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Redox Reactions Involving Sulfur-Containing Amino Acid Complexes

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The Cr^{2+} reductions of the three complexes $[(en)_2Co(Met)]^{2+}$, $[(en)_2Co(MeCys)]^{2+}$, and $[(en)_2Co(Cys)]^{2+}$ (Met = methionine, MeCys = methylcysteine, Cys = cysteine) are described. The Co(III) complexes of methionine and methylcysteine are O,N-bonded chelates. Attack of Cr^{2+} occurs at the O atom in each of these complexes to produce the O-bonded monodentate Cr(III) product which slowly aquates. The kinetic data for the reduction of the methioninato complex are $k^{25°C} = (0.416 \pm 0.006)$ M^{-1} s^{-1}, $\mu = 1.0$ M ($LiClO_4$), $\Delta H^{\ddagger} = 9.7 \pm 0.9$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -28 \pm 3$ eu. The data for the corresponding methylcysteinato complex are $k^{25°C} = 0.56 \pm 0.01$ M^{-1} s^{-1}, $\mu = 1.0$ M ($LiClO_4$), $\Delta H^{\ddagger} = 9 \pm 1$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -28 \pm 4$ eu. The $[(en)_2Co(Cys)]^{2+}$ complex is S,N bonded. Attack of Cr^{2+} occurs at the S atom to give the S-bonded monodentate intermediate which undergoes rapid ring closure, in the presence of excess Cr^{2+}, to produce the S,O-bonded chelated product. If Cr^{2+} is in deficit, a series of reactions ultimately producing the S,N-bonded Cr(III) product also ensues. The rate of Cr^{2+} reduction of $[(en)_2Co(Cys)]^{2+}$ is $(2.4 \pm 0.3) \times 10^5$ M^{-1} s^{-1}, $\mu = 1.0$ M ($LiClO_4$). The S-bonded monodentate intermediate is attacked by Cr^{2+} in both the protonated and unprotonated forms, as evidenced by an inverse hydrogen ion term in the rate law. The rate of reduction through the protonated form is $(6 \pm 3) \times 10^3$ M^{-1} s^{-1}; through the unprotonated form, it is estimated to be $(1.6 \pm 0.4) \times 10^7$ M^{-1} s^{-1}. Comparisons of these results to related systems are made and the results of the cysteine system are discussed in terms of the superexchange and resonance-transfer mechanisms.

Introduction

Sulfur-containing amino acids are frequently found bonded directly to the metal center of proteins having important redox functions. These range from cytochrome *c* in which methionine-80 is found bonded directly to the iron atom of the porphyrin ring[1] to the ferredoxins which have their iron atoms coordinated to one or two cysteine residues.[2,3] Other studies have established that the iron atom in clostridial rubredoxin is surrounded tetrahedrally by four cysteinyl mercaptide residues in solution[4] and in the solid state.[5] Metal–sulfur proteins also appear to play an important role in photosynthesis, in nitrogen fixation, and in the hydroxylation of steroids and other terpenes.[6] The preference for sulfur–metal bonds in biological redox systems suggests that sulfur may have unusual electron-mediating abilities and this has generated considerable interest in sulfur-containing metal complexes in general over the past few years.[7-9]

Our interest in the redox behavior of chelate complexes and in particular those complexes which contain a potential sulfur-bridging atom has led us to investigate the behavior of the cobalt(III) complexes of cysteine, methylcysteine, and methionine toward reduction by chromium(II). Prior to this study, no kinetic information on the ease of electron transfer through these amino acids coordinated to a metal was available, in spite of the prevalence with which these acids are found as ligands bonded to metal atoms in biological systems.

Experimental Section

Reagents. All reagent solutions were prepared in water which was deionized, distilled, and then redistilled from alkaline permanganate in an all-glass apparatus. Lithium perchlorate solutions were made by dissolving anhydrous reagent grade $LiClO_4$ (G. Frederick Smith Chemical Co.) in water and filtering the resulting solution through a 0.50-μ Millipore filter (Millipore Filter Corp.). Triplicate portions of the filtrate were then standardized by determining the amount of hydrogen ion released from an Amberlite IR120(H) analytical grade resin (BDH Chemicals Ltd.).

The perchloric acid solutions were prepared by dilution of 70%, doubly distilled, reagent grade $HClO_4$ (G. Frederick Smith Chemical Co.). Aliquots of this solution were titrated to a bromothymol blue end point to determine the concentration.

Chromium(II) perchlorate solutions were prepared by reduction of chromium(III) perchlorate (G. Frederick Smith Chemical Co.) in aqueous perchloric acid solution using zinc–mercury amalgam. The solutions were standardized as reported earlier[10] and were stored and handled using standard syringe techniques, in an atmosphere of high-purity argon.

Ion-Exchange Procedures. All ion-exchanges were performed at 5 °C in a cold room. Solutions prepared for elution were made with doubly distilled water.

Preparation of $[(en)_2Co(Cys)]^{2+}$ (6). The complex was prepared according to the method of Kothari and Busch[12] except that the ligand was dissolved in the aqueous solution of sodium hydroxide and then to this solution the solid *trans*-$[(en)_2CoCl_2]Cl$ was added. The resulting product was ion-exchanged on Rexyn 102 (Na^+).[11] The desired brown band was eluted from the resin and the solution was concentrated on a Rotovap. After the pH of the solution was adjusted to about 1, sodium perchlorate (G. Frederick Smith Chemical Co.) was added to precipitate the complex. Analyses were found to vary from sample to sample, prepared in this way, especially when large amounts of complex were precipitated quickly. However, all gave satisfactory C:N ratios and could be analyzed by assuming that some of the complex was protonated and some unprotonated. The sample used in the kinetics studies was found to be 62% protonated and 38% unprotonated. Anal. Calcd for 62% $[Co(C_2N_2H_8)_2(SCH_2CH(NH_2)COOH)](ClO_4)_2$ + 38% $[Co(C_2N_2H_8)_2SCH_2CH(NH_2)COO](ClO_4)$: C, 18.26; H, 4.78; N, 15.21. Found: C, 18.18; H, 4.94; N, 15.18.

Preparation of $[(en)_2Co(MeCys)]^{2+}$ (3). The complex was prepared according to the method of Kothari and Busch[12] using *S*-methyl-L-cysteine as ligand. The complex was ion-exchanged as described previously[11] and eluted from the resin with a concentrated solution of NaCl. With the addition of solid $NaClO_4$, crystals of the desired product appeared. Anal. Calcd for $[Co(C_2N_2H_8)_2(NH_2CH(CH_2SCH_3)COO)](ClO_4)_2 \cdot H_2O$: C, 18.23; H, 4.40; N, 13.28. Found: C, 18.29; H, 4.88; N, 13.50.

