such as Fe(I) and Co(I) and cathodic of M(IV) species such as TiO and VO.[12]

The use of these data in the design of photoredox catalysts will be the subject of a future communication.[13]

Acknowledgment. This research is part of a joint project with Professor A. J. Bard (University of Texas at Austin) funded by the Office of Naval Research, to whom we are indebted. We also thank Professor I. M. Walker for useful discussion.

Registry No. (O-^{t}Am)$_2$Si^{IV}(phthalocyanine), 18897-03-5; ClAl^{III}(phthalocyanine)·DMF, 78638-46-7; ClGa^{III}(phthalocyanine)·DMF, 78638-47-8; ClIn^{III}(phthalocyanine)·DMF, 78656-73-2; Mg^{II}(phthalocyanine)·2DMF, 78638-48-9; Zn^{II}(phthalocyanine)·2DMF, 78638-49-0; Cd^{2+}, 22537-48-0; Hg^{2+}, 14302-87-5; Pb^{2+}, 14280-50-3; phthalocyanine, 574-93-6.

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Intramolecular Redox Decomposition of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and Related Complexes

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Received November 26, 1980

Intramolecular electron-transfer (IET) rates are not affected by precursor complex formation[1] and therefore directly reflect the extent of coupling between the electron-donor and -acceptor portions of the molecule. Recent strategies employed to measure IET rates include (1) formation of metastable coordinated ligand radicals (often by pulse radiolytic techniques) which subsequently decay by IET,[2-4] (2) formation of metastable binuclear complexes which then decay by IET,[5-7] and (3) evaluation of intervalence electron transfer between metals of stable binuclear complexes.[8-10] Another approach to measuring IET rates has appeared sporadically in the literature[11-14] but has not been systematically exploited since it depends on the availability of complexes with very specific properties. These complexes must contain a potentially reducing ligand coordinated to a metal ion that can function as a one-equiv oxidant (usually cobalt(III)) in an array that is kinetically inert but thermodynamically unstable. In addition, upon thermal activation these complexes must undergo IET to yield the one-equiv reduced metal center and a ligand free radical rather than suffering the usual metal–ligand bond fission. This type of IET reaction is of interest not only because it allows the intrinsic rate of inner-sphere ligand-to-metal electron transfer to be probed but also because it is the thermally induced analogue to photochemically induced ligand-to-metal charge-transfer excitation.[15,16]

During our research into the chemistry of (thiolato)cobalt(III) complexes,[17-19] we noted that while the prototype complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ has remarkable kinetic stability under ordinary conditions, it does slowly undergo intramolecular redox decomposition upon thermal activation. This thiol-to-metal IET reaction is of special interest in view of the prevalence of thiol–metal interactions in redox enzyme systems[20,2] and in view of the possibility that it is the harbinger for a large number of IET reactions of (thiolato)cobalt(III) complexes, the composition of which can be systematically and extensively varied. In this paper we report on the kinetics of the intramolecular redox decomposition of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and some of its derivatives.

Experimental Section

Triply distilled, charcoal-filtered water and doubly vacuum distilled perchloric acid (G. F. Smith, 70–72%) were used for all kinetic experiments. Lithium perchlorate solutions were prepared by neutralization of Baker "Ultrex" lithium carbonate. The perchlorate salts of (2-mercaptoethylamine-*N,S*)bis(ethylenediamine)cobalt(III) and ((methyl 2-aminoethyl thioether)-*N,S*)bis(ethylenediamine)cobalt(III) were prepared and purified as previously described.[22] Spectrophotometric determinations were conducted on a Cary 14, Cary 210, or Cary 118B recording spectrophotometer. Temperature was maintained to +0.5 °C (as measured with a National Bureau of Standards certified thermometer) by means of a Neslab constant-temperature bath.

