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Multiple-Ligand Bridging by Thiocyanate in the Electrochemical Oxidation of Chromium(II) at Mercury Electrodes

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The electrooxidation of Cr(II) at mercury in thiocyanate solutions produces mixtures of Cr(III) products containing as many as four or five coordinated thiocyanate ions. Under a wide range of conditions $Cr(NCS)_2^+$ and $Cr(NCS)_3$ are the predominant products. The *cis* isomer of $Cr(NCS)_2^+$ is certainly formed preferentially and the same preference probably obtains in the case of $Cr(NCS)_3$. The preferential formation of *cis* isomers and the potential dependence of the product distribution are evidence that the mechanism of the electrode reaction involves ligand bridging by adsorbed thiocyanate between the mercury electrode and Cr(II) in the transition state. The chromium(III)–thiocyanate products are very extensively adsorbed on the mercury electrode because of a strong chemical interaction between the positively charged mercury and the sulfur atom of the nitrogen-bonded thiocyanate ion.

Experiments demonstrating that ligand bridging by halide occurs in the oxidation of Cr(II) at mercury electrodes were first described by Aikens and Ross[1] and additional evidence has been presented recently.[2] It includes the facts that $CrCl^{2+}$ and $CrBr^{2+}$, rather than Cr^{3+}, are the predominant Cr(III) products in chloride- and bromide-supporting electrolytes and that the rate of the electrochemical oxidation is enhanced by addition of iodide, bromide, or chloride.[1,2] The rate enhancement decreases in the order $I^- > Br^- > Cl^-$ which is also the order of decreasing specific adsorption of these anions on mercury. The transition state proposed to account for the data involves bridging between the mercury surface and the Cr^{2+} ion by the adsorbed, catalyzing anion.

The properties required of potential bridging ligands at mercury electrodes according to this scheme are strong adsorption on mercury and good electron-bridging characteristics in the same sense as this term is applied in the analogous homogeneous redox processes which proceed by an inner-sphere mechanism.[3] The thiocyanate anion meets both of these requirements because it is known to be strongly adsorbed on mercury by a sulfur–mercury bond and thus has the correct configuration for functioning as a good electron bridge to a cation such as Cr^{2+}.[4] The present study was therefore initiated to determine if thiocyanate does function as a bridging ligand during the electrochemical oxidation of Cr(II). As the work proceeded it became apparent that the thiocyanate complexes of Cr(III) which were the products of the reaction displayed peculiarly strong affinities for the mercury surface. This feature of their chemistry was extensively examined because of its implications with respect to the transition state involved in the thiocyanate-catalyzed electrooxidation of Cr(II).

Experimental Section

Electrochemical Techniques.—Solutions of the Cr(III) products resulting from the electrooxidation of Cr(II) in various electrolytes were prepared for analysis by controlled-potential oxidation of Cr(II) at stirred mercury pool electrodes in a nitrogen atmosphere. The cell and procedure followed standard practice.[5] A Wenking potentiostat (Brinkmann Instruments, Inc.) was employed with solutions of high ionic strength (0.1–1.0 *M*) and a higher voltage potentiostat (Chemical Electronics Co., Newcastle, England) was used with the less conducting solutions. The solutions of Cr(II) were prepared just prior to each run by controlled-potential reduction of Cr(III) on a mercury pool at −1050 mV *vs.* sce. The Cr(II) solutions were oxidized at diverse potentials in the presence of varying concentrations of sodium thiocyanate and the resulting solutions of Cr(III) were analyzed spectrophotometrically, in some cases following ion-exchange separation of the mixture of products.

Cyclic voltammetric[6] and chronocoulometric[7] experiments were performed with conventional two- or three-compartment cells and a commercially available (Brinkmann Instruments, Inc.) hanging mercury drop electrode modified to provide better electrical contact.[8] A drop of area 0.032 cm^2 was employed. A saturated sodium chloride–calomel reference electrode was employed but all potentials are quoted *vs.* the saturated calomel electrode (sce).

The electronic apparatus employed to impose potential variations on the mercury drop electrode and to measure the resulting current and coulomb responses consisted of appropriately connected operational amplifiers (Philbrick Type 656), mercury wetted relays, bias potentiometers, and switches. The design and operation of essentially identical apparatus have been described.[9,10] For the chronocoulometric experiments, in which the extent of adsorption of the various chromium(III)–thiocyanate complexes was measured, a previously described,[11] computer-based data acquisition and analysis system was also employed.