Preparation of $[(en)_2Co(Met)]^{2+}$ (1). The methionine complex was prepared in a fashion analogous to the cysteine (**6**) and methylcysteine (**3**) derivatives. The ligand DL-methionine (3.0 g) was dissolved in a solution of 1.60 g of NaOH in 40 mL of water. Then 5.7 g of *trans*-$[(en)_2CoCl_2]Cl$ was added and the mixture was stirred at ~50 °C for 4 h during which time it changed color from purple to red. Fine orange crystals were precipitated from the cooled solution by the addition of 12 g of sodium iodide. The crystals were dissolved in water and ion-exchanged[11] on Rexyn 102 (Na^+). Unreacted *cis*-$[(en)_2CoCl_2]Cl$ came off the column first, followed by the orange band of the desired product. Other bands of higher charge remained at the top of the column and were not identified. After being eluted from the column in a concentrated solution, the complex was precipitated by the addition of solid $NaClO_4$, filtered, washed with ether, and dried at the pump. Anal. Calcd for $[Co(C_2N_2H_8)_2(NH_2CH(CH_2CH_2SCH_3)COO)](ClO_4)$: C, 20.54; H, 4.98; N, 13.31. Found: C, 20.16; H, 4.89; N, 13.42.

Preparation of $[(OH_2)_5CrOOCCH(CH_2SCH_3)NH_3]^{3+}$ (4) and $[(OH_2)_4Cr(OOCCH(CH_2SCH_3)NH_2)]^{2+}$ (5). Chromatographic separation, on Dowex 50WX8-200, of reaction mixtures of $[(en)_2Co(MeCys)]^{2+}$ (**3**) with a fourfold excess of Cr(II) over Co(III) or vice versa yielded the monodentate carboxylate bonded complex

Table I. Electronic Spectra of Amino Acid Complexes and Related Species

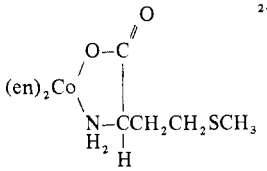
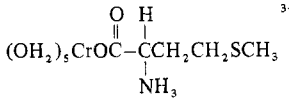
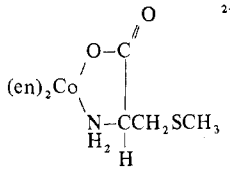
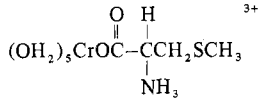
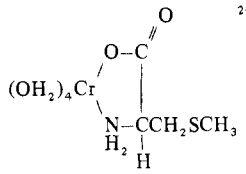
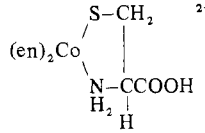
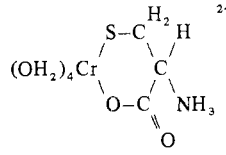
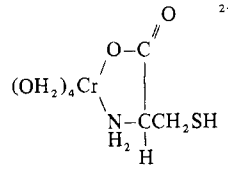
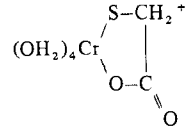
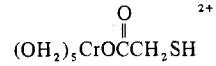
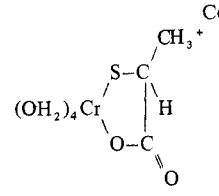
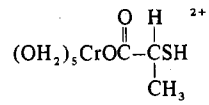
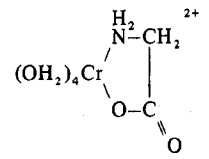
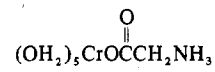
No.	Complex	λ_{max} (ϵ_{max}), nm (M^{-1} cm^{-1})	Ref
	Complexes of Methionine		
1		486 (93.6 ± 0.3) 344 (112 ± 2)	This work
2		573 (22.6 ± 0.2) 409 (22.4 ± 0.4) } ET[a] 573 (22.2 ± 0.5) 410 (21.9 ± 0.7) } SUB[b]	This work
	Complexes of Methylcysteine		
3		486 (106 ± 1) 341 (135 ± 1)	This work
4		572 (22.1 ± 0.6) 409 (21.9 ± 0.7) } ET[a] 572 (21.5 ± 0.4) 409 (22.3 ± 0.1) } SUB[b]	This work
5		533 (40.8 ± 0.9) 403 (34.6 ± 0.5)	This work
	Complexes of Cysteine		
6		580 sh (50.3 ± 0.7) 483 (136 ± 2) 282 (26 000 ± 600)	This work[c]
7		549 (68 ± 1) 441 (43.8 ± 0.7) 267 (6300 ± 200)	This work
8		531 (41.6 ± 0.4) 402 (34.2 ± 0.2)	This work
	Complexes of Mercaptoacetate		
9		548 (68.3) 437 (53.4) 264 (5070)	16
10		568 (26.0) 411 (25.1)	16
	Complexes of 2-Mercaptopropionate		
11		545 (71.2) 440 (52.2) 265 (5050)	17

Table I (*Continued*)

No.	Complex	λ_{max} (ϵ_{max}), nm (M^{-1} cm^{-1})	Ref
12		568 (25.0) 411 (24.3)	17
	Complexes of Glycine		
13		555 (38.0) 420 (41.0)	17
14		572 (22.0) 412 (23.0)	17

[a] ET = electron transfer. [b] SUB = substitution. [c] Spectrum in 1.0 M $HClO_4$.

(**4**) as the sole reduction product. The assignment of this structure was made by comparison of the electronic spectrum of this species to the spectra of other known monodentate carboxylate-bonded Cr(III) compounds (complexes **10**, **12**, and **14** in Table I). The blue color of these species is an additional indicator of oxygen coordination.

This complex was also prepared by substitution of the free ligand on $[(OH_2)_6Cr]^{3+}$. The ligand *S*-methyl-L-cysteine (4.2 g, 0.031 mol) was placed in a flask fitted with a serum cap, which was subsequently degassed with high-purity argon. Degassed $[Cr(OH_2)_6]^{3+}$ (12 mL of 0.5 M solution in 0.2 M $HClO_4$) was then added via syringe. After 48 h of stirring at room temperature, the ligand had dissolved and a violet-colored solution was produced. Ion-exchange on Dowex 50WX8-200 produced four bands. The first was a pink band which eluted as a 2+ ion and had the spectral characteristics of the chelated N,O-bonded complex (**5**). It was assigned to be a chelate on the basis of its high extinction coefficients which are comparable to those of known N,O-bonded chelates (complex **14** in Table I). Sulfur bonding is unlikely since the spectrum lacks a peak at ~270 nm (see Table I).

The second band eluted as a 3+ ion and was identified as $[Cr(OH_2)_6]^{3+}$. The third band, also a blue 3+ species, was spectrally identical with the O-bonded isomer (**4**) produced in the kinetic studies. A purple band of 4+ or higher charge remained on the top of the column and was not recovered.

Preparation of $[(OH_2)_5CrOOCCH(CH_2CH_2SCH_3)NH_3]^{3+}$ (2). As in the methylcysteine product analysis described above, a fourfold excess of $[Cr^{2+}]$ over $[(en)_2Co(Met)]^{2+}$ (**1**) or vice versa yielded the monodentate carboxylate-bonded complex **2** as the only reduction product. This assignment was again made by comparison of the electronic spectrum to those of similar known compounds (complexes **10**, **12**, and **14** in Table I).

This species was also prepared by substitution of the free ligand on $[Cr(OH_2)_6]^{3+}$ using exactly the same molar ratios and conditions as for the methylcysteine study described above. Surprisingly, very little of the O,N-bonded chelate was formed and there was an insufficient amount of this material to allow characterization. A small amount of $[Cr(OH_2)_6]^{3+}$ and a purple band of 4+ or higher charge, which was not identified, were obtained in this study, as well.

