] initially with isotropic and then with anisotropic vibration parameters. A difference map computed at an intermediate stage in the refinement revealed maxima in positions expected for all the hydrogen atoms; these were then allowed for in geometrically idealized positions (C–H = 1.08 Å) and included in the final rounds of calculations but not refined. Scattering factors used in the structure factor calculations were taken from ref 5 and 6, and allowance was made for anomalous dispersion.[7] Refinement converged with R = 0.0343 and $R_w = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$ = 0.0369 for the 1717 reflections with $I > 3\sigma(I)$. The weights in the refinement calculations were derived from the counting statistics ($w = 1/\sigma(F)^2$). A final difference map had no chemically significant features. Figure 1 is a perspective view of the cation with our numbering scheme. Final coordinates for the non-hydrogen atoms are given in Table I. Cation dimensions are summarized in Table II; full details are in the deposition data along with lists of hydrogen-bond distances involving the ions and water molecules. Lists of anisotropic thermal parameters, calculated hydrogen coordinates, and observed and calculated structure factors have also been deposited.

Table I. Final Fractional Coordinates for I, X = CNH_2OH, with Estimated Standard Deviations in Parentheses

atom	x	y	z
Co	0.98575 (9)	0.11234 (5)	0.24976 (8)
O(1)	1.4015 (4)	0.2368 (3)	0.3618 (4)
O(2)	0.5366 (4)	0.0508 (3)	0.2583 (4)
N(1)	1.3850 (5)	0.1657 (3)	0.3199 (4)
N(2)	0.5860 (5)	0.0600 (3)	0.1732 (4)
N(3)	1.0557 (5)	0.2015 (3)	0.2035 (4)
N(4)	0.8833 (5)	0.1028 (3)	0.1122 (4)
N(5)	1.0868 (5)	0.1245 (3)	0.3871 (4)
N(6)	0.8603 (5)	0.1730 (3)	0.2902 (4)
N(7)	1.1128 (5)	0.0506 (3)	0.2132 (4)
N(8)	0.9158 (5)	0.0228 (3)	0.2927 (4)
C(1)	1.2500 (7)	0.1479 (4)	0.2981 (5)
C(2)	0.7204 (6)	0.0777 (4)	0.2019 (5)
C(3)	0.9785 (7)	0.2236 (4)	0.1021 (5)
C(4)	0.9302 (7)	0.1544 (4)	0.0444 (5)
C(5)	1.0071 (7)	0.1559 (4)	0.4515 (5)
C(6)	0.9147 (7)	0.2072 (4)	0.3902 (5)
C(7)	1.0748 (7)	−0.0277 (4)	0.2134 (6)
C(8)	1.0045 (7)	−0.0391 (4)	0.2955 (6)
C(11)	1.1883 (6)	0.1941 (4)	0.2053 (5)
C(12)	1.2026 (6)	0.1657 (4)	0.3924 (5)
C(13)	1.2393 (7)	0.0652 (4)	0.2731 (5)
C(21)	0.7493 (6)	0.1114 (4)	0.1069 (5)
C(22)	0.7432 (6)	0.1337 (4)	0.2872 (5)
C(23)	0.7912 (6)	0.0066 (4)	0.2313 (5)
W(1)	0.9576 (5)	0.4218 (3)	0.1639 (4)
W(2)	0.6120 (5)	0.2983 (3)	0.3638 (4)
W(3)	0.5503 (5)	−0.0669 (3)	0.0694 (4)
W(4)	1.4800 (6)	−0.0871 (3)	0.5276 (4)
Cl(1)	1.21599 (19)	−0.00528 (12)	0.51914 (15)
Cl(2)	0.74643 (20)	0.31877 (11)	0.18774 (16)
Cl(3)	1.18630 (19)	0.05296 (11)	0.00587 (15)
Cl(4)	1.44861 (20)	0.19902 (12)	0.11819 (16)
Cl(5)	1.13781 (20)	0.35124 (11)	0.33450 (16)