The metal-containing reaction product was quantitatively determined to be cobalt(II) by means of a modified Kitson[23] procedure; the Kitson procedure was also used to monitor the amount of cobalt(II) produced as a function of time. The organic reaction products were qualitatively identified by the following procedures. After reaction of the title complex in 0.1 M $HClO_4$ at 70 °C for 4 days, the reaction solution was made basic with an excess of 1 M NaOH and the organic products were extracted into chloroform. (1) TLC analysis of the $CHCl_3$ layer (Eastman 6060 SiO_2 sheets; 1/1 acetone/methanol mobile phase; visualization by either molecular iodine or phosphomolybdic acid) shows only two components. These components have the same respective R_f values as authentic samples of ethylenediamine and cystamine ($NH_2CH_2CH_2SSCH_2CH_2NH_2$) treated in the same fashion. (2) During visualization with phosphomolybdic acid, the component identified as cystamine behaves in the same fashion as does authentic cystamine and as is typical for disulfides; i.e., no color develops until the chromatogram is heated at 110 °C for about 30 min. Thiols generate color with phosphomolybdic acid immediately at room temperature, while sulfonic acids do not generate color even on heating. (3) The ultraviolet spectrum of the chloroform layer exhibits a broad peak at 247 nm, while a similarly treated sample of authentic cystamine exhibits an analogous peak at 248 nm. Absorption in this region is typical for dialkyl disulfides.[24]

The kinetics of the redox decompositions were monitored at 428 or 278 nm for $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$, at 482 or 500 nm for the methylmercury adducts,[18] and at 487 nm for the thioether complex; observed reaction rates are not dependent upon the monitoring wavelength. The intial concentration of the cobalt(III) complex ranged from 0.07 to 5.4 mM, and ionic strength was maintained at 1.00 ± 0.01 M with $HClO_4$ and $LiClO_4$. In a typical kinetics experiment, 100 mL of a $HClO_4$/$LiClO_4$ solution containing the cobalt(III)

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Table I. Observed Rate Parameters for the Intramolecular Redox Decomposition of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ in Aqueous Perchloric Acid Media[a]

t, °C	$[H^+]$, M	$10^6 k_{obsd}$, s^{-1}
56	1.00	2.10 ± 0.07
67	0.10	8.4 ± 0.1
67	0.50	8.0 ± 0.5
67	0.50	8.5 ± 0.5
67	1.00	7.6 ± 0.2
75	0.10	22.6 ± 0.5
75	0.25	25.1 ± 0.9
75	0.50	24.4 ± 0.6
75	1.00	29.1 ± 0.8
85	0.10	101 ± 1
85	1.00	101 ± 1
85	1.00	112 ± 1[b]
85	1.00	99 ± 5
85	1.00	114 ± 2[b]
85	1.00	96 ± 6[b]

[a] Conditions: $\mu = 1.00$ M ($LiClO_4$); $\lambda = 482$ nm unless otherwise noted. [b] $\lambda = 275$ nm.

complex was deaerated with a constant stream of nitrogen gas (which had been scrubbed by passage through a solution of chromous ion) for ca. 2 h. Then 12 8-mL aliquots of this solution were added to serum-capped test tubes and deaerated for another 15 min. At this point the reaction was initiated by placing the capped test tubes in a constant-temperature bath, the increasing pressure accompanying temperature equilibration being relieved by periodic insertion of syringe needles through the serum caps. At regular time intervals, individual test tubes were removed from the bath and immediately cooled to 0 °C to quench the reaction. Subsequently, all aliquots were spectrophotometrically monitored to determine A_t. At high temperatures the final aliquot provided an A_∞ measurement, and for these experiments, plots of log $(A_t - A_\infty)$ vs. time are linear, showing that the reaction is first order in cobalt(III); values of the observed first-order rate constant, k_{obsd}, and the associated standard deviation $\sigma_{k_{obsd}}$, were determined from the A_t–t data by standard nonlinear least-squares analysis.[25] At low temperatures the reactions proceeded too slowly to allow an experimental determination of A_∞; for these reactions, the aliquots were removed at constant time intervals and the k_{obsd} and $\sigma_{k_{obsd}}$ values determined by Kezdy analysis[26] as previously described.[27] Activation parameters were calculated by a linear least-squares analysis, individual values of k_{obsd} being weighted as $1/\sigma_{k_{obsd}}^2$. All reported errors are standard deviations.

