rections should have only a minor influence on the force field.

To obtain an estimate for the uncertainties of the F_{1u} force constants of ClF_6^+, the relevant parts of the F_{33} and F_{44} ellipses of ClF_6^+ and the corresponding $^{35}Cl-^{37}Cl$ isotopic shifts of ν_3 and ν_4 were computed as a function of F_{34}. As can be seen from Figure 3, the resulting uncertainties in the force constants are very small and the force field of ClF_6^+ is rather well determined.

A comparison of the GVFF of ClF_6^+ (see Figure 3 and Table II) with the two previously published modified valence force fields[5,16] shows that F_{44} = minimum is a much better constraint than the transfer of the $f_{rr'}$ value from SF_6 to ClF_6^+. Also, the resulting Cl–F stretching force constant value of 4.97 mdyn/Å for ClF_6^+ is, as expected for a perfluoro cation in its highest oxidation state,[40] the highest value found to date for a Cl–F bond and agrees with the good thermal stability found for these ClF_6^+ salts. A comparison of the ClF_6^+ force field with those of BrF_6^+[16] and IF_6^+[33] (see Table II) shows the expected trends.[40] The stretching force constant drops slightly from ClF_6^+ to BrF_6^+ and then markedly increases for IF_6^+. The deformation constants decrease from ClF_6^+ toward IF_6^+, as expected from the increase in bond lengths. The stretch–stretch interaction constants f_{rr} and $f_{rr'}$ show smooth trends from ClF_6^+ toward IF_6^+, similar to those observed for the isoelectronic SF_6, SeF_6, TeF_6 series, although the relative contributions from f_{rr} and $f_{rr'}$ are different within each series. A comparison of the GVFF of ClF_6^+ with that of SF_6 (see Table II)[36] also shows excellent agreement, except for the above noted difference in the relative contribution from f_{rr} and $f_{rr'}$.

Conclusion. The KrF^+ cation is capable of oxidizing ClF_5 to ClF_6^+ and provides a method for the synthesis of pure ClF_6^+ salts. Thus, KrF^+ is the first oxidative fluorinator capable of producing all three of the presently known coordinatively saturated complex fluoro cations, NF_4^+, BrF_6^+, and ClF_6^+. The synthesis of pure ClF_6AsF_6 permitted a better characterization of the ClF_6^+ cation and the determination of a general valence force field for ClF_6^+. The Cl–F bond in ClF_6^+ (4.97 mdyn/Å) is the strongest Cl–F bond presently known, suggesting highly covalent bonds with sp^3d^2 hybridization of the valence electrons of chlorine. By analogy with the known NF_4^+ chemistry, the existence of numerous stable ClF_6^+ salts is predicted.

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Registry No. ClF_6AsF_6, 86527-33-5; ClF_6SbF_6, 86527-34-6; ClF_6^+, 38217-33-3; KrF_2, 13773-81-4; AsF_5, 7784-36-3; ClF_5, 13637-63-3; SbF_5, 7783-70-2.

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trans-[(en)$_2$Co(Cl)(S$_2$O$_3$)], Na[***trans***-[(en)$_2$Co(C$_2$O$_4$)(S$_2$O$_3$)]], ***trans***-[(en)$_2$Co(NCO)(S$_2$O$_3$)], and the Nature of [(en)$_2$Co(OH$_2$)(S$_2$O$_3$)]$^+$ in Aqueous Solution

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The preparation and characterization of the title complexes are described. The chloro complex rapidly aquates at pH 5–6, and the oxalato and cyanato complexes undergo acidolyses in dilute $HClO_4$, to form a common intermediate, *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$, which subsequently equilibrates to a mixture of cis and trans isomers. Kinetics of the cyanato complex acidolysis are presented and compared with those of HNCO and of $[(NH_3)_5Co(NCO)]^{2+}$.

Introduction

In a previous report,[1] the synthesis of *trans*-(thiosulfato)(aniono)bis(ethylenediamine)cobalt(III) complexes by anation of a brown aqueous cation has been described. This cation, isolated by ion-exchange chromatography, was formulated as *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ largely on the basis of its UV spectroscopic parameters and its labile substitution chemistry; although its stoichiometry appeared certain, its geometric configuration was only inferred. No corresponding brown solid was obtained; indeed, attempts to prepare the perchlorate salt produced a red, bidentate (O,S) thiosulfato complex, $[(en)_2Co(S_2O_3)]^+$,[2] and attempts to isolate a chloride salt[1] resulted in the production of a green solid of variable composition containing excess Cl. Although the aqua in *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ is readily substituted,[1] the corresponding thiocyanato- and nitrito-*N* complexes are relatively inert to aquation even in dilute acid. In an attempt to produce complexes with more labile trans substituents, we have prepared three new complexes in the series *trans*-$[(en)_2Co(X)(S_2O_3)]^{0,-}$, X = Cl^-, NCO^-, $C_2O_4^{2-}$. We report here their isolation, characterization, and chemistry, which establishes the nature of aqueous $[(en)_2Co(OH_2)(S_2O_3)]^+$.

Experimental Section

General Data. For chromatographic elutions, LiCl and hydrated $NaClO_4$ and $LiClO_4$, as obtained from G. F. Smith Chemical Co., were prepared as concentrated stock solutions and filtered before use. For the acidolysis kinetic experiments, doubly vacuum-distilled $HClO_4$ (70–72%, G. F. Smith) and $LiClO_4$ recrystallized from H_2O were used to prepare stock solutions. A chloroacetic acid–chloroacetate buffer was prepared from Li_2CO_3 and aqueous chloroacetic acid, and the pH values were determined with a pH meter calibrated at μ = 1.00 M ($LiClO_4$). Deuterium oxide (99.85 atom % D) was obtained from Aldrich Chemical Co. Other common chemicals were of reagent