Preparation of $[(OH_2)_4Cr(SCH_2CH(NH_3)COO)]^{2+}$ (7). This S,O-bonded chelated species was the sole product formed with an excess of Cr(II) over $[(en)_2Co(Cys)]^{2+}$ (**6**) as determined by ion exchange of kinetic reaction mixtures in 0.1 M $HClO_4$. The assignment of this structure was based on electronic spectral comparisons to known S,O-bonded species (complexes **9** and **11** in Table I). The peak at ~270 nm is assigned to ligand → metal charge transfer from sulfur and is very diagnostic of sulfur bonding in these complexes.

This S,O-bonded chelate **7** slowly aquated to produce $[Cr(OH_2)_6]^{3+}$. This aquation reaction was observed to be catalyzed by the cation-exchange resin (Dowex 50WX8-200). Usually, the blue $[Cr(OH_2)_6]^{3+}$ could be seen forming on the column before all of the S,O-bonded chelate could be eluted. However, the spectra obtained from samples of the S,O-bonded complex immediately upon elution were very reproducible (Table I, complex **7**). In a typical Cr^{2+} excess analysis, 0.244 mm of $[(en)_2Co(Cys)]^{2+}$ (**6**) and 0.374 mm of Cr^{2+} (total volume 20 mL) were reacted for a few seconds and then subjected to ion exchange.

In the corresponding Co(III) excess studies, typically the reaction mixtures contained 5.14×10^{-2} M $[(en)_2Co(Cys)]^{2+}$ (**6**) and 1.74×10^{-2} M Cr^{2+}. Reproducible results were apparently not obtained under experimental conditions which were as closely similar as possible. In an attempt to establish some trend in these results, a series of experiments under different conditions were performed. Variations in the method of reaction included adding the Cr(II) to the solution of complex in times ranging from complete addition in 4.0 s to gradual addition over a period of 2.6 min, rapid or slow stirring during the addition of Cr(II), and adding concentrated (0.45 M) or dilute (3.5×10^{-2} M) solutions of the reductant. Samples which were 5 times more dilute during reaction than those mentioned above also were studied. Ionic strengths varied from 0.14 to 1.0 M and the acidity range covered was 0.1–0.9 M $HClO_4$.

Only one band, purplish pink in color, was obtained in each case but the spectral details differed dramatically from analysis to analysis. The longest wavelength bands had peak maxima ranging from 523 to 547 nm with extinction coefficients of 35–72 M^{-1} cm^{-1}. A shoulder also appeared between 409 and 456 nm with extinction coefficients of 28–45 M^{-1} cm^{-1}. The UV spectra of this product, likewise varied with peaks in the range 267–272 nm and extinction coefficients of 880–5110 M^{-1} cm^{-1}.

These spectra were indicative of a mixture of at least two species, each having a 2+ charge. The amounts of each 2+ species formed depended on the variations described above as well as on the time required for ion-exchange isolation. The results obtained are consistent if it were assumed that a mixture of the S,O- and N,O-bonded chelated species (complexes **7** and **8** in Table I) was present. The low values of the extinction coefficients in the UV spectrum corresponded to lower values in the visible spectrum and shifts to shorter wavelengths in the visible as expected for a solution of predominantly the N,O-bonded chelate **8**. Similarly, high values of the extinction coefficients of the UV–visible spectrum and shifts to longer wavelengths in the visible were consistent with a solution of primarily the S,O-bonded chelate **7**.

Preparation of $[(OH_2)_4CrOOCCH(CH_2SH)NH_2]^{2+}$ (8). This N,O-bonded chelate was prepared by substitution of the free ligand, L-cysteine, on $[(OH_2)_6Cr]^{3+}$. The ligand (2.75 g, 9.923 mol) was added to $[(OH_2)_6Cr]^{3+}$ (10 mL of 0.5 M solution in 0.2 M $HClO_4$). After 1 week of stirring, aliquots of this solution were ion-exchanged on Dowex 50WX8-400. Three bands were obtained. The first band was a pink species which eluted as a 2+ ion and was formulated to be the N,O-bonded chelate **8**. It was assigned to be a chelate on the basis of its high extinction coefficients (see complexes **5** and **8** in Table I) and because of the similarity of its spectrum to that of the methylcysteine N,O-bonded complex **5**. Sulfur-bonding is unlikely since the UV spectrum lacks a peak at about 270 nm.

The second band, a 3+ ion, was $[(OH_2)_6Cr]^{3+}$ and the third band, also blue, was a 4+ or higher charged species and this was not identified.

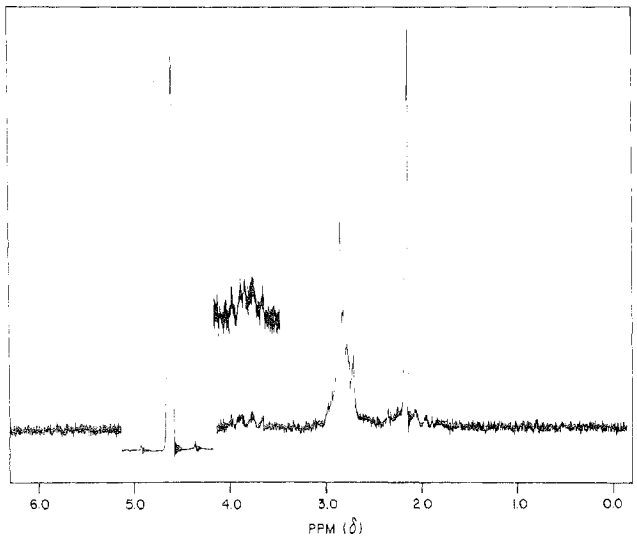


Figure 1. Proton magnetic resonance spectrum of $[(en)_2Co(Met)]^{2+}$ in D_2O. All shifts are relative to DOH at δ 4.61.

Kinetic Measurements. The rates of reduction of the $[(en)_2Co(MeCys)]^{2+}$ (**3**) and $[(en)_2Co(Met)]^{2+}$ (**1**) complexes were followed by observing the changes in absorbance of the longest wavelength maximum of the respective cobalt complex. The runs at 25.0 and 35.0 °C were performed on a Beckman Acta CIII spectrophotometer with the temperature controls described previously.[13] All reactions were carried out at μ = 1.0 M ($LiClO_4$) under pseudo-first-order conditions in cylindrical cells sealed with rubber serum caps in the absence of oxygen. The runs at 45.0 °C were performed on a Durrum Model D-110 stopped-flow spectrophotometer.

The rate of reduction of the $[(en)_2Co(Cys)]^{2+}$ (**6**) complex was followed by observing the change in absorbance of the charge-transfer peak at 282 nm, using the stopped-flow instrument. The stopped-flow spectrophotometer was modified to facilitate the handling of low concentrations of Cr(II) which are extremely air sensitive.[14] The reagent solutions were degassed with high-purity argon which had all traces of oxygen removed by passing the gas stream over a BASF catalyst R-3-11 maintained at 120–140 °C. A kinetic run in the visible region of the spectrum using excess cobalt showed a decrease in absorbance and the rate constant obtained was the same, within experimental error, as that obtained in the UV studies. The very small absorbance changes in the visible spectrum and the extremely rapid rates of reaction precluded a complete study using excess $[(en)_2Co(Cys)]^{2+}$.