In the chronocoulometric experiments the electrode was adjusted to an initial potential, E_i, where the Cr(III) complex was not reduced. The potential was then stepped to a new potential, E_f, where the reduction of the Cr(III) complex was diffusion controlled and the resulting charge flow was measured. To obtain the quantity of an adsorbed reactant from this charge–time data it is necessary to know how much of the total charge was consumed by the double-layer capacitance at the electrode–

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[1] D. A. Aikens and J. W. Ross, Jr., *J. Phys. Chem.*, **65**, 1213 (1961).

[2] J. J. Ulrich and F. C. Anson, *Inorg. Chem.*, **8**, 195 (1969).

[3] H. Taube, "Advances in Inorganic and Nuclear Chemistry," Vol. 6, Academic Press, Inc., New York, N. Y., 1959, Chapter 1.

[4] R. Parsons and P. C. Symons, *Trans. Faraday Soc.*, **64**, 1077 (1968).

[5] J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, N. Y., 1958, Chapter XIX.

[6] R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969, Chapter 5.

[7] F. C. Anson, *Anal. Chem.*, **38**, 54 (1966).

[8] F. C. Anson and B. Epstein, *J. Electrochem. Soc.*, **115**, 1155 (1968).

[9] G. Lauer, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1967.

[10] F. C. Anson and D. A. Payne, *J. Electroanal. Chem.*, **13**, 35 (1967).

[11] G. Lauer, R. Abel, and F. C. Anson, *Anal. Chem.*, **39**, 765 (1967).

electrolyte interface. When the electrode reaction can be caused to reverse itself by stepping the potential back to E_i, the charge consumed by the double layer is obtainable from an analysis of the charge–time data for the reverse step.[7,12] This procedure has been employed successfully in a number of previous studies.[13-15] It failed, however, in the present instance because with many solution compositions the oxidation of Cr(II) during the reverse potential step did not produce the same chromium(III)–thiocyanate complex that was initially reduced to Cr(II). This difficulty required that the change in double-layer charge between E_i and E_f be measured in a separate experiment. This was accomplished by measuring the charge flowing into a dropping mercury electrode potentiostated at E_i in the presence of the initial chromium(III)–thiocyanate complex and again at E_f. The measurements at E_f (−1000 mV *vs.* sce) were not made in the presence of Cr(II) because there was no evidence of adsorption of any Cr(II) complexes. The theory and practice of this charge-measuring procedure have been described.[14,16,17]

Ion-Exchange Procedures.—Cation and anion exchange[18] were employed to separate mixtures of chromium(III)–thiocyanate complexes for analysis. Dowex 50W-X8 resin in the acid form was used for separation of cations and Bio-Rad AG2-X8 in the perchlorate form was used to separate the anionic complexes. Columns 10 cm in length and 2 cm² in area were utilized. After collecting all cationic Cr(III) species on the column, $Cr(NCS)_2^+$ was eluted with 0.1 *M* $HClO_4$ followed by $Cr(NCS)^{2+}$ with 1 *M* $HClO_4$. The elution rate was 2–3 ml/min.

$Cr(NCS)_3$ was isolated from mixtures by passing the initial effluent from the cation-exchange column through the anion-exchange column and collecting the initial effluent and that resulting from elution with 0.01 *M* $HClO_4$. The anionic chromium(III)–thiocyanate complexes remained on the column and no attempt was made to isolate them.

Analytical Methods.—Quantitative analysis of the solutions of $Cr(NCS)^{2+}$ and $Cr(NCS)_2^+$ resulting from the ion-exchange separations were accomplished spectrophotometrically on the basis of published molar absorbances at 570 nm. These molar absorbances were confirmed by converting the Cr(III) to chromate and measuring the chromate absorbance at 374 nm. The average number, $\bar{n}$, of coordinated thiocyanate ions in the Cr(III) products resulting from controlled-potential oxidations of Cr(II) was established in the following manner. The molar absorptions of $Cr(H_2O)_6^{3+}$, $CrNCS^{2+}$, $Cr(NCS)_2^+$, $Cr(NCS)_3$, and $Cr(NCS)_6^{3-}$ at 570 nm are known[18,19] and increase monotonically with increasing number of coordinated thiocyanate ions (Figure 1). The molar absorptions of $Cr(NCS)_4^-$ and $Cr(NCS)_5^{2-}$ were approximated by interpolation from the known values and $\bar{n}$ was estimated by measuring the absorbance of the oxidized solution at 570 nm. That the values of $\bar{n}$ resulting from this procedure were reasonably accurate was established by applying it to a solution containing known quantities of $Cr(NCS)_3$, $Cr(NCS)_2^+$, $CrNCS^{2+}$, and $Cr(H_2O)_6^{3+}$. The $\bar{n}$ value obtained from the absorbance at 570 nm and Figure 1 was within 10% of the true value.