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grade and were used without further purification. Chromatographic separations were accomplished[1] with use of Sephadex resins (SP-C25, Na^+ form; QAE-Q25, Cl^- and ClO_4^- forms; G-10 to desalt). Elemental analyses of solid samples were performed by Galbraith Laboratories Inc., Knoxville, TN. Solution absorptivities were based on total Co as determined by the Kitson method[3] and calibrated against the absorbance of stock $Co(ClO_4)_2$ solutions.[4] Visible–UV spectra were recorded on either a Beckman DB-GT or a Hitachi 100A spectrophotometer in MilliQ (Millipore) water; IR spectra were recorded on a Perkin-Elmer 337 in KBr pellets. pH values were determined on a Corning Model 12 pH meter using a Sensorex semimicro combination-glass reference electrode, calibrated against standard buffers except as noted. Amine deuteration of the oxalato complex was performed as previously described.[5] ^{13}C and ^1H NMR spectra were obtained on a JEOL FX90Q instrument at 22.50 and 89.55 MHz, respectively. In general, resonances are reported in ppm downfield from the methyl groups in TSP (2,2-dimethyl-2-silapentanoate, sodium salt), which was the internal reference. The ^{13}C spectra were run in the proton-decoupled mode; up to 34 000 pulses were performed for the ^{13}C spectra, and up to 1000 for the ^1H. The thiosulfato cyanato and thiosulfato aqua complexes were found to undergo substitution by the TSP carboxylate within the times (>5 h) required to obtain ^{13}C spectra. In the cyanato case, the spectrum was recorded with the reference set at 69.34 ppm for dioxane as a secondary internal reference. Peak positions for the oxalato complex measured vs. TSP or dioxane, agreed within 0.002 ppm.

Solutions Containing the (Thiosulfato)aquabis(ethylenediamine)cobalt(III) Cation, $[(en)_2Co(OH_2)(S_2O_3)]^+$. The brown cation prepared as previously described[1] contains a trace of a yellow cationic impurity, which absorbs strongly ca. 370 nm. Elution from SP-C25 cation resins does not effect complete separation of this impurity, and the absorptivity of the shoulder previously reported in this spectral range, ca. 390 nm, is high. To prepare highest purity solutions of the brown cation, a stoichiometric mixture of aqueous iodine and *trans*-$[(en)_2Co(S_2O_3)_2]^-$ is passed through a QAE-Q25 column (15 cm × 2- cm i.d.) (ClO_4^- form) and eluted with 0.03 M $NaClO_4$. The brown cation separates cleanly from the yellow cationic impurity and is then separated from other more highly charged cations by elution from a SP-C25 column (Na^+ form).[1] Reproducible visible–UV spectral parameters, obtained at 25.0 °C (0.25 M $NaClO_4$), are λ_{max}/nm ($\epsilon_{max}/M^{-1}\ cm^{-1}$) 530 (65.2), 390 sh (188), 289 (9500), and 215 (12 000); these absorptivities are lower in the UV than those previously reported.[1] In most of the following synthetic work, $[(en)_2Co(OH_2)(S_2O_3)]^+$ was prepared and isolated on only SP-C25 columns. For the kinetic experiments, the preliminary separation, using QAE-Q25 (ClO_4^- form), was also employed.

***trans*-(Thiosulfato)(chloro)bis(ethylenediamine)cobalt(III), *trans*-$[(en)_2Co(Cl)(S_2O_3)]$.** When $[(en)_2Co(OH_2)(S_2O_3)]^+$ is displaced from an SP-C25 column with 0.25 M aqueous LiCl, the initially brown band divides into an upper red band and a lower contiguous green band. Either band is collected and flash evaporated at $T < 20$ °C to near dryness and further dehydrated by successive additions of absolute ethanol, flash evaporating off the azeotrope. On the first appearance of a dark green solid, the solution is refrigerated at −10 °C and the desired product, formulated as *trans*-$[(en)_2Co(Cl)(S_2O_3)]\cdot H_2O$, precipitates and is collected by filtration, rinsed with EtOH, and air-dried. Anal. Calcd for $[(en)_2Co(Cl)(S_2O_3)]\cdot H_2O$: C, 13.93; H, 5.27; N, 16.26; Co, 17.12; S, 18.61; Cl, 10.30. Found: C, 13.91; H, 5.41; N, 16.10; Co, 16.90; S, 18.88; Cl, 10.47. If, on the first appearance of solid, the dehydration is continued, a green solid settles out, which is a microscopic mixture of LiCl and anhydrous *trans*-$[(en)_2Co(Cl)(S_2O_3)]$. This mixture is triturated with damp methanol and the suspended salt repeatedly decanted. When the supernatant remains clear, the residual green solid is rinsed with dry methanol, filtered, and air-dried. Anal. Calcd for $[(en)_2Co(Cl)(S_2O_3)]$: C, 14.70; H, 4.90; N, 17.15; Co, 18.07; S, 19.60; Cl, 10.87. Found: C, 14.78; H, 4.87; N, 16.94; Co, 17.92; S, 19.98; Cl, 10.92. In either case, monohydrate or anhydrous, no difference is detected between the properties of the green solid derived either from the red or the green band on the cation column or from their mixture. In aqueous solution, the complex aquates rapidly (see below) and solution spectra of the pure complexes are unobtainable. IR (KBr) (cm^{-1}): thiosulfato 1190, 1135, 1000, 635.

***trans*-(Thiosulfato)(cyanato)bis(ethylenediamine)cobalt(III), *trans*-$[(en)_2Co(NCO)(S_2O_3)]$.** Two procedures, analogous to those previously reported,[1] have been employed to produce the trans isomer. In the first, a 50% molar excess of solid NaNCO is stirred into a 0.03 M solution of $[(en)_2Co(OH_2)(S_2O_3)]^+$ at room temperature and the resultant mixture is allowed to stand ca. 90 min. The desired product is purified by passage through QAE-Q25 and SP-C25 columns in the Cl^- and Li^+ forms, respectively, eluting with H_2O and collecting the single, red, charge-neutral band. The eluate is concentrated by flash evaporation ($T < 20$ °C) to a convenient volume (ca. 10 mL) and passed through a Sephadex G-10 column to remove residual salt. The red effluent is flash evaporated to the first appearance of a permanent solid and refrigerated overnight at 0 °C. The dark red crystals are filtered and air-dried; yields are typically 70%, based on the starting $[(en)_2Co(OH_2)(S_2O_3)]^+$. The aqueous solubility is ca. 25 mg/mL at 25 °C. Anal. Calcd for $[(en)_2Co(NCO)(S_2O_3)]\cdot 2H_2O$: C, 16.26; H, 5.46; N, 18.96; Co, 15.96; S, 17.36. Found: C, 16.30; H, 5.08; N, 18.94; Co, 15.78; S, 17.56. IR (KBr) (cm^{-1}): cyanato 2260, 2230, 1330, 643; thiosulfato 1185, 1148, 1003, 635. UV–vis λ_{max}/nm ($\epsilon/M^{-1}\ cm^{-1}$): 532 (94.8), 380 sh (289), 283 (13 200), 217 (13 400). ^{13}C NMR (ppm): ethylenediamine 47.62. ^1H NMR (ppm): CH_2 2.92.