Results and Discussion

In aqueous acidic media, under anaerobic conditions, $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ decomposes by a first-order process to yield cobalt(II) quantitatively. Within experimental error the rate of production of cobalt(II) is equal to the rate of disappearance of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ as monitored spectrophotometrically. These observations indicate that decomposition occurs via rate-determining intramolecular electron transfer to yield cobalt(II) and a thiyl radical.

$$5H^+ + (en)_2Co(SCH_2CH_2NH_2)^{2+} \xrightarrow{k_{obsd}} Co^{2+} + H_3NCH_2CH_2S^{+}\cdot + 2enH_2^{2+} \quad (1)$$

Two thiyl radicals eventually combine to form the disulfide cystamine;[17] the disulfide and ethylenediamine are the only organic reaction products detectable by TLC analysis. Attempts to trap the proposed thiyl radical intermediate, using large excesses of acrylic acid, crotonic acid, or conventional spin trapping reagents, were unsuccessful.

Values of k_{obsd} as a function of temperature and $[H^+]$ are given in Table I. These data show that the rate of intramolecular electron transfer is independent of acid over the range $[H^+] = 0.10$–1.0 M as would be expected from the fact that the sulfur atom of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ is only a poor Bronsted base.[28] However, the sulfur atom of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ has a high affinity for soft Lewis acids such as methylmercury(II),[18] and consequently addition of CH_3Hg^+ markedly retards intramolecular electron transfer. When 0.5 equiv of CH_3Hg^+ is added to $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ to form predominantly $[[(en)_2Co(SCH_2CH_2NH_2)]_2HgCH_3]^{5+}$, $10^6 k_{obsd}$ drops from 101 to 58 s^{-1} (85 °C, $[H^+] = \mu = 1.00$ M), and when 1.0 equiv is added to form predominantly $[[(en)_2Co(SCH_2CH_2NH_2)]HgCH_3]^{3+}$, $10^6 k_{obsd}$ further drops to 15 s^{-1}. This retardation is in harmony with the intramolecular electron transfer from sulfur to cobalt(III) depicted in eq 1—coordination of CH_3Hg^+ to the sulfur atom of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ decreases the polarizability of the sulfur atom and therefore its ability to function as a reductant. The polarizability and reducing ability of the coordinated sulfur atom can also be reduced by covalently bonding it to CH_3^+, i.e., by converting the thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ to the thioether complex $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$.[22] As expected, the thioether complex is very stable toward intramolecular redox decomposition, no reaction being detected even after 10 days at 85 °C ($10^6 k_{obsd} < 0.05$ s^{-1}). This total inertness of the covalently bonded CH_3^+ derivative implies that the methylmercury derivatives decompose through the small amounts of free $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ always present in equilibrium with the methylmercury adducts.[18] The fact that intramolecular electron-transfer rates can be controlled by the addition of exogeneous substances raises the possibility of using this phenomenon to synthesize complexes that are currently inaccessible because of rapid intramolecular redox decomposition.

Table II. Activation Parameters Governing the Intramolecular Redox Decomposition of Some Cobalt(III) Complexes

complex	ΔH^*, kcal/mol	ΔS^*, eu	ref
$(en)_2Co(SCH_2CH_2NH_2)^{2+}$	33 ± 2[a]	15 ± 4	this work
trans-$(en)_2Co(OH_2)(SO_3H)^{2+}$	33[b]	9	12
trans-$(NH_3)_4Co(OH_2)(SO_3)^{+}$	26[a,c]	12	13
$(NH_3)_5Co(OClO)^{2+}$	25[d]	3	14
cis-$(en)_2Co(Cl)(NH_2OH)^{2+}$	12[e]	−34	11

[a] $\mu = 1.00$ M. [b] In 2.36 M $HClO_4$. [c] Rate-determining step involves isomerization rather than electron transfer.[13] [d] $\mu = 0.5$ M. [e] $\mu = 0.1$ M. Parameters calculated from data of ref 11. Mechanism not unambiguously established.