Physical Measurements. The ultraviolet and visible spectra were measured on a Beckman Acta CIII spectrophotometer. The proton magnetic resonance spectrum was obtained on a Varian A-60 spectrometer. The infrared spectra were recorded on a Beckman IR 12 spectrophotometer, as KBr pellets.

Results

Since the $[(en)_2Co(Met)]^{2+}$ (**1**) complex had not previously been prepared, we carefully characterized this species. The infrared spectrum shows a C=O stretching band at 1652 cm^{-1} which is typical of a coordinated carboxylate group. This compares favorably with the value of 1656 cm^{-1} obtained[12] for the analogous *S*-methylcysteine derivative. If the NH_2 group were uncoordinated, two bands in the region of 3500–3300 cm^{-1} should be present in the spectrum. However, the NH_2 stretching absorptions occurred at 3120, 3200, 3260, and 3300 cm^{-1} for the ethylenediamine and methionine NH_2 groups. That these bands were actually NH_2 vibrations was verified by deuteration studies of the amine groups by equilibration in D_2O. Upon deuteration the bands at 3120–3300 cm^{-1} decreased markedly in intensity and new ND_2 stretching absorptions appeared at 2300, 2370, 2400, and 2460 cm^{-1}. These results suggest that the methionine ligand is coordinated to the metal by N and O donor atoms.

The ^1H NMR spectrum (Figure 1) shows the methyl protons at δ 2.15 ppm and a poorly resolved multiplet centered at δ 3.80 ppm. Since the remaining signals occur in the region of δ 2.84 ppm, the spectrum cannot be analyzed; i.e., the broad peak due to the methylene protons on the ethylenediamine ligands obscures most of the signals due to the methionine protons. One interesting observation is that there is only one methyl resonance in this spectrum whereas in the spectrum of $[(en)_2Co(MeCys)]^{2+}$ (**3**),[12] two signals, attributed to the presence of diastereoisomers, were noted.

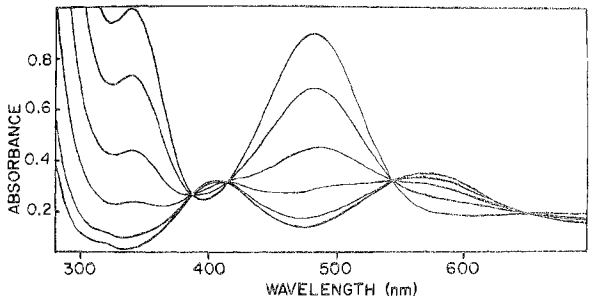


Figure 2. Changes in the visible spectrum during the Cr^{2+} reduction of methylcysteinatobis(ethylenediamine)cobalt(III) (1.85×10^{-3} M) by Cr^{2+} (7.40×10^{-3} M); $[H^+]$ = 0.1 M; path length 5 cm; 25 °C. The spectral scans were started at 15, 315, 915, 1815, 3515, 8115, and 9615 s after mixing. The last two show no change.

Perhaps the best evidence that the methioninato ligand is N,O bonded is the electronic spectrum which lacks a ligand → metal charge-transfer band, typical of metal–sulfur coordination at ~270 nm. The visible spectrum of the methioninato complex is very similar to that of the structurally analogous methylcysteinato derivative (see Table I).

The scan runs of the reactions of $[(en)_2Co(MeCys)]^{2+}$ (**3**) and $[(en)_2Co(Met)]^{2+}$ (**1**) with Cr(II) showed that both species were reduced at similar rates. The Cr^{II}–$[(en)_2Co(Met)]^{2+}$ (**1**) reaction showed isosbestic points at 390, 422, 549, and 660 nm. However, the first scan of the reduction of the $[(en)_2Co(MeCys)]^{2+}$ (**3**) species did not go through the isosbestic points at 387, 415, 545, and 639 nm formed by the remaining scans in this reaction (see Figure 2). The deviation was particularly bad at the first isosbestic point at 639 nm. This peculiar observation was consistently made on every one of the 13 experiments of this type attempted on the $[(en)_2Co(MeCys)]^{2+}$ (**3**) complex, at various acidities, ionic strengths, reagent concentrations, and ages of sample. It does not appear to be an artifact of the isolation procedure since different preparations were used or of the instrument since the scan runs on the $[(en)_2Co(Met)]^{2+}$ (**1**) complex were run within a 3-h period of the methylcysteine study and the spectra produced were normal. The anomaly may have been due to a small amount of decomposition of the complex since the smell of sulfur was quite noticeable in solutions of $[(en)_2Co(MeCys)]^{2+}$ (**3**) but not in solutions of $[(en)_2Co(Met)]^{2+}$ (**1**) or $[(en)_2Co(Cys)]^{2+}$ (**6**). However, the visible spectrum of a 0.1 M $HClO_4$ solution of $[(en)_2Co(MeCys)]^{2+}$ (**3**) did not change over a period of 1 week which would indicate that the amount of decomposition, if any, was slight. In any event, the effect was small and did not appear to affect the kinetics.

The kinetics of the reductions of $[(en)_2Co(Met)]^{2+}$ (**1**) and $[(en)_2Co(MeCys)]^{2+}$ (**3**) by chromium(II) follows the rate law

$$\frac{-d[\text{Co(III) complex}]}{dt} = k[Cr^{2+}][\text{Co(III) complex}] \qquad (1)$$

Summaries of the kinetic data obtained for the methioninato and methylcysteinato complexes are given in Tables II and III, respectively. Product analyses of kinetic reaction mixtures of both systems showed that the only product formed with either Cr(II) or Co(III) in excess was the monodentate carboxylate-bonded Cr(III) product (**2** or **4**, respectively). With a fourfold excess of Cr(II), the measured ligand transfer

Table II. Kinetic Data for the Reduction of Methioninatobis(ethylenediamine)cobalt(III) by Chromium(II)

Temp,[a] °C	$10^3 \times$ $[[(en)_2Co(Met)]^{2+}]$[b]	$10^2 \times$ $[Cr(II)]$[b]	$[H^+]$[b]	k_2, M^{-1} s^{-1}
15.0	1.74	15.4	0.10	0.212
	1.74	15.4	0.10	0.219
	1.78	6.13	0.10	0.213
	1.78	6.13	0.70	0.213
	1.85	3.30	0.10	0.215
25.0	1.76	13.0	0.10	0.437
	1.64	6.03	0.10	0.439
	1.70	3.25	0.10	0.435
	1.70	3.25	0.20	0.444
	1.76	3.25	0.80	0.435
	1.64	3.02	0.40	0.433
45.0	2.68	9.95	0.10	1.19
	2.56	7.45	0.20	1.21
	2.56	6.55	0.40	1.19
	2.63	4.97	0.10	1.18

[a] The temperature was accurate to ±0.1 °C. [b] Concentrations are initial values in molar units.

