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LETTER

Isomerization and Conformational Equilibria Coupled to Electron Transfer in a Macrocyclic Cobalt(III/II)-cyclam System in Sodium Hydroxide Solution

COSTAS TSINTAVIS, HU-LIN LI*,
JAMES Q. CHAMBERS**

Department of Chemistry, University of Tennessee, Knoxville, TN 37996 (U.S.A.)

and DAVID T. HOBBS

Westinghouse Savannah River Co., Aiken, SC 29808 (U.S.A.)

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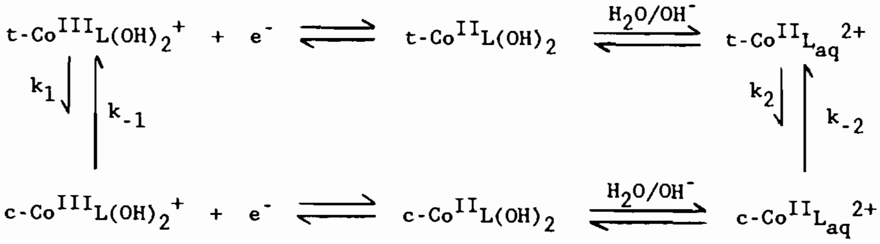
Intrigued by the moderately complex cyclic voltammetric behavior of the $Co^{III/II}$(1,4,8,11-tetraazacyclotetradecane) couple, or $[Co([14]aneN_4(OH)_2)]^+$ commonly known as Co(cyclam) [1], in alkaline solution observed in a previous study in our laboratory [2], we decided to study more closely this classical redox system in sodium hydroxide solution. In this medium, cyclic voltammograms of the Co^{III}(cyclam) complex exhibit a quasi-reversible wave at mercury and gold working electrodes. We find that an electrochemical square scheme (see Scheme 1) is operative under these conditions, where the coupled chemical reactions involve *cis*/*trans* isomerization of the coordinated macrocyclic ring. Since the $Co^{III/II}([14]aneN_4)$ couple is a prototypical macrocyclic transition metal redox system, the results have important implications for the understanding of the mechanism of both heterogeneous and homogeneous electron transfer for macrocyclic Co(III/II) complexes.

Experimental

Literature procedures were employed for the synthesis of the *trans*- [3] and *cis*-$Co([14]aneN_4Cl_2)Cl$ [4] compounds. Elemental analysis, UV–Vis absorption spectra and IR spectra confirmed the structures. It should be noted that the coordinated ligand has an *R,S,S,R* configuration for the *trans*-complex and an *R,R,R,R* (or *S,S,S,S*) configuration for the *cis*-complex [5, 6]. Reagent grade NaOH and doubly distilled water that had been passed through a Millipore Model Milli-Q column were used to prepare all solutions. All solutions were thoroughly flushed with 'high purity' argon that had been passed through a 3-ft column containing Mn(II) dispersed on vermiculite.

Upon dissolution of *trans*- and *cis*-$Co([14]aneN_4Cl_2)Cl$ in 3 M NaOH, rapid hydrolysis [7, 8] took place to yield the respective *trans*- and *cis*-$Co^{III}([14]aneN_4)(OH)_2^+$ species, as evidenced by their subtlely distinctive and different absorption spectra: *trans*-, $\lambda_{max} = 386$ nm (52.8 M^{-1} cm^{-1}), 474sh nm (8.1 M^{-1} cm^{-1}), 538 nm (45.9 M^{-1} cm^{-1}) [2]; *cis*-, $\lambda_{max} = 377$ nm (112.1 M^{-1} cm^{-1}), 534 nm (111.2 M^{-1} cm^{-1}) [4]. Alternatively, for the *trans*-complex, identical spectra and electrochemical results were obtained when the dihydroxide form was prepared by passing the dichloro complex through an anion exchange column in the hydroxide form. The spectrum of the *cis*-$Co^{III}([14]aneN_4)(OH)_2]^+$ complex slowly changed to that of the *trans*-complex (half-life = 66 min).

The inner disk of a gold disk–gold ring electrode (Pine Instruments Model AFDT27, diameter = 0.25 cm) was used as the working electrode for most of the measurements. This electrode surface was polished and electrochemically pretreated by cycling through the surface oxidation/reduction process at 0.5 V versus SCE. The reference electrode was either a double-bridge SCE (Corning) or a Ag/AgCl



Scheme 1. (L = cyclam; c = *cis*, t = *trans*).