In an alternative procedure, 0.43 g of *trans*-$[(en)_2Co(Cl)_2]Cl$[6] is dissolved in 10 mL of H_2O and 0.098 g of NaNCO stirred in. The mixture is heated to 35 °C and 0.38 g of $Na_2S_2O_3\cdot 5H_2O$ added with stirring. After 2 h the solution is filtered and the filtrate is diluted to 100 mL and chromatographed successively through QAE-Q25 and SP-C25 columns as above. *Two* neutral, incompletely resolved bands are obtained; the leading edge of the front, predominant, red band has visible–UV parameters consistent with those of the *trans*-$[(en)_2Co(NCO)(S_2O_3)]$ isolated above. A sample from the trailing edge of the second, minor, faint pink band exhibited the following visible–UV spectral parameters: λ_{max}/nm ($\epsilon/M^{-1}\ cm^{-1}$) 514 (215), 390 sh (295), 292 (14 600), 199 (15 500). Insufficient quantities were prepared to isolate a solid or obtain an NMR spectrum, but by analogy with the preparations, the visible–UV spectra, and the column behavior of other complexes of the form $[(en)_2Co(X)(S_2O_3)]^{0,-}$ ($X = NO_2^-$, NCS^-, N_3^-, $S_2O_3^{2-}$),[7] we believe this second neutral species to be the cis isomer, *cis*-$[(en)_2Co(NCO)(S_2O_3)]$. The total yield of neutral Co(III) species was ca. 40% on the basis of the starting *trans*-$[(en)_2CoCl_2]Cl$.

Sodium *trans*-(Thiosulfato)(oxalato)bis(ethylenediamine)cobaltate(III), Na[*trans*-$[(en)_2Co(C_2O_4)(S_2O_3)]]\cdot 4H_2O$. A solution containing 1 mmol of $[(en)_2Co(OH_2)(S_2O_3)]^+$ is prepared and assayed at 530 nm, and 0.132 g of solid $Na_2C_2O_4$ is stirred in. The reaction appears complete in 30 min, but better yields are obtained if the solution is gently heated at 35–40 °C for 1 h and allowed to stand overnight in the dark. Anionic products are separated from unreacted $[(en)_2Co(OH_2)(S_2O_3)]^+$ by passage through an SP-C25 (Na^+ form) column, eluting with H_2O. The purple band is collected, flash evaporated to ca. 10 mL, and passed through a G-10 column to desalt. The purple effluent is further flash evaporated to the first appearance of a permanent solid and diluted with a 4-fold excess of absolute ethanol. When the mixture is allowed to stand in a freezer at −10 °C, a pale purple solid settles out and is filtered, rinsed with ethanol, and air-dried. Yields are typically 45% on the basis of the starting $[(en)_2Co(OH_2)(S_2O_3)]^+$. The solubility at 25 °C in H_2O is ca. 18 mg/mL. Anal. Calcd for Na [*trans*-$[(en)_2Co(C_2O_4)(S_2O_3)]]\cdot 4H_2O$: C, 15.26; H, 5.16; N, 11.82; Co, 12.42; S, 13.75. Found: C, 15.19; H, 5.06; N, 11.81; Co, 12.44; S, 13.50. IR (KBr) (cm^{-1}): oxalato 1620, 1590, 1305, 770; thiosulfato 1210, 1155, 1005, 635. UV–vis λ_{max}/nm ($\epsilon/M^{-1}\ cm^{-1}$): 538 (68), 301 (14 000), 218 (13 500). ^{13}C NMR (ppm): ethylenediamine 47.13. ^1H NMR (ppm): CH_2 2.92, 2.89, 2.86, 2.83.

Stoichiometry of the Acidolysis of *trans*-$[(en)_2Co(NCO)(S_2O_3)]$. Hydrogen ion consumption was determined, in 3-fold molar excess $HClO_4$, after 90% completion, by titration of excess acid to pH 5.0. The Co(III) species were subsequently isolated on an SP column and identified by their visible–UV spectra and elution characteristics. Carbonic acid was determined gravimetrically as $BaCO_3$ after 100% consumption of *trans*-$[(en)_2Co(NCO)(S_2O_3)]$ in 20-fold excess $HClO_4$

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Table I. Kinetic Parameters Describing the Temperature, Ionic Strength, and $[H^+]$ Dependence of the Acidolysis of *trans*-$[(en)_2Co(NCO)(S_2O_3)]^a$

T/°C	μ/M	$10^2[H^+]$/M	$10^3 a/s^{-1}$	$10^4 b/s^{-1}$
25.0	0.0996	4.01	1.55 ± 0.02^b	2.99 ± 0.18^b
25.0	0.200	4.01	1.69 ± 0.02	3.45 ± 0.08
25.0	0.500	4.01	1.92 ± 0.02	3.36 ± 0.06
25.0	1.00	4.01	2.43 ± 0.04^b	3.74 ± 0.10^b
25.0	1.00	8.00	4.72 ± 0.02	4.15 ± 0.04
25.0	1.00	12.0	7.18 ± 0.03	4.14 ± 0.3
25.0	1.00	16.0	9.08 ± 0.06	4.27 ± 0.06
25.0	1.00	20.0	11.6 ± 0.9^b	4.45 ± 0.07^b
25.0	1.00	24.0	13.2 ± 0.9^b	4.47 ± 0.09^b
25.0	1.00	28.0	15.7 ± 0.1	4.42 ± 0.04
25.0	1.00	32.1	18.1 ± 0.1	4.46 ± 0.05
25.0	1.00	36.0	20.3 ± 0.2	4.75 ± 0.05
25.0	1.00	40.0	23.7 ± 0.3^b	4.58 ± 0.08^b
15.0	1.00	4.01	0.986 ± 0.005	0.860 ± 0.006
15.0	1.00	16.0	3.90 ± 0.01	0.99 ± 0.01
15.0	1.00	32.1	8.01 ± 0.03	1.07 ± 0.01
15.0	1.00	40.0	9.90 ± 0.04	1.06 ± 0.01
35.0	1.00	4.01	5.14 ± 0.03	12.3 ± 0.1
35.0	1.00	8.00	10.05 ± 0.06	12.9 ± 0.1
35.0	1.00	12.0	14.9 ± 0.1	14.1 ± 0.1
35.0	1.00	16.0	19.3 ± 0.1	13.5 ± 0.1