Table III. Kinetic Data for the Reduction of Methylcysteinatobis(ethylenediamine)cobalt(III) by Chromium(II)

Temp,[a] °C	$10^3 \times$ $[[(en)_2Co(Me\text{-}Cys)]^{2+}]$[b]	$10^2 \times$ $[Cr(II)]$[b]	$[H^+]$[b]	k_2, M^{-1} s^{-1}
15.0	1.74	13.3	0.10	0.289
	1.77	13.2	0.10	0.282
	1.77	6.18	0.70	0.280
	1.77	3.30	0.10	0.292
25.0	1.43	11.8	0.10	0.605
	1.39	5.49	0.10	0.574
	1.39	2.78	0.10	0.608
	1.43	2.79	0.20	0.578
	1.39	2.79	0.40	0.584
	1.41	2.81	0.80	0.580
45.0	5.18	9.95	0.10	1.63
	4.82	7.25	0.20	1.51
	4.81	6.05	0.40	1.48
	5.18	4.84	0.10	1.53

[a] The temperature was accurate to ±0.1 °C. [b] Concentrations are initial values in molar units.

in the methioninato system **1** ranged from 81 to 89% in typical analyses, whereas in the methylcysteinato system **3**, 85–99% of the substituted Cr(III) product **4** was recovered. These results along with those of the scan runs indicate that these reductions proceed solely by the inner-sphere pathway. The only reaction which the Cr(III) products appear to undergo upon equilibrating at room temperature for 1 week was slow hydrolysis to $[Cr(OH_2)_6]^{3+}$. About 45% of the original material for the methioninato species **2** and about 24% of the methylcysteinatochromium(III) complex hydrolyzed during this time period.

Kinetics and Product Analyses of the $[(en)_2Co(Cys)]^{2+}$ (6) System. The reduction of $[(en)_2Co(Cys)]^{2+}$ by Cr(II), unlike that of the previous two systems, occurred extremely rapidly and was complete within the time of manual mixing. The kinetics were studied on the specially modified stopped-flow instrument described in the Experimental Section. Two reactions were detected, the first producing a rapid decrease in absorbance followed by a slower decrease which depended on the hydrogen ion concentration. The kinetic data for these two reactions are collected in Tables IV and V.

The initial reaction was first order in Cr(II) and Co(III) concentrations and was independent of the concentration of acid. The observed rate law was identical with that obtained for the methionine and methylcysteine complexes.

Table IV. Kinetic Data for the Reduction of Cysteinatobis(ethylenediamine)cobalt(III) by Chromium(II) at 25 °C[a]

$10^5[[(en)_2Co(cys)]^{2+}]$[b]	$10^4 \times$ $[Cr(II)]$[b]	$[H^+]$[b]	$10^{-5}k_2$, M^{-1} s^{-1}
3.06	17.8	0.80	2.35
2.55	9.00	0.80	2.41
3.06	8.90	0.15	2.12
3.06	8.90	0.20	2.76
3.06	8.88	0.40	2.43
3.06	8.90	0.80	2.64
3.06	4.51	0.10	2.10

[a] The temperature was accurate to ±0.1 °C. [b] Concentrations are initial values in molar units.

Table V. Kinetic Data for the Second Reaction in the Reduction of Cysteinatobis(ethylenediamine)cobalt(III) by Chromium(II) at 25 °C[a]

$10^5[[(en)_2Co(cys)]^{2+}]$[b]	$10^4 \times$ $[Cr(II)]$[b]	$[H^+]$[b]	$10^{-4}k_2$, M^{-1} s^{-1}
3.06	90.0	0.80	1.04
3.06	45.0	0.80	0.98
3.06	45.0	0.40	1.67
3.06	8.90	0.20	1.99
3.06	8.90	0.10	3.97

[a] The temperature was accurate to ±0.1 °C. [b] Concentrations are initial values in molar units.

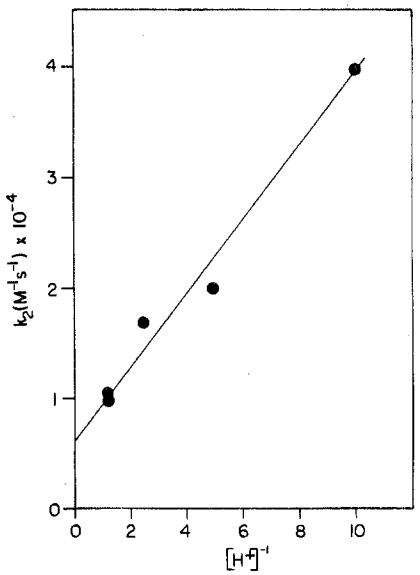


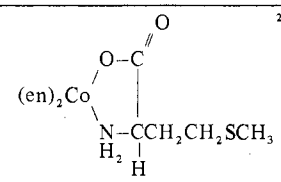
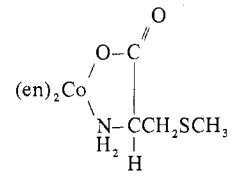
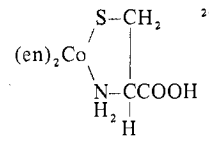
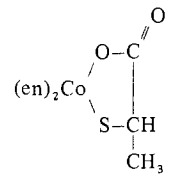
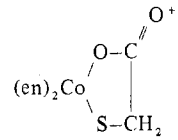
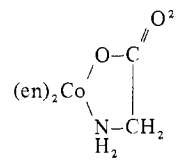
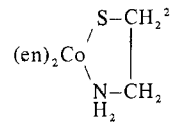
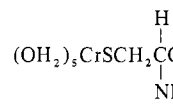
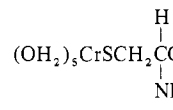
Figure 3. Plot of k_2 (M^{-1} s^{-1}) vs. $[H^+]^{-1}$ for the Cr(II) reduction of the intermediate S-bonded monodentate chromium(III)–cysteine product (**21**,**22**).

The second reduction was also first order in [Cr(II)] but had an inverse hydrogen ion dependence, as shown in Figure 3. The data indicate that the initially formed product of the reduction of $[(en)_2Co(Cys)]^{2+}$ exists as an equilibrium mixture of protonated and unprotonated forms which are reduced at different rates by Cr(II). This second reduction obeys the rate law

$$\frac{-d[Cr(III)]}{dt} = \left[a + \frac{b}{[H^+]}\right][Cr(III)]\,[Cr(II)] \qquad (2)$$

A computer least-squares fit to the line in Figure 3 gave an intercept $a = (6 \pm 3) \times 10^3$ M^{-1} s^{-1} and a slope $b = (3.3 \pm 0.6) \times 10^3$ s^{-1}.