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*Permanent address: Department of Chemistry, Lanzhou University (China).

**Author to whom correspondence should be addressed.

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electrode of conventional design. The latter quasi-reference electrode was *c.* 80 mV versus SCE in 3 M NaOH. Error limits given in the text are standard deviations of at least three measurements on separate solutions.

Results and Discussion

A cyclic voltammogram of the *trans*-Co^{III}(cyclam) complex at a gold disk electrode is shown in Fig. 1. On the initial sweep a quasi-reversible couple is seen at $E_{1/2} = -0.884 \pm 0.005$ V versus SCE. On the initial return sweep, a two-step process is seen in the cyclic voltammogram, a pattern which persists on subsequent cycles. The new couple in these voltammograms has the characteristics of a nearly reversible one-electron redox couple ($E_{1/2} = -0.667 \pm 0.008$ V versus SCE).

Figure 2 shows the cyclic voltammogram of the *cis*-complex obtained less than a minute after dissolution in the NaOH solution. At this sweep rate, two nearly reversible waves are seen which have roughly equal peak heights. The half-wave potentials are identical to the couples in the voltammograms of the *trans*-complex. Under these conditions, the solution absorption spectra indicated that the major portion (close to 100%) of the complex was in the *cis*-form. Addition of the *trans*-complex to the solution increased the height of the second couple, as shown in Fig. 2(B).

These results are consistent with the square scheme shown in Scheme 1. Schemes of this type involving geometrical isomerizations have ample precedent in organometallic electrochemistry [9–11]. Electrochemically induced *cis*/*trans* isomerization has been observed for related cobalt redox couples [12].

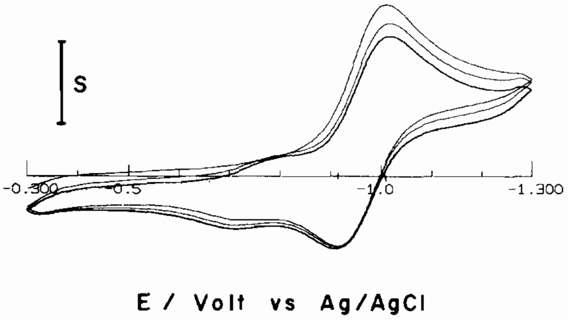

Fig. 1. Cyclic voltammogram of 3.04 mM *trans*-Co^{III}-(cyclam)$(OH)_2^+$ in 3.0 M NaOH at a gold disk electrode (0.196 cm^2); sweep rate, 0.1 V s^{-1}; current scale, 0.222 mA cm^{-2}. The first, second and fifth cycles are shown.

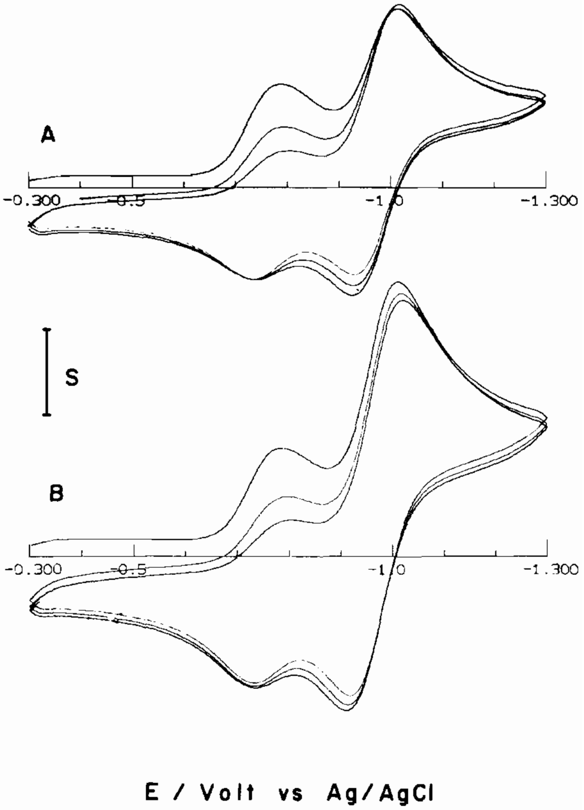

Fig. 2. Cyclic voltammograms of (A) 1.23 mM *cis*-Co^{III}-(cyclam)$(OH)_2^+$ in 3.0 M NaOH and (B) solution A plus 1.2 mM *trans*-Co^{III}(cyclam)$(OH)_2^+$ at a gold disk electrode (0.196 cm^2); sweep rate, 0.05 V s^{-1}; current scale, 0.111 mA cm^{-2}. The first, second and fifth cycles are shown.