[a] $[trans\text{-}[(en)_2Co(NCO)(S_2O)_3]]_0 = 2.01 \times 10^{-3}$ M. [b] Average of two determinations.

and transfer of the CO_2 to carbonate-free $Ba(OH)_2$ solutions with N_2 carrier gas. Ammonium ion was detected but not quantitatively recovered. Stoichiometric ratios, based on $[(en)_2Co(NCO)(S_2O_3)]$: H^+, 1.96 ± 0.02; $[(en)_2Co(OH_2)(S_2O_3)^+]$, 1.01 ± 0.03; H_2CO_3, 1.05 ± 0.03.

Kinetic Measurements and Calculations. Spectrophotometric kinetic data were obtained on a Beckman DBGT, equipped with a thermostated cell-housing accommodating 1.00- and 4.00-cm cells. Fixed-wavelength experiments were performed for the acidolysis of *trans*-$[(en)_2Co(NCO)(S_2O_3)]$ at 532 nm, the absorbance maximum of the starting material. Initial concentrations of *trans*-$[(en)_2Co(NCO)(S_2O_3)]$ were in the range of $(2.0–3.5) \times 10^{-3}$ M, and A_{532}–t data were taken over at least 4 half-lives of the long-half-life parameter (below). In 10-fold or greater stoichiometric excess $[H^+]$, the A_{532}–t data were biphasic, exhibiting a minimum after 5–10 min, and were successfully fit to the biexponential expression eq 1 with the nonlinear

$$A_{532} = A_\infty + A_1 e^{-at} + A_2 e^{-bt} \qquad (1)$$

regression Biomed BMD-P3R.[8] Between 50 and 100 A_{532}–t data pairs were chosen evenly to weight the two exponential terms. The optimized a and b parameters and their asymptotic standard deviations are reported in Table I. a and b were fit to linear relationships in $[H^+]$ (eq 2). Apparent activation parameters ΔH^* and ΔS^* were obtained

$$a = k_0 + k_1[H^+] \qquad b = k_2 + k_3[H^+] \qquad (2)$$

from a linear least-squares fit of the ln (k_i/T) data vs. T^{-1}, according to the Eyring formalism.[9] Ionic strength was maintained with $LiClO_4$, and the D kinetic isotope effect was measured at 25 °C in an average 95.3 D atom % D_2O.

A_{532} and pH of an acidolysis of *trans*-$[(en)_2Co(NCO)(S_2O_3)]$ were monitored vs. time under second-order conditions: T/°C = 25.0; $10^2[H^+]$/M = 3.00; $10^3[trans\text{-}[(en)_2Co(NCO)(S_2O_3)]]_0$/M = 9.34; μ/M = 0.100 ($LiClO_4$). The pH meter was calibrated with dilute $HClO_4$, μ/M = 0.100 ($LiClO_4$), and $[H^+]$ was calculated from $[H^+] = 10^{-pH}$. A fourth-order Runge–Kutta algorithm[10] was used to simulate the A_{532}–t and $[H^+]$–t data b integrating rate equations with ionic-strength-corrected rate parameters: $10^2k_0/s^{-1} = 0.00$; $10^2k_1/M^{-1}\,s^{-1} = 3.68$; $10^4k_2/s^{-1} = 3.16$; $10^4k_3/M^{-1}\,s^{-1} = 2.17$. A two-step process, B → C → D, was considered, and a simulation executed for which (i) 2 equiv of H^+ was consumed in the first step, (ii) parameters a and b (eq 1) were assigned to the first and second steps, respectively, and (iii) initial and final absorptivities at 532 nm were the observed values and that of the intermediate C, was assigned $\epsilon_{532} = 46\ M^{-1}\,cm^{-1}$. Agreement between observed and calculated A_{532}–t and $[H^+]$–t profiles was within experimental uncertainty. After 4 half-lives of the short-half-life process, the calculated H_2CO_3 production was 97% of that isolated as $BaCO_3$ under similar conditions. Simulations for which the assignments of a and b were interchanged, or for which only 1 equiv of H^+ was consumed in the first step, gave unsatisfactory agreement with the observed profiles.

The intermediate formed in the acidolyses of *trans*-$[(en)_2Co(NCO)(S_2O_3)]$ and of *trans*-$[(en)_2Co(C_2O_4)(S_2O_3)]^-$ and in the aquation of *trans*-$[(en)_2Co(Cl)(S_2O_3)]$ was isolated and characterized as follows. Each reacting solution at ca. 25 °C was allowed to react 5–13 min, quenched rapidly to 4 °C, and chromatographed on a short (7 cm × 2.2-cm i.d.) SP column (Na^+ form) maintained at 4 °C. Unreacted anionic and neutral species were rinsed from the column with ice-cold H_2O, and the green brown intermediate was eluted in 10–15 min with cold 0.25 M $NaClO_4$. The cold effluent was warmed rapidly (ca. 2 min) to 25 °C, and spectrophotometric scans (700–350 nm) were repeated at specific times in 4.00- and 1.00-cm cells. The visible–UV spectrum of the product solution was identical in each case with that of $[(en)_2Co(OH_2)(S_2O_3)]^+$ (above). Isosbestic-point spectral parameters and apparent first-order rate coefficients, b', obtained from a nonlinear least-squares fit[8] of the A_{530}–t data to the first-order kinetic expression eq 3 are given in Table II.

$$A_{530} = A_\infty' + A_2' e^{-b't} \qquad (3)$$

The red upper band and the green lower band, formed on elution of $[(en)_2Co(OH_2)(S_2O_3)]^+$ with 0.25 M NaCl (see above), were cleanly separated at 4 °C on an SP column, 20 cm × 2.2-cm i.d. Each band was collected, adsorbed on a short SP column at 4 °C (as above), rinsed with cold H_2O to elute Cl^-, and displaced with 0.25 M $NaClO_4$. Each solution was rapidly warmed to 15, 25, or 35 °C; kinetic data were obtained as above, and the product, again, was $[(en)_2Co(OH_2)(S_2O_3)]^+$. Spectral parameters for the isosbestic points and b' are included in Table II. Unless otherwise noted, all reported uncertainties are standard deviations.