That the chromium(III)–thiocyanate species which was retained by neither the cation- nor the anion-exchange resin was indeed $Cr(NCS)_3$ was confirmed by direct analysis for chromium and thiocyanate. Chromium was determined by oxidation to CrO_4^{2-} with hydrogen peroxide in alkaline solution and measurement of the absorbance of the resulting chromate ion at 374 nm. Thiocyanate was determined by degradation of the complex in NaOH followed by acidification to pH 1.0 and potentiometric titration with Ag^+ or measurement of the absorbance of the ferric thiocyanate complex at 460 nm. When the latter method was used, any free NCS^- which might be present and which would lead to erroneous results for the thiocyanate to chromium ratio was determined prior to degradation of the complex, a correction being made for the absorbance of $Cr(NCS)_3$ at 460 nm. In some instances it was found that a small amount of free NCS^- passed through the anion-exchange column. Because of the extensive reaction between $Cr(NCS)_3$ and Ag^+, such free NCS^- could not be determined by titration with Ag^+ in the presence of $Cr(NCS)_3$ so the ferric thiocyanate method was preferred in general. Ratios of thiocyanate to chromium of 3.02, 2.98, and 2.88 were obtained from analysis of aliquots from three different electrochemical preparations. The molar absorptivity of the $Cr(NCS)_3$ which resulted from the electrochemical oxidation of Cr(II) in 0.02 *M* NaNCS was ϵ 67, λ_{max} 569 nm. The stereochemical purity and configuration of this species were not established.

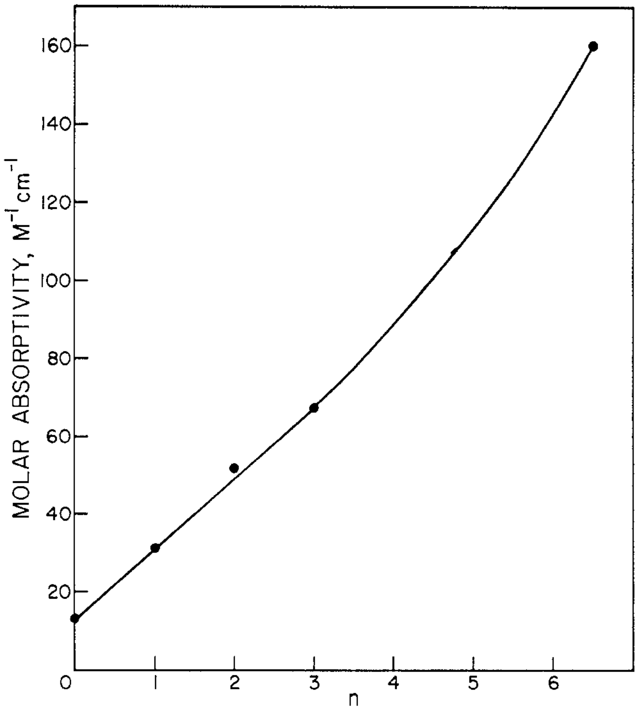

Figure 1.—Molar absorptivities at 570 nm of the $Cr(NCS)_n^{3-n}$ complexes as a function of *n*. The values at *n* = 2 and *n* = 3 are from ref 18. For *n* = 0 and *n* = 6 values given in ref 19 were used, although they refer to 575 and 565 nm, respectively. (The absorptions show very little wavelength dependence in this portion of the spectrum.) The value for *n* = 3 resulted from the present study.

Reagents.—All reagents were analytical grade and solutions were prepared with triply distilled water. Chromium(III) perchlorate was obtained by reduction of $Na_2Cr_2O_7$ with H_2O_2 in an excess of $HClO_4$. The Cr(III) solutions were kept acidic, 0.1 *M* $HClO_4$, to minimize polymer formation and were periodically examined spectroscopically according to the criteria of Posthmus and King[20] to ensure the absence of significant polymerization. Most experiments were performed with solutions containing 0.01 *M* $HClO_4$ but the Cr(III) was exposed to this higher pH only for the duration of the experiment (never more than 4 hr). Sodium perchlorate stock solutions (8 *M*) were prepared by mixing equivalent amounts of concentrated perchloric acid and sodium carbonate. The resulting solution (pH 8) was heated overnight on a hot-water bath and then filtered through sintered glass. CO_2 was eliminated by bubbling N_2 through the filtrate. The pH was finally adjusted to 2 with $HClO_4$.

Sodium thiocyanate solutions were prepared from reagent

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[12] J. H. Christie, R. A. Osteryoung, and F. C. Anson, *J. Electroanal Chem.*, **13**, 236 (1967).

[13] F. C. Anson, J. H. Christie, and R. A. Osteryoung, *ibid.*, **13**, 343 (1967).