Table II. Summary of Cation Dimensions (A or deg)[a]

bond or angle type	range	no. of bonds/ angles	mean
Co–N	1.966–1.979 (6)	6	1.973 (5)
N–C	1.487–1.516 (9)	12	1.499 (9)
C–C	1.504–1.554 (10)	9	1.535 (10)
N–O	1.413 and 1.420 (7)	2	1.417 (7)
N(3)–Co–N(4)	87.3–87.6 (2)	3	87.4 (2)
N(3)–Co–N(5)	91.0–91.7 (2)	6	91.5 (2)
C(1)–C(11)–N(3)	108.2–110.0 (5)	6	108.9 (5)
C(11)–C(1)–C(12)	110.2–113.4 (6)	6	111.7 (6)
Co–N(3)–C(11)–C(1)	−33.1 to −35.9	6	−34.9
N(3)–C(3)–C(4)–N(4)	43.8 to 44.8	3	44.4

[a] See Figure 1 for numbering scheme.

Results and Discussion

When sodium dithionite is mixed with Co(dinosar)$^{3+}$ under anaerobic conditions, two reactions are observed. The first reaction results in complete loss of the low energy visible band exhibited by Co(dinosar)$^{3+}$ at 474 nm and corresponds to production of Co(dinosar)$^{2+}$. The stoichiometry of this step was determined at 474 nm by spectrophotometric titration. One-half mole of dithionite ions was required per mole of Co(III) complex. The second reaction results in the production of a cobalt(III) species that has been identified as I, X = CNHOH. The overall stoichiometry was determined by spectrophotometric titration at 325 nm (a maximum for sodium dithionite) and showed that 4.0 ± 0.1 mol of $Na_2S_2O_4$ was consumed per mol of Co(dinosar)$^{3+}$. Thus the second reaction requires 3.5 mol of $Na_2S_2O_4$. The overall reaction can be represented as

$$Co(C_{14}H_{30}N_6)(NO_2)_2{}^{3+} \xrightarrow{e^-} Co(C_{14}H_{30}N_6)(NO_2)_2{}^{2+} \xrightarrow[(-2H_2O)]{8H^+ + 7e^-} Co(C_{14}H_{30}N_6)(NHOH)_2{}^{3+} \quad (1)$$

Reaction 1 was shown to be quantitative by cation-exchange

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Table III. Kinetic Data for the Reaction of $S_2O_4^{2-}$ with $Co(dinosar)^{3+}$ [a,b]

$[Co(dinosar)^{3+}]$, mM	$[S_2O_4^{2-}]$, mM	first stage k_{obsd}, s^{-1}	second stage k_{obsd}, s^{-1}
1.70	124	4.54	0.22
1.70	70	3.50	0.16
1.70	33	2.42	0.11
2.56	2.5	0.69	0.023

[a] $I = 0.50$ M maintained with Na_2SO_4, pH 6.3, MES buffer. [b] Each run is an average of at least three separate experiments.

chromatography after reaction of $Co(dinosar)^{3+}$ with excess dithionite (kinetic conditions). In all cases the major product (>95%) was the hydroxylamine complex I, X = CNHOH.

The kinetics of reaction 1 were studied by stopped-flow spectrophotometry at 474 nm, 25 °C, pH 6.3 MES buffer, and $I = 0.5$ M (Na_2SO_4). The data are collected in Table III. With dithionite in excess, each step was clearly first order. Varying the dithionite concentration showed a square-root dependence on reductant concentration for each step. This is easily interpreted in terms of the mechanism shown in (2) and (3). Since $k_{obsd}\,[S_2O_4^{2-}]^{-1/2} = = K_1^{1/2}k_2$, where k_{obsd} is