Table VI. Rate Constants and Activation Parameters for the Chromium(II) Reduction of Amino Acid Complexes and Related Species[a]

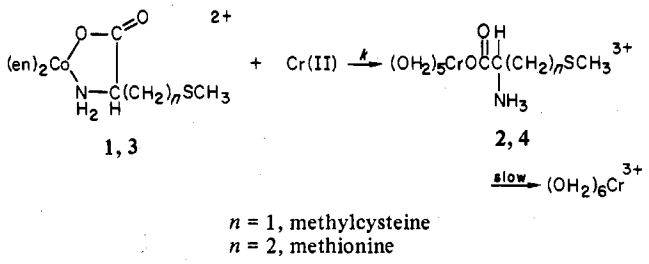
No.	Complex	$k^{25\,°C}$, $M^{-1}\,s^{-1}$	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	Ref
1		0.416 ± 0.006[b,c]	9.7 ± 0.9	−28 ± 3	This work
3		0.56 ± 0.01[b,c]	9 ± 1	−28 ± 4	This work
6		(2.4 ± 0.3) × 10[5 c]			This work
15		1.5 × 10[5 d]	1.1 ± 0.2	−31 ± 1	17, 28
16		6.4 × 10[6 e]			16, 28
17		2.22	8.9 ± 0.1	−27 ± 0.4	17, 28
18		3.3 × 10[4]	7.3 ± 0.3	−13.5 ± 1	18, 28
19	$(OH_2)_5CrSCHCOOH^{2+}$ (CH₃)	>2 × 10[4]			17, 27
20	$(OH_2)_5CrSCH_2COOH^{2+}$	>2 × 10[4]			16, 27
21		(1.6 ± 0.4) × 10[7 c,f]			This work
22		(6 ± 3) × 10[3 b]			This work

[a] I = 1.0 M ($LiClO_4$) unless otherwise noted. [b] The rate constant shown was calculated from the transition-state equation. [c] The errors are standard deviations. [d] I = 0.10 M (ClO_4^-). [e] I = 0.10 M (ClO_4^-), T = 18.6 °C. [f] Depends on the estimated K_a and may be lower. See text.

Since the intermediate is so short-lived, an estimate of the K_a for this equilibrium is difficult. By use of the value of pK_a = 3.7 which was measured for the $[(en)_2Co(Cys)]^{2+}$ (**6**) complex[12] and which should be comparable to that of a cysteine complex of Cr(III), the second-order rate constant through the unprotonated species can be estimated to be (1.6 ± 0.4) × 10^7 $M^{-1}\,s^{-1}$. Reduction through the protonated form of the intermediate proceeded much more slowly, with a second-order rate constant of (6 ± 3) × 10^3 $M^{-1}\,s^{-1}$ (see Table VI and Scheme II).

Product analysis of kinetic reaction mixtures produced the S,O-bonded chelate **7** as the only inner-sphere reduction product with Cr^{2+} in excess. Ligand-transfer studies appeared to indicate that not all of the cysteine ligand was transferred from cobalt to chromium during the act of electron transfer. The low values obtained are probably due to the hydrolysis of this species which occurs during the ion-exchange process (vide supra) since $[Cr(OH_2)_6]^{3+}$ could be seen forming on the column maintained at 5 °C, as charging and elution procedures were carried out. There was an inverse correlation between the amount of time required for the ion-exchange process and the amount of S,O-bonded chelate **7** recovered. By ion-exchanging the reaction mixture as quickly as possible, the amount of ligand transfer as S,O-bonded chelate **7** observed

Scheme I



n = 1, methylcysteine
n = 2, methionine

in typical analyses ranged from 70 to 79%. In view of the rapid decomposition of this species, however, we feel that the transfer is probably quantitative. The fact that the S,O-bonded chelate breaks down to form only $[Cr(OH_2)_6]^{3+}$ has important mechanistic implications (vide infra).

The sole product isolated from an attempt to prepare the chromium(III) product by substitution of cysteine on $[(OH_2)_6Cr]^{3+}$ was the O,N-bonded chelate **8**. As was found by earlier workers[15] chromium(III) sulfur-bonded products are difficult to make by the usual substitution procedures. None of the three amino acids used in this study gave an S-bonded chromium(III) product by substitution of the free ligand on $[Cr(OH_2)_6]^{3+}$. However, Cr^{2+} reduction of $[(en)_2Co(Cys)]^{2+}$ (**6**) did produce a sulfur-bonded product, in agreement with observations of others[15] that electron-transfer methods may succeed in producing sulfur-bonded chromium(III) products when substitution methods fail.

Discussion

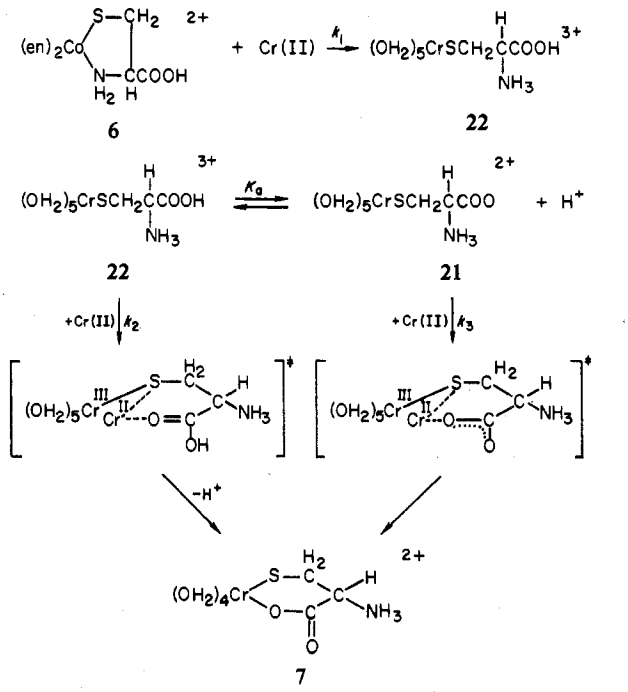
The reactions of Cr(II) with the methylcysteine– and methionine–cobalt(III) complexes were found to have very similar rate constants and activation parameters. These results are strongly indicative of a common mechanism for reduction of these two species as might have been anticipated from the similarity of their molecular structures. Product analysis studies indicate that the Cr(II) attacks at the carbonyl oxygen of the coordinated carboxylate in both cases to produce the monodentate oxygen-bonded chromium(III) product as shown in Scheme I. Equilibration studies showed that these products did not undergo any reaction other than slow aquation to the $[Cr(OH_2)_6]^{3+}$ ion.

This type of behavior was also noted in the reduction of the glycinato analogue $[(en)_2Co(OOCCH_2NH_2)]^{2+}$ (**17**) which reacted by attack at the carboxylate oxygen to give the monodentate oxygen-bonded species **14** and had a second-order rate constant of 2.2 M^{-1} s^{-1}.[16] Presumably the $-(CH_2)_nSCH_3$ side chain on the carbon bearing the carboxyl group for the methionine and methylcysteine complexes **1** and **3**, respectively, is sufficiently electron-withdrawing to slow down the rate of reduction to about one-fifth of its value when the oxidant is the glycinatocobalt(III) complex (**17**).

The reduction of the cysteinato species **6** was extremely fast, as was found for other systems in which a cobalt–sulfur bond was present, e.g., the mercaptoacetato[16] (**16**), 2-mercapto-propionate[17] (**15**), and 2-aminoethanethiolato[18] (**18**) complexes (see Table VI). Two reactions were detected in the stopped-flow traces, the first of which was extremely fast with a second-order rate constant of $(2.4 \pm 0.3) \times 10^5$ M^{-1} s^{-1}. The second reaction, which had an inverse hydrogen ion dependence and was again first-order in the reductant concentration, was slower than the first reaction at all acidities studied.