[14] F. C. Anson and D. J. Barclay, *Anal. Chem.*, **40**, 1791 (1968).

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[18] E. L. King and E. B. Dismukes, *J. Am. Chem. Soc.*, **74**, 1074 (1952).

[19] A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier Publishing Co., Amsterdam, 1968, p 275.

[20] C. Posthmus and E. L. King, *J. Phys. Chem.*, **59**, 1216 (1955).

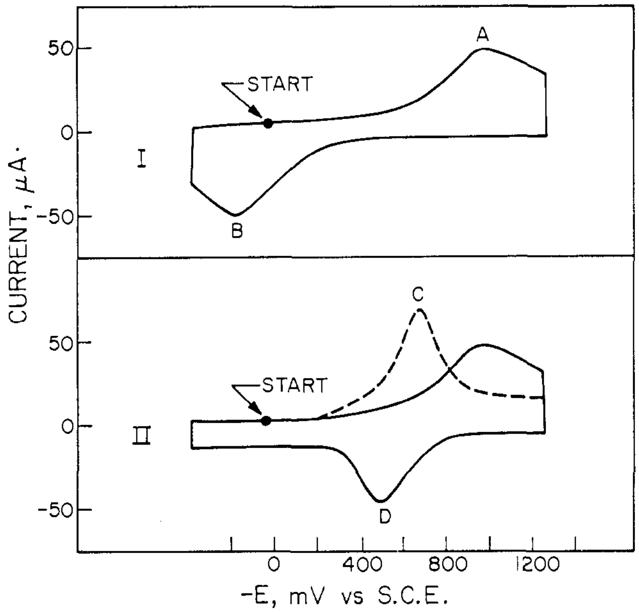

Figure 2.—Cyclic voltammetry of Cr(III) in thiocyanate. I: 0.5 m*M* Cr^{3+}, 1 *M* $NaClO_4$, and 0.01 *M* $HClO_4$; scan rate 25 V/sec. II: identical with I except the solution also contained 2 m*M* NaNCS.

grade salt and were discarded after *ca.* 12 hr. Prepurified nitrogen was further purified by passing it through heated copper turnings, then through a Dry Ice–acetone trap, and, finally, through 1 *M* $HClO_4$ to adjust its humidity. All experiments were performed at room temperature (25 ± 2°).

Results

Cyclic Voltammetry.—The cyclic-voltammetric behavior of Cr^{3+} in the absence and presence of thiocyanate (shown in Figure 2) gives a clear qualitative picture of the catalytic effect of small amounts of thiocyanate on the oxidation rate of Cr^{2+}. Curve I shows the typical pair of cathodic and anodic waves obtained with solutions of Cr^{3+} in perchlorate electrolytes. Curve II shows the different behavior resulting from the presence of 2 m*M* sodium thiocyanate. At the peak of the anodic wave in curve II, peak D, the rate of oxidation of Cr^{2+} is proceeding about 250 times greater than at the same potential in curve I. The cathodic peak labeled C in curve II appears only on the second and all subsequent cycles. This indicates that the species being reduced at peak C was not initially present in the solution but was produced during the first anodic-going half-cycle of the potential sweep. The proximity of peak C to the anodic peak D suggests that the product or products of the anodic reactions proceeding at peak D are the species which subsequently give rise to cathodic peak C. This interpretation is supported by the observation that peak A, which corresponds to the reduction of Cr^{3+} to Cr^{2+}, and peak B, which corresponds to the reverse of this reaction, remain undiminished on repeated cycling in the absence of thiocyanate but virtually disappear in the presence of thiocyanate because the Cr^{2+} is oxidized almost exclusively to chromium(III)–thiocyanate complexes which are reduced at potentials near peak C.

That N-bonded Cr(III)–NCS complexes are responsible for peak C in Figure 2 was verified by examining the cyclic-voltammetric behavior of $CrNCS^{2+}$ and $Cr(NCS)_2^+$ (prepared chemically by the method of King, *et al.*[18]) and $Cr(NCS)_3$ (isolated by passing the chemically prepared mixture of Cr(III)–NCS species successively through cation- and anion-exchange resins). At a scan rate of 25 V/sec the cathodic peak potentials of $CrNCS^{2+}$, $Cr(NCS)_2^+$, and $Cr(NCS)_3$ were −930, −670, and −700 mV, respectively. Thus, peak C, which occurs at −680 to −700 mV on the second and subsequent potential sweeps, apparently arises from the reduction of Cr(III) complexes that contain at least two coordinated thiocyanate ions.