$$S_2O_4^{2-} \rightleftarrows 2SO_2^- \qquad K_1 \qquad (2)$$

$$SO_2^- + Co(dinosar)^{3+} \rightarrow \text{product} \qquad k_2 \qquad (3)$$

the pseudo-first-order rate constant and $K_1 = 1.4 \times 10^{-9}$ M,[8] the value (k_2) for direct attack by SO_2^- in each stage of (1) is determined to be 3.5×10^5 M^{-1} s^{-1} and 1.6×10^4 M^{-1} s^{-1} respectively. The second-order rate constant for reduction of $Co(dinosar)^{3+}$ by SO_2^- is somewhat larger than the corresponding values for a number of cobalt(III) amines and aminocarboxylate complexes.[9,10] This difference is more real when the much smaller driving force is considered ($E°$ values for cobalt(III) complexes examined in ref 10 are positive; that for $Co(dinosar)^{3+}$ is 0.0 V). The relative ease of reduction of $Co(dinosar)^{3+}$ may result from the $-NO_2$ group channeling electrons to the metal center. This is supported by the observation that I, X = N, I, X = CNHOH, and I, X = CNH_2, are reduced extremely slowly (no reduction by dithionite at pH 6.3 for 24 h with $[S_2O_4^{2-}] \geq 0.2$ M).

The second stage of (1), the production of a cobalt(III) complex in a reducing medium, was unexpected. This reaction resembles the induced electron transfer reactions described by Taube,[11] although it is uncertain how essential is the role of the cobalt oxidation in the $-NO_2$/$-NHOH$ transformation. Since both $-NO_2$ groups are reduced, the oxidation of one Co(II) may be incidental. The step associated with the rate constant 1.6×10^4 M^{-1} s^{-1} must involve reaction of the SO_2^- entity with the NO_2 group or a subsequently reduced species. This step must precede the intramolecular oxidation of cobalt(II), which is the monitored process. Presumably the reactive intermediate formed scavenges an electron from Co(II) with the same facility as from SO_2^-. It would be interesting to determine how general this reaction might be with cobalt(II) complexes of other ligands containing reducible substituents. A study of complex I with one X = CMe and the other X = CNO_2 may eliminate some of the mechanistic ambiguities referred to above.

The selectivity of the reaction was also surprising. When the reduction was carried out over zinc dust under anaerobic conditions, a total of four cobalt(III) products were eventually isolated. Three of these were identified as I, X = CNO_2; I, X = CNH_2OH; and I, X = CNH_2. Furthermore, preliminary results of a polarographic study of $Co(dinosar)^{3+}$ indicate several complex reactions.

Due to the difficulty in characterizing unambiguously the product of reaction 1 by spectroscopic methods, the crystal structure of the complex was determined. The X-ray analysis unequivocally establishes the structure of the cation to be as shown in Figure 1, with the Co atom at the center of the cryptate ligand, and apical NH_2OH moieties. The cation dimensions summarized in Table II define a structure with normal geometry.[2] The cation has almost ideal D_3 symmetry (if the apical NH_2OH groups are excluded), with the 3-fold axis running through C(1), Co, and C(2) (Figure 1) and the 2-fold axis passing through Co and the midpoints of the ethylenediamine CH_2–CH_2 type bonds. All hydrogen atoms were located in difference maps and all 20 N–H or O–H hydrogens in the asymmetric unit are involved in an extensive hydrogen bonding network with the Cl^- ions or each other (N–H···Cl^- 2.983–3.293, water–H···Cl^- 3.011–3.342, O–H···water 2.590 and 2.609, water–H···water 2.869, N–H···water 2.702 and 2.719 Å).

Acknowledgment. We thank Professor Alan M. Sargeson for information on the Zn reduction of $Co(dinosar)^{3+}$ and Dr. I. I. Creaser for a gift of I, X = CNH_2. This work was partly supported by a National Science Foundation grant and the Natural Sciences and Engineering Research Council of Canada.

Registry No. I, X = CNO_2, 71935-78-9; I, X = CNH_2OH, 87655-56-9; I, X = CNHOH, 87655-57-0; $[Co(en)_3]Cl_3$, 13408-73-6; $Na_2S_2O_4$, 7775-14-6; dinosar, 87655-55-8; formaldehyde, 50-00-0; nitromethane, 75-52-5.

Supplementary Material Available: Tables of interatomic distances and angles, bond lengths, bond angles, torsion angles, hydrogen-bonding distances, anisotropic thermal parameters, calculated hydrogen coordinates, and structure factors (27 pages). Ordering information is given on any current masthead page.

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