Results and Discussion

1. Preparation and Characterization. All three complexes can be formed at room temperature from a common starting material, the brown cation $[(en)_2Co(OH_2)(S_2O_3)]^+$, via substitution (eq 4). This reaction mode is analogous to that

$$[(en)_2Co(OH_2)(S_2O_3)]^+ + X^{-,2-} \rightleftharpoons [(en)_2Co(X)(S_2O_3)]^{0,-} + H_2O \qquad (4)$$

$$X = Cl^-,\ NCO^-,\ C_2O_4^{\ 2-}$$

previously reported;[1] strongly dehydrating conditions are required to produce the solid Cl^- complex. In addition, the thiosulfato cyanato complex can be prepared via successive substitutions on *trans*-$[(en)_2CoCl_2]^+$ with gentle heating.

a. Chloro Complex. The IR spectra of both the anhydrous and the monohydrate complexes show bands characteristics of $(en)_2Co$ and of coordinated S_2O_3 (1200–1100, 1000, 635 cm^{-1}). The inner-sphere coordination of the Cl is indicated by the similar green color of the two solids, either of which dissolves in water to give initially a forest green solution that fades to dull green-brown in ca. 3 min at room temperature. At 4 °C this green-brown intermediate can be isolated as a discrete band with a mobility, under $NaClO_4$ elution, characteristic of a 1+ band; no other species is evident than a trace of a green neutral band that hydrolyzes to the 1+ green-brown band on the column. The freshly eluted green-brown cation exhibits relative maxima at 542, 394, 289 and 215 nm, but due to its labile equilibration (see below), ϵ_{max} and other solution properties are not reported. The 289-nm charge-transfer band is characteristic of Co(III)–S coordination[11] and the trans designation is adopted for the solids on the basis of (a) the acute lability of the Cl^- in solution, in accord with the well-

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Table II. Isosbestic Points and Rate Parameters for Equilibration of Intermediates

source	λ/nm (ε/M^{-1} cm^{-1})			$10^4 b'/s^{-1}$ [a]
trans-$[(en)_2Co(NCO)(S_2O_3)]$	602 (31.3)	462 (51.9)	380 (199)	3.76 ± 0.04
trans-$[(en)_2Co(C_2O_4)(S_2O_3)]^-$	604 (30.8)	458 (56.9)	382 (201)	3.90 ± 0.06
trans-$[(en)_2Co(Cl)(S_2O_3)]$	605 (30.6)	460 (51.1)	382 (198)	3.92 ± 0.04
$[(en)_2Co(OH_2)(S_2O_3)]^+$, Cl^- elution				
"lower green band" *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$	606 (30.6)	457 (55.5)	382 (197)	3.94 ± 0.06
"upper red band" *cis*-$[(en)_2Co(OH_2)(S_2O_3)]^+$	607 (30.6)	454 (58.1)	382 (199)	4.19 ± 0.08

[a] 25.0 °C, 0.25 M $NaClO_4$, pH 5–6.

established trans-labilizing effect of thiolato ligands in Co(III) complexes,[1] and (b) the weak single peaks in the IR at 890 cm^{-1} in the CH_2 rocking region and at 790 cm^{-1} in the NH_2 rocking region.[12]

b. Oxalato and Cyanato Complexes. Initially the purple oxalato and the red cyanato complexes are each rapidly formed at room temperature by substitution on $[(en)_2Co(OH_2)(S_2O_3)]^+$. However in the oxalato case, the absorbance of the reaction mixture passes through a maximum vs. time at 530–540 nm, where both reactant and product complexes absorb comparably. This behavior suggests a more complex anation mechanism than that previously invoked[1] for the thiosulfato aqua species.

The cyanato complex is eluted with water from either an SP or a QAE column; thus, the complex is charge neutral. The oxalato complex is eluted from an SP column with water and binds to a QAE column, behavior indicative of an anionic species. The oxalato complex is eluted, with minor decomposition, from the QAE column by 0.25 M Cl^-, as expected for a 1− species. We attribute this decomposition on the QAE column to the reversal of the equilibrium (eq 4) as oxalate binds to the anion resin.

Both the oxalato and cyanato complexes exhibit bands characteristic of $(en)_2Co$ and the coordinated thiosulfato ligand. The oxalato complex exhibits bands at 1620 and 1590 cm^{-1} that are not removed by deuteration of the amines, and at 1305 and 770 cm^{-1}, as found previously for monodentate oxalato coordination.[5] The asymmetric NCO stretch of the cyanato appears at 2260–2230 cm^{-1}, and the symmetric, at 1330 cm^{-1}. Intense charge-transfer bands at 302 and 283 nm in the UV for the oxalato and cyanato complexes, respectively, are indicative of an S-bonded thiosulfato to Co(III)[1,11] in each. In D_2O the ^1H NMR spectrum of the oxalato exhibits a symmetric pattern of four resonances at 2.92–2.83 ppm for the CH_2's; for the cyanato, a single broad resonance at 2.92 ppm is observed. The single resonance in the ^{13}C NMR, at 47.13 and 47.62 ppm for the oxalato and for the cyanato complex, respectively, and weak single peaks in the IR spectra of each complex at ca. 890 and 815 cm^{-1} [12] are charactersitic of the trans configuration in $(en)_2CoXY$ complexes. Neither the cyanato nor the oxalato carbons were observed on account of the low solubility of the complexes, their sensitivity to decomposition during the times required (>5 h) in the spectrometer, and the inherently low intensity of ^{13}C resonances in NCO^- or $C_2O_4^{2-}$ groups. Thus, we are unable conclusively to demonstrate the monodentate coordination of the oxalato; however, the charge type and presence of the second ligand, $S_2O_3^{2-}$, and the similarity of the IR spectrum to that of *trans*-$[(en)_2Co(NO_2)(C_2O_4)]$[5] strongly imply a monodentate oxalato. No evidence for a *cis*-$[(en)_2Co(C_2O_4)(S_2O_3)]^-$ species was found, and attempts to prepare it via substitution on *cis*-$[(en)_2Co(X)(C_2O_4)]$, X = Cl^-, OH^-,[13] were frustrated by our inability to isolate the latter. The mode of cyanato ligation, N or O bonded, remains ambiguous in the absence of a definitive structural determination.