The potential of the anodic peak D in Figure 2 is a very sensitive function of the concentration of free thiocyanate ion, Table I. The shift of the peak potential for Cr(II) oxidation to more cathodic values as the concentration of thiocyanate increases reflects the strong catalytic effect of the thiocyanate anion. That the site of the catalysis is the electrode surface is indicated by the temperature dependence of the anodic peak potential, Table II. The shift in the peak potential to more anodic values at the higher temperature corresponds to a *decreased* overall reaction rate at the higher temperature. This seems surely to reflect the decrease in specific adsorption of thiocyanate at the higher temperature[21] which results in a decline in the surface catalysis. More positive potentials are required to achieve the same rate at 70° because it is necessary to bring the thiocyanate adsorption back to the value prevailing at 25°.

Table I

Effect of Thiocyanate Concentration on the Peak Potential for Oxidation of Cr(II) (Peak D in Figure 2)[a]

[Thiocyanate], m*M*	[Cr(II)], m*M*	Peak potential, mV *vs.* sce
0	0.5	+50
0.4	0.2	−330
0.5	0.5	−360
1.0	0.5	−407
1.34	0.67	−424
1.5	0.5	−450

[a] Potential sweep rate 25 V/sec.

Table II

Temperature Dependence of the Peak Potential for Cr(II) Oxidation in Thiocyanate[a]

Temp, °C	Peak potential, mV *vs.* sce
25	−470
70	−330

[a] [Cr(II)] = 2 m*M*; [SCN] = 1.5 m*M*; sweep rate 20 V/sec.

To confirm that the catalysis resulting from the addition of thiocyanate arises entirely from thiocyanate ions which are adsorbed on the mercury surface, the cyclic voltammetry of a solution containing both thiocyanate and a larger amount of iodide was examined. Iodide ion is more strongly adsorbed on mercury than thiocyanate[4,22] but has a very much smaller tendency

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(21) S. Minc and J. Andzejczak, *J. Electroanal. Chem.*, **17**, 101 (1968).

(22) D. C. Grahame, *J. Am. Chem. Soc.*, **80**, 4201 (1958).

to coordinate with Cr^{2+} in the bulk of the solution.[23] Therefore the addition of iodide to a thiocyanate solution of Cr^{2+} should not alter the concentrations or rate of formation of any chromium(II)–thiocyanate complexes but should decrease the amount of thiocyanate adsorbed on the mercury surface by replacing it with iodide. The result of this experiment was that the chromium(II) oxidation wave (peak D, Figure 2) shifted from −550 to −520 mV when the 0.5 m*M* chromium(III)–10 m*M* NaNCS solution was made 0.1 *M* in NaI. This anodic shift in peak potential reflects a marked decrease in the catalytic effect of thiocyanate in the presence of excess iodide ion.

TABLE III

AVERAGE NUMBER OF COORDINATED THIOCYANATE IONS IN THE Cr(III) PRODUCTS RESULTING FROM ELECTROOXIDATION OF Cr(II)[a]

[Thiocyanate], m*M*	Potential at which Cr(II) was oxidized, mV *vs.* sce[b]	Absorbance of product solution at 570 nm	$\bar{n}$	Calcd equil value of $\bar{n}$[c] Cr(III)	Cr(II)
10	−150	0.27	0.75 ± 0.1	0.3	0.01
20	−250	0.49	1.80 ± 0.2	0.9	0.02
100	−350	0.76	3.5 ± 0.3	2.7	0.10
1000	−550	1.04	4.5 ± 0.4	4.2	1.00

[a] The Cr(II) concentration was 10 m*M*. [b] The oxidation potentials were chosen to avoid any oxidation of mercury while keeping the amount of adsorbed thiocyanate fairly constant at each concentration. [c] Calculated from equilibrium constants given in ref 24. The values of $\bar{n}$ for Cr(II) are probably somewhat too low at the two highest concentrations of thiocyanate because no constants are available for higher complexes than $Cr(NCS)_2$.

Controlled-Potential Electrolyses.—Exhaustive electrolyses of Cr(II) solutions at stirred mercury pools were carried out to obtain sufficient quantities of the Cr(III) products for ion-exchange separation and/or spectrophotometric analyses. The average number, $\bar{n}$, of coordinated thiocyanate ions in the Cr(III) products was estimated spectrophotometrically as explained in the Experimental Section. Table III shows the variation of $\bar{n}$ with the thiocyanate concentration and compares the measured values of $\bar{n}$ with the values that would be observed if the chromium(III) or chromium(II) were allowed to reach equilibrium in each thiocyanate solution.[24] The significant feature of these data is the coordination of much more than the equilibrium quantity of thiocyanate in the Cr(III) product. The inertness of Cr(III) toward substitution of thiocyanate means that all of the coordinated thiocyanate ions appearing in the product must have been present in the transition state for the electrode reaction.