A mechanism consistent with the kinetics and product analysis results is outlined in Scheme II. In this mechanism, the reductant attacks the coordinated sulfur atom to produce the sulfur-bonded monodentate chromium(III) product **21,22**. The intermediate formed in this manner is then attacked by a second Cr(II) at the sulfur and oxygen atoms in a chelated

Scheme II



transition state to give the final S,O-bonded product **7**. The intermediate exists in both the protonated and unprotonated forms and these are reduced at different rates by Cr^{2+} (see Table VI).

The rate expression derived for the second reduction is

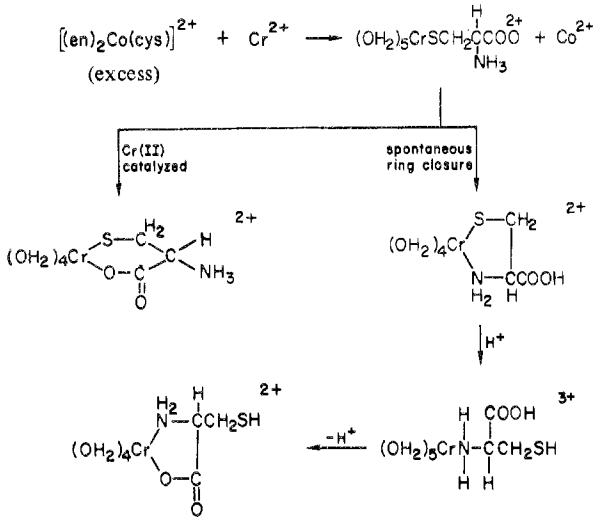
$$\frac{-d[Cr(III)]}{dt} = \left[\frac{k_2[H^+] + k_3K_a}{K_a + [H^+]}\right][Cr(III)]\,[Cr(II)] \qquad (3)$$

where [Cr(III)] represents the total concentration of the protonated and unprotonated forms of the chromium(III) product. Assuming that the K_a of this initially formed product is not much different from that of the bis(ethylenediamine)cobalt(III) complex of cysteine (**6**) containing a free carboxylate group, i.e., $K_a = 2 \times 10^{-4}$,[12] then $[H^+]$ is always much greater than K_a in the denominator of eq 3. Thus, the form of the rate expression reduces to that given in eq 2 (see Figure 2).

An examination of a molecular model of the monodentate chromium(III) sulfur-bonded products **21,22** shows that either the nitrogen atom of the amine group or the oxygen of the carboxylate group must be very close to the sulfur atom at all times since the sulfur imposes a bent or curled structure on the entire ligand. When the oxygen atom is adjacent to the sulfur, the ligand is in an extremely favorable position for attack by a second chromium(II) simultaneously at the oxygen and sulfur atoms of the initially formed chromium(III) product **21,22** in a chelated transition state. This would result in formation of the S,O-bonded species **7** which was the observed product.

A similar reduction mechanism was proposed for the reaction of chromium(II) with pentaamminecobalt(III) complexes of dicarboxylic acids.[19] In this case, reduction through the conjugate base was only observed when a strain-free molecular model of a chelated transition state could be constructed, although chelated products were not isolated. It was concluded that an inverse acid term, which is associated with reduction of a deprotonated form of the complex, is indicative of reduction through a chelated transition state.[20] Our results are in support of this general conclusion, and in addition, we obtained the S,O-bonded chelate as the only reduction product.

Scheme III



A different series of events accompanies the reaction when $[(en)_2Co(Cys)]^{2+}$ (**6**) is in excess over Cr^{2+}. Two reduction products were obtained, the S,O-bonded and N,O-bonded chelates (complexes **7** and **8**, respectively). The N,O-bonded chelate could not have arisen directly by electron transfer since the reduction was several orders of magnitude too fast to be consistent with this hypothesis. It also could not be the direct result of ring closure of the initially formed S-bonded monodentate intermediate **21,22**. Attack of a second Cr(II) at the N and O atoms simultaneously is ruled out since this path was not observed in the Cr^{2+} excess studies and, if slow, this reaction would not be observed in the presence of excess Co(III) since all of the Cr(II) would have been used up in electron transfer. It could not have been a secondary product of S,O-bonded chelate (**7**) rearrangement either, since equilibration studies established that the only reaction that this chelate undergoes is aquation to form $[Cr(OH_2)_6]^{3+}$.

A mechanism consistent with all of the experimental data is that shown in Scheme III. In the presence of excess Cr^{2+}, attack of Cr^{2+} occurs at the S and O atoms of the intermediate **21,22** simultaneously to give the S,O-bonded chelate **7**. With $[(en)_2Co(Cys)]^{2+}$ in excess, some of the Cr^{2+} is still used in a fast second electron-transfer step to give the S,O-bonded product **7** but all of the Cr^{2+} is used up in electron transfer before all of the monodentate S-bonded intermediate **21,22** can undergo this reaction. The intermediate then follows a different pathway. Ring closure occurs across the nitrogen atom to give an S,N-bonded intermediate which is presumably favored because a five-membered ring is formed in preference to the six-membered ring produced in the S,O-bonded chelate. The S,N chelate might be expected to be less stable than the N,O chelate due to the presence of the Cr(III)–S bond. The N,O complex could be formed by ring opening at sulfur in the S,N chelate followed by rapid ring closure across oxygen.[21] In fact, the stable product formed from substitution of cysteine on $Cr(OH_2)_6^{3+}$ is the N,O-bonded chelate. Also, for the 2-aminoethanethiolato system,[18] the S,N-bonded chromium(III) chelate equilibrated slowly to the N-bonded monodentate product at low acidity. Equilibration was complete in 5–7 days.

As mentioned in the Results, the S,O-bonded chelate **7** rapidly aquates, especially on the ion-exchange column, to $[Cr(OH_2)_6]^{3+}$. Other workers have established that for the corresponding chromium(III) S,O-bonded chelates of mercaptoacetate (**10**)[16] and 2-mercaptopropionate (**12**)[17] systems, an equilibrium mixture of S,O-bonded chelate, O-bonded monodentate product, and $[Cr(OH_2)_6]^{3+}$ was gradually formed. The chelates **7**, **10**, and **12** were characterized in all cases by high extinction coefficients ($\sim$70 M^{-1} cm^{-1} at $\sim$550 nm) and a peak in the UV spectrum at about 265 nm (see Table I). The O-bonded monodentate products **9**, **11**, and **13**) have much lower extinction coefficients, no peak in the UV spectrum indicating a lack of a metal–sulfur bond, and a shift of the longest wavelength band in the visible spectrum, to lower energy. The fact that we did not observe any O-bonded monodentate product for the cysteine–chromium(III) system must mean that this species is more unstable to hydrolysis than the S,O-bonded chelate which is surprising in light of the fact that the corresponding methionine– and methylcysteine–chromium(III) complexes (**2** and **4**, respectively) are relatively stable.

The enhancement of reduction rate observed in ethylenediamine complexes of cobalt(III) bonded to sulfur was not observed in the corresponding chromium(III) complexes. However, with the weaker field aquo nonbonding ligands, the reduction of the chromium(III)–thiolato complexes was also very fast[22] (see Table VI, complexes **19–22**). In this case the chromium–sulfur σ bonding was apparently strong enough to labilize the OH_2 trans to the sulfur. A correlation for these kinds of complexes has been shown[22] to exist between the efficiency of electron-transfer bridging and the ability of the sulfur to exert a trans-labilizing effect. Both effects are enhanced by the presence of nonbonding ligands in the order $OH_2 > NH_3 >$ en.