2. Reactivity. a. Equilibration. The red and the green 1+ species, obtained by Cl^- elution of $[(en)_2Co(OH_2)(S_2O_3)]^+$ from an SP column, equilibrate in aqueous media at 25 °C (0.25 M $NaClO_4$) to the original brown species $[(en)_2Co(OH_2)(S_2O_3)]^+$ with comparable isosbestic points and apparent rate parameters, b' (Table I). We identify this equilibration with the isomerization in eq 5, where $k_f + k_r = b'$ (eq 3) and

$$cis\text{-}[(en)_2Co(OH_2)(S_2O_3)]^+ \underset{k_r}{\overset{k_f}{\rightleftharpoons}} trans\text{-}[(en)_2Co(OH_2)(S_2O_3)]^+ \qquad (5)$$

the red and green species are assigned the cis and trans thiosulfato aqua configurations, respectively, on the basis of their relative mobilities on the cation column, trans greater than cis,[14] and the relative intensity of their d–d visible absorption bands, cis greater than trans. The apparent absorptivities, 101 and 40 M^{-1} cm^{-1}, at 530 nm for the freshly separated red and green bands in dilute 0.25 M $NaClO_4$ are the lower and upper limits for the absorptivities of *cis*- and *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$, respectively.

Apparent absorptivities, ϵ_∞, at 530 nm of equilibrated preparations of *trans*- and *cis*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ were obtained from A_∞' (eq 3). These ϵ_∞ were independent of their source, cis or trans, but were temperature dependent, and the above estimates for ϵ_{cis} and ϵ_{trans}, 101 and 40 M^{-1} cm^{-1}, respectively, were used with eq 6 to estimate the equilibrium

$$\epsilon_\infty = \frac{\epsilon_{cis} + \epsilon_{trans}K_5}{1 + K_5} \qquad (6)$$

constant K_5 for the isomerization (eq 5) at $\mu = 0.25$ ($NaClO_4$). ϵ_∞/M^{-1} cm^{-1} (T/°C) K_5: 62.7 (15.0) 1.69; 65.2 (25.0) 1.42; 70.2 (35.0) 1.02. The corresponding thermodynamic parameters for eq 5 (0.25 M $NaClO_4$) are $\Delta H°$/kcal mol^{-1} = −4.4 ± 0.9 and $\Delta S°$/cal mol^{-1} K^{-1} = −14.3 ± 2.9. Rate parameters, b' (eq 3), for equilibrating *trans*- or *cis*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ were as follows for trans, cis $10^4b'$/s^{-1} (T/°C): 1.05 ± 0.04, 1.07 ± 0.03 (15.0); 3.94 ± 0.06, 4.19 ± 0.08 (25.0); 13.4 ± 0.1, 14.0 ± 0.2 (35.0). The apparent activation parameters for b' are $\Delta H^\ddagger$/kcal mol^{-1} = 22.0 ± 0.2 and $\Delta S^\ddagger$/cal K^{-1} mol^{-1} = −0.2 ± 0.9. Attempts to demonstrate the presence of cis–trans isomers in an equilibrated mixture with ^{13}C NMR were frustrated by decomposition of the sample in the probe.

b. Aquation. The thiosulfato chloro complex aquates rapidly ($t_{1/2}$ ca. 3 min, 25 °C), liberating one Cl^- per Co and producing a green-brown cation, which equilibrates to the brown $[(en)_2Co(OH_2)(S_2O_3)]^+$ with the same isosbestic points and apparent rate parameters b' (Table II), as those found above and with an initial apparent absorptivity of 43 cm^{-1} M^{-1} at 530 nm. These data are consistent with the predominant

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formation of *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ on aquation of the chloro complex and the subsequent isomerization of the trans isomer according to eq 5.

At room temperature and pH ca. 5, both the oxalato and the cyanato complexes decompose slowly ($t_{1/2} > 1$ week) in aqueous solution. For the oxalato, the principal Co-containing product is the bidentate complex, $[(en)_2Co(C_2O_4)]^+$; for the cyanato, the initial product is the thiosulfato aqua, which undergoes slow ligand exchange, with production principally of *cis*- and *trans*-$[(en)_2Co(S_2O_3)_2]^-$ and $[(en)_2Co(OH_2)_2]^{3+}$.

c. Acidolyses. In dilute aqueous $HClO_4$, both the thiosulfato oxalato and the thiosulfato cyanato complexes undergo acidolysis, with initial production of a green-brown cationic intermediate that equilibrates to the brown $[(en)_2Co(OH_2)(S_2O_3)]^+$ with the same isosbestic points and apparent rate parameter b' (Table II), as found above. The initial absorptivities of the intermediates at 530 nm, 47 and 48 M^{-1} cm^{-1} for the oxalato and cyanato complexes, respectively, are consistent with predominant initial formation of the trans thiosulfato aqua cation. In the oxalato acidolysis, approximately 10% Co^{2+} is also formed: in the cyanato case, the overall H^+ consumption and the production of CO_2 and of $[(en)_2Co(OH_2)(S_2O_3)]^+$ are consistent with the stoichiometry in eq 7. At 15, 25, and 35 °C, the first-order rate parameters,

$$\textit{trans-}[(en)_2Co(NCO)(S_2O_3)] + 2H^+ + 3H_2O \rightarrow [(en)_2Co(OH_2)(S_2O_3)]^+ + NH_4^+ + H_2CO_3 \tag{7}$$