The possibility that Cr^{2+} coordinates with several thiocyanate ions in a homogeneous chemical reaction just prior to formation of the transition state for the electrode reaction could not be ruled out by resorting to the arguments given previously[2] to demonstrate the absence of such prior complexation reactions in the cases of chloride and bromide ligands, because the equilibrium stability of chromium(II)–thiocyanate complexes is considerably greater than the halide complexes. However, strong evidence against the likelihood of prior complexation between chromium(II) and thiocyanate is provided by the potential dependence of the composition of the chromium(III)–thiocyanate products. Table IV gives the results of a series of controlled-potential oxidations of chromium(II) in a 20 m*M* thiocyanate solution at three different potentials. It is evident from these data that more thiocyanate is incorporated into the chromium(III) product, the more positive is the potential at which the chromium(II) is oxidized.

TABLE IV

POTENTIAL DEPENDENCE OF THE AMOUNT OF COORDINATED THIOCYANATE IN THE Cr(III) PRODUCTS RESULTING FROM ELECTROOXIDATION OF Cr(II)[a]

Potential of oxidn, mV *vs.* sce	Fraction of Cr(III) appearing as Cr^{3+}[b]	$CrNCS^{2+}$	$Cr(NCS)_2^+$	$Cr(NCS)_3$	Higher complexes
−150[c]	~0.2	<0.05	0.25	0.5	<0.05
−300[c]	~0.2	<0.05	0.25	0.5	<0.05
−550[d]	~0.3	0.2	0.45	0.05	<0.05
Equil distribution[e]	0.18	0.68	0.09	0.05	. . .
Equil distribution of corresponding Cr(II) complexes[e]	0.80	0.18	0.02	. . .	. . .

[a] Each solution contained 10 m*M* Cr(II), 20 m*M* NaSCN, and 0.01 *M* $HClO_4$. Analyses were performed spectrophotometrically following separation of the products by ion exchange. [b] Cr^{3+} was found by difference. Incomplete reduction of the Cr^{3+} during the preparation of the Cr^{2+} solution and some oxidation of Cr^{2+} by residual oxygen probably account for the bulk of this species in the product. [c] Oxidation was complete in *ca.* 60 min. [d] At this potential the electrode reaction proceeded so slowly that 6 hr was required to complete the oxidation. To check that the initial electrode products would persist during this period it was ascertained that $Cr(NCS)_3$ could be kept over a stirred mercury pool for 8 hr without appreciable decomposition. [e] Calculated from equilibrium constants given in ref 24.

Stereochemistry of the Chromium(III) Products.—The appearance of $Cr(NCS)_2^+$ and $Cr(NCS)_3$ among the oxidation products of Cr(II) permitted an investigation of possible stereospecificity in the electrode processes which lead to these products: King, *et al.*,[25a] have shown that in an equilibrium mixture of the two isomers of $Cr(NCS)_2^+$ the ratio of the *trans* to the *cis* isomer is 0.53 and that the two isomers can be distinguished by measuring the ratio of their absorbances at 300 and 270 nm. For the *trans* isomer this ratio of A_{300}/A_{270} is 1.31 while for the *cis* isomer the same ratio is 0.95.[25a]

The products from the controlled-potential oxidations of a series of solutions containing 10 m*M* Cr(II) and 20 m*M* NaNCS were separated by ion exchange and the absorbance ratio A_{300}/A_{270} was measured for the most readily eluted aliquots containing a mixture of the *cis* and *trans* isomers of $Cr(NCS)_2^+$. In four experiments in which oxidation potentials of −550,

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(23) S. Arhland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

(24) A. Martell and L. G. Sillén, "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964, p 126.

(25) (a) J. T. Hougen, K. Schug, and E. L. King, *J. Am. Chem. Soc.*, **79**, 519 (1957); (b) D. W. Carlyle and E. L. King, private communication.

−300, −200, and −150 mV were employed, the distribution of products varied (Table IV) but the $Cr(NCS)_2^+$ fraction in each case gave the same absorbance ratio, $A_{300}/A_{270} = 1.01 \pm 0.01$. A linear interpolation from King's values for the pure isomers leads to a ratio of 0.17 for the ratio of *trans* to *cis* isomers in the electrochemically prepared complex compared with 0.53 for an equilibrium mixture. The numerical value (0.17) of this experimentally measured ratio is probably a reasonably good estimate of the amount of *cis* isomer produced because the rate of *cis* to *trans* isomerization is too slow to alter the ratio during the several hours required for the ion-exchange separation and elution.[25b] It seems certain, therefore, that the *cis* isomer is produced in greater than equilibrium amount during the electrochemical production of $Cr(NCS)_2^+$ and that this preferential formation of the *cis* isomer is independent of the fraction of the total Cr(II) that is oxidized to this complex.