The observation of a well-formed wave for the reduction of the *trans*-complex in the first sweep of the voltammogram of the solution of the *cis*-complex implies the existence of an electron-transfer catalyzed isomerization of the labile Co^{II}([14]ane-N_4) complex

$$cis\text{-}Co^{III} + e \rightleftharpoons cis\text{-}Co^{II} \xrightarrow[k_{-2}]{\text{fast}} trans\text{-}Co^{II} \rightleftharpoons trans\text{-}Co^{III} - e \qquad (1)$$

In support of this process, chronoamperometric measurements of freshly prepared solutions of *cis*-$Co^{III}([14]aneN_4)(OH)_2^+$ at potentials between the *cis* and *trans* couples gave apparent *n*-values less than unity, which decreased with time in agreement with the theory of Feldberg and Jeftic [13]. A detailed kinetic study is in progress.

Identical steady-state cyclic voltammograms were obtained from solutions of either the *trans*- or the *cis*-isomer. From the peak heights of the two waves in these voltammograms, one can estimate that 10% of the Co^{II} is in the *cis*-form at equilibrium. This estimate is consistent with the sweep-rate dependence of the wave for the oxidation of the *cis*-$Co^{II}(cyclam)_{aq}$ species which is almost absent at 1 V s^{-1} in the cyclic voltammograms obtained using freshly prepared solutions of the *trans*-complex.

TABLE 1. Voltammetric parameters of $Co^{III}(cyclam)(OH)_2^+$ in 3 M NaOH at a gold disk electrode, 22 ± 2 °C[a]

Ligands	E_p^{cath} (V vs. SCE)	E_p^{anod} (V vs. SCE)	E_p (mV)	$i_p/ACv^{1/2}$ (Amp cm^{-2} M^{-1} $(V/s)^{-1/2}$)
trans-$(OH)_2$[(*R,S,S,R*)cyclam]	−0.924	−0.848	76 (4)[b]	0.46
trans-$(OH)_2$[(*R,R,R,R*)cyclam][c] or (*S,S,S,S*)	−0.912	−0.846	67 (6)	0.46
cis-$(OH)_2$[(*R,R,R,R*)cyclam] or (*S,S,S,S*)	−0.696	−0.642	54 (3)	d

[a]Sweep rate = 0.1 V s^{-1}. [b]Number of determinations are in parentheses. [c]Formed by electrocatalyzed isomerization of *cis*-$Co^{III}(cyclam)(OH)_2^+$. [d]Decreases with time.

Voltammetric data are collected in Table 1. The observed behavior in NaOH solution reveals greater mechanistic detail of the $Co^{III/II}([14]aneN_4)$ redox process than seen previously in acetonitrile [14].

It is noted that the $E^{0\prime}$ value for the *trans*-complex is consistent with a pH dependence for a one-electron, two-proton process [2]. This implies that the acid/base equilibria embodied in Scheme 1 are fast on the voltammetric timescale. It is also realized that the stable conformation of the *cis*-Co^{III} complex has the coordinated ligand in an *R,R,R,R* (or *S,S,S,S*) conformation where the four coordinated nitrogen atoms have the same configuration [3, 15]. The corresponding conformation of the *trans*-complex is not the thermodynamically stable form. Distinctive differences in the voltammetric wave shape are seen in the region of the diffusion tail of the cyclic voltammogram of the *trans*-complex, depending on whether the complex is generated by the above process (eqn. (1)) in the diffusion layer or by synthesis and dissolution in NaOH solution. In the former case, a peak separation of 67 mV indicative of a nearly reversible couple is seen for the *trans*-$Co^{III/II}([14]aneN_4)$ couple. These differences, which are suspected to involve conformational changes of the cyclam ligand, are under active investigation.

Thus we have demonstrated the existence of electron-transfer-induced *cis*/*trans* isomerization for the $Co^{III/II}([14]aneN_4)$ couple in basic solution. The overall process is complex, involving both proton transfer reactions and conformational rearrangements as well as the *cis*/*trans* isomerization equilibria between labile Co(II) species. As noted by others [9, 16], this study emphasizes the role of coupled equilibria on wave shape and apparent heterogeneous rate constants obtained from cyclic voltammograms of macrocyclic complexes.

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