a and b (eq 1), were fit to linear functions (eq 2) of $[H^+]$ over the range 0.04–0.40 M, $\mu = 1.00$ ($LiClO_4$). The short-half-life parameter, a, was cleanly first order in $[H^+]$, k_0 being insignificantly different from zero at each temperature. $10^3k_1/M^{-1}$ s^{-1} ($T/°C$): 24.9 ± 0.2 (15.0), 57.6 ± 1.6 (25.0), 124 ± 4 (35.0). The long-half-life parameter, b, consisted of a predominant, acid-independent term, k_2, and a minor term first order in $[H^+]$, characterized by k_3. $10^4k_2/s^{-1}$, $10^4k_3/M^{-1}$ s^{-1} ($T/°C$): 0.87 ± 0.04, 0.56 ± 0.15 (15.0); 3.86 ± 0.09, 2.2 ± 0.4 (25.0); 11.9 ± 0.5, 13 ± 4 (35.0). Apparent activation parameters $\Delta H^\ddagger$/kcal mol^{-1}, $\Delta S^\ddagger$/cal K^{-1} mol^{-1} for k_1, k_2, and k_3, respectively: 13.6 ± 0.2, −18.7 ± 0.5; 22.6 ± 1.4, 1.4 ± 4.0; 27 ± 3, 15 ± 8. At 25 °C, log k_1 and log k_2 were only weakly dependent on $\mu^{1/2}$: d log $k/d\mu^{1/2} = 0.28 \pm 0.02$ and 0.13 ± 0.04 $M^{-1/2}$, respectively. The ionic strength dependence of k_3 was not well-defined. In 95.3% D_2O at 25.0 °C, the short-half-life parameter, a, was cleanly first order in $[D^+]$, $k_{1D} = 0.116 \pm 0.007$ M^{-1} s^{-1}, for an inverse deuterium isotope effect $k_{1D}/k_{1H} = 2.0 \pm 0.1$. In the long-half-life parameter, b, the weak acid dependence was not well resolved in D_2O but the overall isotope effect, $b_D/b_H = 0.87 \pm 0.14$, was not significantly different from unity. General-acid catalysis was sought in the k_1 term in a chloroacetic acid–lithium chloroacetate buffer. At pH 2.58, $[ClCH_2COOH] = 0.57$ M, no evidence of general acid catalysis was detected.

Under pseudo-first-order excess $[H^+]$, the mechanism in eq 8, where B = *trans*-$[(en)_2Co(NCO)(S_2O_3)]$, C = *trans*-

$$B \xrightarrow{k_B} C \underset{k_D}{\overset{k_C}{\rightleftharpoons}} D \tag{8}$$

$[(en)_2Co(OH_2)(S_2O_3)]^+$, and D = *cis*-$[(en)_2Co(OH_2)(S_2O_3)]^+$, leads[15] to a time-dependent absorbance, $A(t)$, of the form in eq 1. Identification of the parameters a, for the short-half-life process, and b, for the long-half-life process, with k_B and ($k_C + k_D$), respectively, is in general not possible on the basis of A–t data alone.[16] In this case, the following points substantiate this assignment: (i) The computer simulation, using measured absorptivities at 532 nm for the thiosulfato cyanato and equilibrated thiosulfato aqua complexes and 46 M^{-1} cm^{-1} for the intermediate, was successful only if a and b were assigned as above. (ii) The agreement between b' (Table I), obtained from the equilibration of the isolated intermediate, C, and b (25.0 °C), obtained from the cyanato acidolysis, $10^4b/s^{-1} = (3.86 \pm 0.09) + (2.2 \pm 0.4)[H^+]$, confirms the identification of the long-half-life process with the isomerization of the initially formed *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$. A_∞ (eq 1) at 532 nm was used to obtain apparent absorptivities, ϵ_∞, for the equilibrated product. These ϵ_∞ were found to be $[H^+]$ and μ independent, but temperature dependent, and equilibrium constants K_5 for the isomerization in eq 5 were estimated as in eq 6. At $\mu = 1.00$ ($LiClO_4$), ϵ_∞/M^{-1} cm^{-1} ($T/°C$) K_5: 64.8 (15.0) 1.46; 69.0 (25.0) 1.10; 73.6 (35.0) 0.82. The corresponding thermodynamic parameters for eq 5 are $\Delta H°$/kcal mol^{-1} = −5.2 ± 0.3 and $\Delta S°$/cal mol^{-1} K^{-1} = −18 ± 1. The agreement with the values obtained for the isomerization (above) in 0.25 M $NaClO_4$ is fair. Although the cis–trans isomerization of $[(en)_2Co(OH_2)(S_2O_3)]^+$ is more rapid than that of many Co(III) complexes, the first-order rate parameter, b', is comparable to that of $[(en)_2Co(OH_2)(N_3)]^{2+}$,[17] 10^4k (25 °C)/s^{-1} = 0.98, and is more than 1 order of magnitude less than that of $[(en)_2Co(OH_2)(OH)]^{2+}$,[18] 10^3k (25 °C)/s^{-1} = 5.0. In 0.10 M $LiClO_4$, the bidentate complex $[(en)_2Co(S_2O_3)]^+$ aquates[2] with rate parameters and isosbestic points comparable to those of the thiosulfato aqua complex: 10^4k_{aq}(25 °C)/s^{-1} = 2.75 ± 0.14; $\Delta H^\ddagger$/kcal mol^{-1} = 22.3 ± 0.8; $\Delta S^\ddagger$/cal K^{-1} mol^{-1} = 0.0 ± 2.4; λ_{isos}/nm (ϵ_{isos}/M^{-1} cm^{-1}) 609 (32), 460 (58). We suggest these parameters may describe the isomerization of *cis*-$[(en)_2Co(OH_2)(S_2O_3)]^+$, formed following an initial, rapid aquation of the bidentate thiosulfato complex.

Nonretention of configuration in the spontaneous and induced aquations of $[(en)_2CoXY]^{n+}$ complexes is well established,[19] and the acidolyses of the thiosulfato cyanato and the oxalato thiosulfato complexes, as well as the aquation of the thiosulfato chloro complex, appear not to be wholly retentive. For each complex, the apparent absorptivity of the intermediate, ϵ_{532}/M^{-1} cm^{-1} = 48 (cyanato) and ϵ_{530}/M^{-1} cm^{-1} = 47 (oxalato), 43 (chloro), is larger than the upper bound, ca. 40 M^{-1} cm^{-1}, estimated above for the *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$. These larger apparent absorptivities are consistent both with some isomerization between separation and initiation of the kinetics and with production of some *cis*-$[(en)_2Co(OH_2)(S_2O_3)]^+$, ϵ_{530} ca. 101 M^{-1} cm^{-1}. The latter interpretation is supported by the computer simulation of the thiosulfato cyanato acidolysis; in this calculation an apparent absorptivity of 46 M^{-1} cm^{-1} was required for the intermediate.