The stereochemical configuration of the $Cr(NCS)_3$ obtained from electrolyses was not established. The electronic spectra of chemically and electrolytically prepared solutions of this complex were not different enough to enable an unambiguous differentiation to be made. However, samples of $Cr(NCS)_3$ prepared chemically display a slightly smaller tendency to adsorb on the surface of mercury electrodes than do electrochemical preparations of the same complex. As is elaborated in the following section, this difference is in the direction to be expected if the electrochemically prepared complex contains a higher percentage of the *cis* isomer.

Adsorption of Chromium(III)–Thiocyanate Complexes on Mercury.—Tanaka and coworkers[26] established from electrocapillary measurements that a number of mixed-ligand thiocyanate complexes of chromium(III) are adsorbed on mercury electrodes. As part of the present study we investigated the adsorptions on mercury of the four complexes $Cr(H_2O)_5NCS^{2+}$, $Cr(H_2O)_4(NCS)_2^+$, $Cr(H_2O)_3(NCS)_3$, and $Cr(NCS)_6^{3-}$. The magnitude and strength of the adsorptions seemed worth pursuing quantitatively because the adsorbed chromium(III) complex is a good model for the transition state in the thiocyanate-catalyzed electrooxidation of chromium(II).

Tables V and VI summarize the adsorption data obtained. The most important features to be noted are the increase in adsorption as the number of coordinated thiocyantes increases from 0 to 3, the slightly but uniformly higher adsorption of the electrolytically prepared $Cr(NCS)_2^+$ and $Cr(NCS)_3$, the relatively minor potential dependence of the adsorption, and the decrease in adsorption produced by the presence of free thiocyanate ions.

The increase in adsorption with the number of coordinated thiocyanates reflects both the increasing number of bonding sites and the decreasing coulombic repulsion between the positively charged electrode and the adsorbing cation. The maximum adsorption attained with the neutral and presumably most weakly hydrated complex, $Cr(NCS)_3$ would probably be sharper except that the electrode surface is virtually fully covered by 25×10^{-11} mol/cm^2 of $Cr(NCS)_3$ and the fact that the adsorption of the anionic complexes resulting from coordination of additional thiocyante ions is enhanced by their more favorable coulombic interaction with the positively charged electrode. The slightly larger adsorption of the $Cr(NCS)_2^+$ prepared electrochemically is consistent with the previous demonstration that the *cis* isomer of this complex is formed preferentially during the electrolytic synthesis. The parallel behavior displayed by the two preparations of $Cr(NCS)_3$ provides some evidence to support the expectation that preferential formation of the *cis* isomer of this complex is achieved during its electrolytic preparation.

TABLE V

ADSORPTION OF CHROMIUM(III)–THIOCYANATE COMPLEXES ON MERCURY ELECTRODES

Potential, mV *vs.* sce	$10^{11}\Gamma_{Cr(III)}$,[a,b] mol/cm^2						
		$CrNCS^{2+}$	$Cr(NCS)_2^+$		$Cr(NCS)_3$		
	Cr^{3+}	Chemical[c] synthesis	Electrolytic[d] synthesis	Chemical[c] synthesis	Electrolytic[d] synthesis	Chemical[c] synthesis	$Cr(NCS)_6^{3-}$
200	0	0.6	12.5	...	...	...	...
100	0	0.8	10.6	...	...	...	18.2
0	0	1.1	9.8	8.5	25.2[e]	22.7	19.7
−100	0	1.3	9.0	7.9	22.6	21.3	20.0
−200	0	1.3	7.9	7.2	20.3	19.5	19.3
−300	0	1.0	7.6	7.0	19.9	17.5	17.2
−400	0	1.0	...	...	...	...	12.5

[a] The concentration of the complex was 0.5 mM in each case. The supporting electrolyte was 0.01 M $HClO_4$–0.99 M $NaClO_4$. [b] The values of $\Gamma_{Cr(III)}$ were evaluated chronocoulometrically as described in the Experimental Section. The values listed are estimated to be accurate to $\pm 0.5 \times 10^{-11}$ mol/cm.^{2} [c] Synthesis and ion-exchange separation of the product mixtures followed the directions of King and Dismukes.[18] The neutral complex was separated as described in the Experimental Section. [d] Electrolytic synthesis involved oxidation at a stirred mercury pool of a solution containing 10 mM Cr(II) and 20 mM NaNCS (also containing 0.01 M $HClO_4$ and 0.05 M $NaClO_4$) at −300 mV followed by ion-exchange separation of the product mixture. [e] This value may be somewhat too large because of an incipient reaction between the electrode and the complex at this potential.