Table II lists activation parameters governing four reactions related to the intramolecular electron-transfer (IET) reaction investigated in this work. However, the data for *trans*-$[(NH_3)_4Co(OH_2)(SO_3)]^+$ are not relevant to this discussion since the rate-determining step in the decomposition of this complex appears to be isomerization rather than electron transfer.[13] Moreover, the decomposition of *cis*-$[(en)_2Co(Cl)(NH_2OH)]^{2+}$ was monitored only be determination of released chloride,[11] and therefore the assignment as an intramolecular redox reaction must be considered speculative. This leaves a total of only three thermally induced, ligand-to-cobalt(III), IET reactions which can be directly compared. The nearly identical values of the activation parameters governing decomposition of $[(en)_2Co(SCH_2CH_2NH_2]^{2+}$ and *trans*-$[(en)_2Co(OH_2)(SO_3H)]^{2+}$ presumably result from fortuitous cancellation of opposing effects (the driving force for electron loss from coordinated sulfur vs. the Franck–Condon barrier of the cobalt(III) center[29]). The lower ΔH^* value for

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decomposition of $[(NH_3)_5Co(OClO)]^{2+}$ may reflect the smaller Franck–Condon barrier associated with the cobalt(III) center containing only monodentate ligands.[29,30] Finally, the observed ΔS^* values for the three IET reactions fall within a narrow range (3–15 eu) which indicates only little solvent reorganization in the transition state, a result which is entirely in harmony with intramolecular electron transfer.

Acknowledgment. Financial support by the National Science Foundation, Grant No. CHE 79-26497, is gratefully acknowledged. We also thank Mr. Robert Whittle for conducting the cobalt(II) experiments.

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Preparation and Kinetics of Isomerization of *cis*-Ni(cyclam)$(H_2O)_2^{2+}$

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Received December 17, 1980

Complexes of macrocyclic tetraaza ligands commonly exhibit tetragonal stereochemistry with the four nitrogen atoms in the equatorial plane. The in-plane ligand field provided by the four nitrogen donors of the 14-membered-ring saturated macrocycle cyclam ([14]aneN_4, 1,4,8,11-tetraazacyclotetradecane) is sufficiently strong to stabilize low-spin nickel(II). The electronic spectrum of Ni(cyclam)$^{2+}$ exhibits a single band at 22 400 cm^{-1} characteristic of square-planar diamagnetic nickel(II) complexes. Recently Fabbrizzi[1] demonstrated that dilute aqueous solutions of Ni(cyclam)$^{2+}$ also contain 29% of the octahedral species Ni(cyclam)$(H_2O)_2^{2+}$, presumably the trans isomer.

There are few exceptions to coplanar coordination by cyclam, although smaller macrocycles tend to adopt the folded configuration upon coordination to nickel(II).[2] (Both cis and trans isomers of cyclam complexes of cobalt(III),[3] rhodium(III),[4] and ruthenium(III)[5] have been isolated.) The present paper describes the facile conversion of Ni(cyclam)$^{2+}$ to *cis*-Ni(cyclam)$(H_2O)_2^{2+}$ and reports some of its equilibrium and kinetic properties. In acidic solution, the cis isomer isomerizes to the trans isomer extremely slowly; the half-life at pH 3 is approximately 250 days.

Experimental Section

Table I. Electronic Spectral Data of Some Nickel(II) Polyamine Complexes in Aqueous Solution

complex	λ_{max} $(\epsilon)^a$			
Ni(cyclam)(en)$^{2+}$	880 (10.8)	800 (sh)	535 (8.4)	343 (13.6)
Ni(2,3,2-tet)(en)$^{2+\,b}$	880 (7.5)	800 (sh)	535 (7.0)	342 (10.9)
cis-Ni(cyclam)-$(H_2O)_2^{2+}$	890 (14)		548 (8.3)	348 (14)
cis-Ni(2,3,2-tet)-$(H_2O)_2^{2+\,c}$	900 (9.5)		550 (5.5)	345 (11)
trans-Ni(3,2,3-tet)-$(H_2O)_2^{2+\,b,d}$	800 (4), 745 (4)		550 (5)	350 (9)

[a] λ_{max} given in nm, ϵ in M^{-1} cm^{-1}. [b] Reference 9. [c] Reference 7. [d] Reference 8.