The acidolyses of free HNCO[20] and of $[(NH_3)_5Co(NCO)]^{2+}$ [21] both follow kinetics first order in $[H^+]$ with apparent activation parameters comparable to those found above for k_1. $\Delta H^\ddagger$/kcal mol^{-1}, $\Delta S^\ddagger$/cal K^{-1} mol^{-1}: 14.5, −14.2 (cyanic acid); 13.1, −18.0 (cyanato pentaammine). The rate law for the cyanic acid acidolysis is also insensitive to $[ClCH_2COOH]$, and a thorough study[21b] of the cyanato pentaamine acidolysis revealed the presence of a short-lived intermediate, formulated as $[(NH_3)_5Co(NH_2COOH)]^{3+}$, which was rapidly hydrolyzed by solvent H_2O. We conclude that a similar mechanism, consisting of a preequilibrium protonation of the cyanato ligand, with a rate-determining addition of solvent H_2O to form the carbamic acid complex, followed by rapid

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hydrolysis with solvent H_2O, is consistent with the inverse deuterium isotope effect,[22] with the lack of general acid catalysis, and with the apparent activation parameters.

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Registry No. $[(en)_2Co(OH_2)(S_2O_3)]^+$, 86900-35-8; *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$, 62656-34-2; *cis*-$[(en)_2Co(OH_2)(S_2O_3)]^+$, 86900-36-9; *trans*-$[(en)_2Co(Cl)(S_2O_3)]$, 86853-85-2; *trans*-$[(en)_2Co(NCO)(S_2O_3)]$, 86853-86-3; *trans*-$[(en)_2Co(Cl)_2]Cl$, 14040-33-6; Na[*trans*-$[(en)_2Co(C_2O_4)(S_2O_3)]]$, 86853-87-4; *trans*-$[(en)_2Co(S_2O_3)_2]^-$, 62529-95-7; iodine, 7553-56-2.

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Molybdenum(V) and -(VI) Complexes with Deprotonated Aromatic Amino Ligands

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Reaction of $MoO_2(acac)_2$ or MoO_2Cl_2 with tridentate (NOS, NO_2) ligands having aromatic amino groups gives MoL_2 (L = *N*-(2-hydroxybenzyl)-2-mercaptoaniline, *N*-(2-hydroxybenzyl)-2-hydroxyaniline) complexes in which both oxo groups have been displaced and the amino groups deprotonated. The complexes exhibit reversible electrochemical behavior involving $MoL_2/MoL_2^-/MoL_2^{2-}$ complexes. The Mo(V) complex $[Et_4N][MoL_2]$ (L = *N*-(2-hydroxybenzyl)-2-mercaptoaniline) has also been prepared and its structure determined. It has highly distorted octahedral geometry with short Mo–N bonds. The oxygen analogue has been obtained in solution by electrochemical reduction of the corresponding Mo(VI) complex. The EPR parameters of the Mo(V) complexes obtained by computer simulation are reported. Reaction of *N,N'*-bis(2-hydroxybenzyl)-*o*-phenylenediamine and 1,2-bis(2-hydroxyanilino)ethane with $MoO_2(acac)_2$ gives complexes of formula $MoO_2(LH_2)$. One-electron electrochemical reduction gives monomeric Mo(V) complexes, in which the amino ligands are most probably deprotonated. The Mo(V)–oxo complexes are similar in properties to previously reported Mo(V)–oxo complexes with deprotonated tetradentate aromatic N_2S_2 ligands. Their EPR spectra show well-resolved ^{14}N shfs from two equivalent nitrogens. They are reversibly reduced electrochemically in a one-electron step to Mo(IV) species and oxidized irreversibly to $MoO_2(LH_2)$. The generation of the stable Mo(V) intermediates in the electrochemical reduction of the Mo(VI) complexes mimics the redox behavior of molybdenum hydroxylases.

Introduction

The ability of transition metals in high oxidation states to deprotonate coordinated amino ligands is well-known,[2-4] and molybdenum(V) and -(VI) complexes with *o*-aminobenzenethiol having deprotonated amino (amido) groups have been reported.[5,6] Deprotonation of coordinated amino groups may be of importance with respect to molybdenum enzymes, for which coupled proton/electron-transfer processes have been postulated.[7]

Recently we reported preliminary results for two Mo(V)–oxo complexes, $[Et_4N][MoOL]$, where L^{4-} is a tetradentate aromatic amino thiol ligand with an N_2S_2 donor set in which the amino groups are deprotonated.[8] We report here the detailed syntheses and the EPR parameters of these complexes, the syntheses and properties of two new non-oxo Mo(VI) complexes and one new non-oxo Mo(V) complex having deprotonated amino ligands, and the X-ray crystal structure of the latter. In addition, the syntheses and electrochemical behavior of two new Mo(VI)–dioxo complexes with normal (i.e., protonated) amino ligands and the solution properties of three Mo(V) complexes with deprotonated amino ligands,

Table I. Electrochemical Data

complex	Mo(VI)/Mo(V) $E_{1/2}$[a]	Mo(VI)/Mo(V) n[b]	Mo(V)/Mo(IV) $E_{1/2}$[a]	Mo(V)/Mo(IV) n[b]
$Mo(hbma)_2$[d]	−0.02	0.92	−1.15	1[c]
$Mo(hbha)_2$[d]	−0.26	1.04	−1.36	1[c]
$MoO_2(haeH_2)$[e]	−1.41[g] −0.02[h]	1.01	−1.70	1[c]
$MoO_2(hbpdH_2)$[f]	−1.41[g] −0.19[h]	1.04	−1.69	1[c]
$MoO_2(maeH_2)$[e]	−1.03[j] 0.14[h]	2.00[j]	−1.00[i]	1.05[i]
$MoO_2(mabH_2)$[e]	−1.09[j] 0.19[h]	2.05[j]	−1.02[i]	1.10[i]

[a] $(E_{pc} + E_{pa})/2$ vs. SCE; 0.100 V/s scan rate. [b] Electrons/molecule. [c] Estimated by comparison of peak with peak of first reduction. [d] CH_2Cl_2, 0.10 M $[n\text{-}Bu_4N][BF_4]$. [e] DMF, 0.10 M $[Et_4N]Cl$. [f] MeCN, 0.10 M $[Et_4N]Cl$. [g] Irreversible reduction. [h] Irreversible oxidation. [i] $[Et_4N][MoO(mae)]$ and $[Et_4N][MoO(mab)]$, respectively.[8] [j] Reduction from Mo(VI) to Mo(IV).[8]

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