Thus the very fast rate of Cr(II) reduction of the monodentate S-bonded cysteine complex of Cr(III) (**21,22**) is apparently the result of (1) the ability of the sulfur to labilize the OH_2 trans to itself and (2) chelation in the transition state. The Cr^{2+}-catalyzed ring closures of the monodentate chromium(III) complexes of mercaptoacetate, $[(OH_2)_5CrSCH_2COOH]^{2+}$,[23] and 2-mercaptopropionate, $[(OH_2)_5CrSC(CH_3)HCOOH]^{2+}$,[23] are postulated to occur by a similar mechanism. A lower limit of $\sim 10^4$ M^{-1} s^{-1} at $[H^+] = 0.1$ M and $\mu = 1.0$ M ($LiClO_4$) was estimated (see Table VI, complexes **20** and **19**).

In terms of detailed mechanisms, a radical-ion path[24] is not likely for cysteine as ligand since it is readily oxidized rather than reduced. The similar rates obtained for reduction of $[(en)_2Co(Cys)]^{2+}$ (**6**) and $[(OH_2)_5Cr(Cys)]^{2+}$ (**21,22**), both by attack at coordinated sulfur, result from a ground-state trans effect in the cobalt(III) complex and labilization of the trans OH_2 in the chromium(III) complex. These effects contribute to the facile electron transfer observed and apparently increase as the thiol ligand becomes more oxidizable.[25] Thus a superexchange[26] or resonance-transfer[27] mechanism is likely operative. The same conclusions can be drawn for the ligands mercaptoacetate and 2-mercaptopropionate.

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Registry No. **1**, 63121-03-9; **2**, 63058-90-2; **3**, 63058-91-3; **4**, 63058-92-4; **5**, 63058-93-5; **6**, 63058-94-6; **7**, 63058-95-7; **8**, 63058-96-8; **21**, 63058-97-9; **22**, 63058-98-0; Cr^{2+}, 22541-79-3; *trans*-$[(en)_2CoCl_2]Cl$, 14040-33-6.

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Metal Ion Catalyzed Oxidation of o-Dihydroxy Aromatic Compounds by Oxygen. 1. Redox and Acid–Base Properties of the System 1,2-Naphthoquinone-4-sulfonate/1,2-Dihydroxynaphthalene-4-sulfonate

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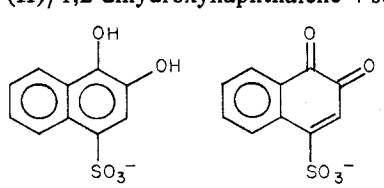
The redox and acid–base equilibria of the oxygen-sensitive couple 1,2-naphthoquinone-4-sulfonate (Q)/1,2-dihydroxynaphthalene-4-sulfonate (PH_2) have been determined at 25 °C and 0.10 M ionic strength. The successive proton formation constants of PH_2, $10^{12.66\pm0.02}$ and $10^{8.14\pm0.04}$ M^{-1}, were obtained by spectrophotometric and potentiometric measurements, respectively. The same values were obtained with both classical and pulsed polarography, and with the latter method the pK of the quinone hydrate was found to be $10^{10.51\pm0.05}$ M^{-1}. From the variation in the slope of the log plot of the polarographic curves with pH, the equilibrium constant for semiquinone (SQ) formation was evaluated as $K(Q + P \rightleftharpoons 2SQ) = 10^{3.2}$. The optical spectrum of the semiquinone was also determined. A special cell was used to carry out simultaneously electrochemical synthesis, potentiometric measurements, and spectrophotometric determinations.

Introduction

Although several authors[1-5] have studied the oxidation reactions of o-dihydroxy aromatic compounds and their metal complexes by dioxygen and by hydrogen peroxide, all of these investigations have been made using benzene derivatives.[6-11] Our preliminary studies[12] have shown that the oxidation of o-phenols such as tiron and catechol by oxygen, even in the presence of a catalyst such as Fe(III), is very slow around neutral pH values. This behavior was attributed to the fact that the standard potential of the Fe^{2+}/Fe^{3+} couple ($E_{Fe}° = 0.749$ V[13]) is lower than the standard potentials of these two catechols.

The literature values[14-19] of the standard potentials of o-dihydroxy aromatic compounds indicate that compounds possessing fused aromatic rings should oxidize more readily than o-diphenols at neutral pH values, i.e., under conditions similar to those found in naturally occurring systems. However, not much work regarding the systematic study of the oxidation–reduction, acid–base, and complexation properties of these compounds has been reported. The practical difficulty of preventing the oxidation of these compounds by atmospheric oxygen has probably been a major deterrent for undertaking such studies.

This paper describes a study of the 1,2-naphthoquinone-4-sulfonate (II)/1,2-dihydroxyhaphthalene-4-sulfonate (I)



I, PH_2 II, Q

couple, Q/PH_2, and also describes the properties of this system from the redox and acid–base points of view.

Experimental Section

Instruments and Reagents. The major apparatus used in this study includes a Beckman pH meter, Model 1019, a Metrohmn pH meter, E 500, Cary 14 and Beckman DBG spectrophotometers, PAR (electrochemistry system No. 170) and Tacussel (modules PRT 30 and UAP 4) polarographs, and a Beckman Electroscan 30 controlled-potential electrolyzer. The cell is described below.

Unless otherwise stated all reagents used were of analytical grade. Solutions were deaerated by purging them with nitrogen gas of 99.99% purity as certified by Bertholet S. A.

Syntheses. Potassium Salt of 1,2-Naphthoquinone-4-sulfonic Acid (Q). A commercially available sample of the potassium salt of 1-amino-2-naphthol-4-sulfonic acid was oxidized to the o-quinone with concentrated nitric acid. The product was recrystallized from water in the presence of bromine.[20,21] Golden yellow needles of the potassium salt of 1,2-naphthoquinone-4-sulfonic acid were obtained and their purity was determined by the UV–visible spectrum of the compound which was found to be identical with that obtained by Rosenblat et al.[22] and by the Danielson test.[23]

Lithium Salt of 1,2-Dihydroxynaphthalene-4-sulfonic Acid (PH_2). Two methods (SO_2[20] or $Na_2S_2O_4$[24]) for reducing Q to PH_2 are described in the literature. In our laboratories neither of these methods gave satisfactory results. The SO_2 reduction was incomplete, and in the second method, the product obtained was found contaminated. PH_2 was therefore prepared by reducing Q with a slight excess of $Na_2S_2O_3$ at pH ~2 using a minimum of water.

After filtration the product was separated from the solution by the addition of a saturated solution of LiCl. If too much LiCl is added, it coprecipitates with the product. The pH of the reaction must be kept at about 2 since the oxidation by air is rapid at higher pH values. For the same reason, filtration must be carried out very rapidly.

Colorless needles of PH_2 were obtained and the following tests showed that the purity of the compound was satisfactory: (1) the UV–visible spectrum obtained after oxidizing an 8×10^{-5} M solution in PH_2 with 1.6×10^{-4} M Ce(IV) in the presence of sulfuric acid (0.005 M) was identical with that of an 8×10^{-5} M solution of Q in the same