***cis*-Ni(cyclam)(en)$(ClO_4)_2$.** Ethylenediamine was added to an aqueous solution of Ni(cyclam)$(ClO_4)_2$ (e.g., 4 mM Ni(cyclam)$^{2+}$, 20 mM en). Sodium perchlorate was added to the resulting violet solution, whereupon violet *cis*-Ni(cyclam)(en)$(ClO_4)_2$ precipitated. Anal. Calcd for $NiC_{12}H_{32}N_6Cl_2O_8$: C, 27.82; H, 6.23; N, 16.23. Found: C, 27.79; H, 6.07; N, 16.16. *Warning: Perchlorate salts of similar complexes are explosive; they are heat and pressure sensitive. Only small amounts of this complex should be prepared and should be handled with care.*

***cis*-Ni(cyclam)Br_2.** A suspension of Ni(cyclam)(en)$(ClO_4)_2$ in boiling methanol was acidified with concentrated HBr, yielding blue *cis*-Ni(cyclam)Br_2.

Kinetic Measurements. The cis to trans isomerization was followed at 450 nm (appearance of planar Ni(cyclam)$^{2+}$). The majority of the rate constants were determined by the initial rate method; an effective molar absorptivity of 50 M^{-1} cm^{-1} was used for Ni(cyclam)$^{2+}$ at $I = 0.1$, $NaClO_4$. The faster reactions were followed to completion, and rate constants were obtained from plots of $\ln (A_\infty - A)$ vs. t. All rates were measured at 25 °C with $I = 0.1$, $NaClO_4$. Reaction pH was adjusted by the addition of perchloric acid (pH 1–3), 0.10 M boric acid (pH 5), 0.01 M borate buffer (pH 7–9), or sodium hydroxide (pH 10). There was no detectable rate enhancement caused by boric acid–borate buffer, but an experiment using acetic acid to obtain a pH near 3 resulted in relatively rapid (overnight) isomerization. Rates were measured beginning either with acidified solutions of Ni(cyclam)(en)$^{2+}$ or with solutions of Ni(cyclam)Br_2. Rates in basic solution were measured with use of only the latter complex. Hydronium and hydroxide ion concentrations were obtained from $-\log [H^+] = pH - 0.11$ and $\log K_w = -13.78$, for 25 °C and $I = 0.10$.

Results and Discussion

Addition of ethylenediamine to a yellow aqueous solution of Ni(cyclam)$^{2+}$ yields in a few minutes a violet solution from which Ni(cyclam)(en)$^{2+}$ can be isolated. Since en can only coordinate to cis positions, the cyclam ligand must adopt the folded configuration (*cis*-β).[6] Acidification of the violet solution to, e.g., pH 3 yields a blue-violet solution of *cis*-Ni(cyclam)$(H_2O)_2^{2+}$ (eq 1). The spectrum of this complex is

$$\textit{cis}\text{-Ni(cyclam)(en)}^{2+} + 2H_3O^+ \rightarrow \textit{cis}\text{-Ni(cyclam)}(H_2O)_2^{2+} + H_2en^{2+} \quad (1)$$

typical of *cis*-$Ni^{II}N_4O_2$ (see Table I). The ν_1 band in the near-infrared spectrum is diagnostic of cis or trans coordination.[7,8] Solutions of *cis*-Ni(cyclam)Br_2 in water have identical spectra with those of acidified *cis*-Ni(cyclam)(en)$^{2+}$.

Violet solutions of *cis*-Ni(cyclam)$(H_2O)_2^{2+}$ isomerize slowly to yellow Ni(cyclam)$^{2+}$. In contrast, addition of ammonia also produces a violet octahedral complex, but the yellow color of Ni(cyclam)$^{2+}$ is regenerated immediately upon acidification; the ligand has remained in the planar configuration.

Depending on the concentration of en added, a small amount of planar Ni(cyclam)$^{2+}$ remains. Spectrophotometric measurements at 450 nm were used to determine the equilibrium constant for reaction 2. Because of the very low solubility

$$\text{Ni(cyclam)}^{2+} + \text{en} \rightleftharpoons \text{Ni(cyclam)(en)}^{2+} \quad (2)$$

of the mixed-ligand complex in the presence of appreciable

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