TABLE VI

DEPENDENCE OF THE ADSORPTION OF $Cr(NCS)_3$ ON THE THIOCYANATE CONCENTRATION[a]

Potential, mV *vs.* sce	Thiocyanate concn, M				
	0	5×10^{-3}	2.5×10^{-2}	10^{-1}	1
	$10^{11}\Gamma_{Cr(III)}$,[b] mol/cm^2				
0	22.7	13.8	...	...	...
−100	21.3	17.9	15.4	...	...
−200	19.5	19.0	17.5	13.6	...
−250	18.9	18.8	17.9	13.9	4.9
−300	17.5	18.5	17.4	15.1	5.3
−350	15.1	17.5	16.9	14.9	5.4
−400	...	...	...	14.5	5.5

[a] The concentration of $Cr(NCS)_3$ was 0.5 mM. The complex was prepared chemically and isolated by ion exchange. [b] The $\Gamma_{Cr(III)}$ values were evaluated chronocoulometrically and are estimated to be accurate to $\pm 0.5 \times 10^{-11}$ mol/cm.^{2}

Discussion

On the basis of the data presented, we conclude that thiocyanate ions, which are adsorbed on the mercury

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(26) N. Tanaka, E. Kyuno, G. Satô, and R. Tamamushi, *J. Phys. Chem.*, **66**, 2706 (1962).

electrode surface, bind to Cr^{2+} in the transition state and serve as electron-transfer bridges during the oxidation of Cr(II). Five aspects of the results support this conclusion.

(1) The dependence of the composition (*i.e.*, number of coordinated thiocyanate ions) of the chromium(III) products on the electrode potential (Table IV) indicates that the number of thiocyanate ions in the transition state is affected by electrode potential. The number of adsorbed thiocyanate ions is known[4,21] to increase steadily as the electrode potential becomes more positive while the concentrations of all unadsorbed ions are unaffected by changes in electrode potential. (This ignores the enhancement and depression of ion concentrations within the diffuse double layer, but the observed potential dependences are in the opposite direction from any expected double-layer contributions which should be very small in any case at $\mu = 1.0$.) The electrode surface seems, therefore, to be the site at which the transition state is assembled from adsorbed thiocyanate ions and a Cr^{2+} ion.

(2) The fact that iodide ion depresses the catalytic effect of thiocyanate even though iodide offers little competition to thiocyanate for the Cr^{2+} ions in the bulk of the solution can be understood in terms of the competition between iodide and thiocyanate for the electrode surface and, thereby, for a place in the transition state which is formed there.

(3) The preferential formation of the *cis* isomers of $Cr(NCS)_2^+$ and (probably) of $Cr(NCS)_3$ during the electrooxidation of Cr(II) provides particularly clear evidence for a surface transition state with bridging thiocyanate ions attached by mercury–sulfur and chromium–nitrogen bonds. The ability of the mercury electrode to stabilize such a configuration is indicated by the unusually strong adsorption of the products, $Cr(NCS)_2^+$ and $Cr(NCS)_3$. The fact that some *trans*-$Cr(NCS)_2^+$ results from the electrooxidation suggests that oxidation of $CrNCS^{2+}$ *via* a single adsorbed thiocyanate ion may be an additional reaction pathway.

(4) The apparently anomalous sign of the temperature dependence of the peak potentials for the oxidation of chromium(II) (Table II) seems less unusual when compared with the temperature dependence of thiocyanate ion adsorption, which has the same sign.[21] The fact that the rate of oxidation of chromium(II) follows the thiocyanate adsorption so closely strongly implicates the electrode surface as the seat of the rate-determining process.

(5) The failure of the chromium(III)–thiocyanate product distribution to follow more closely the equilibrium distribution of chromium(II)–thiocyanate complexes (Table III) argues circumstantially against a homogeneous complexation reaction prior to the electrode reaction as the source of the catalysis of chromium(II) oxidation by thiocyanate. The thiocyanate concentration dependence of the observed product distribution can be understood in terms of a strong kinetic preference for oxidation of Cr^{2+} ions which are attached to the electrode surface by two or three adsorbed thiocyanate ions. Analogous examples of kinetic preference for a multiply bridged transition state are known for a few inner-sphere homogeneous redox reactions.[27] The increase in $\bar{n}$ to values greater than 4 in 1 *M* sodium thiocyanate (Table III) probably reflects a reaction pathway in which $Cr(NCS)_2$ and $CrNCS^+$ ions, formed in the bulk of the solution, coordinate with three additional adsorbed thiocyanate ions prior to electron transfer.

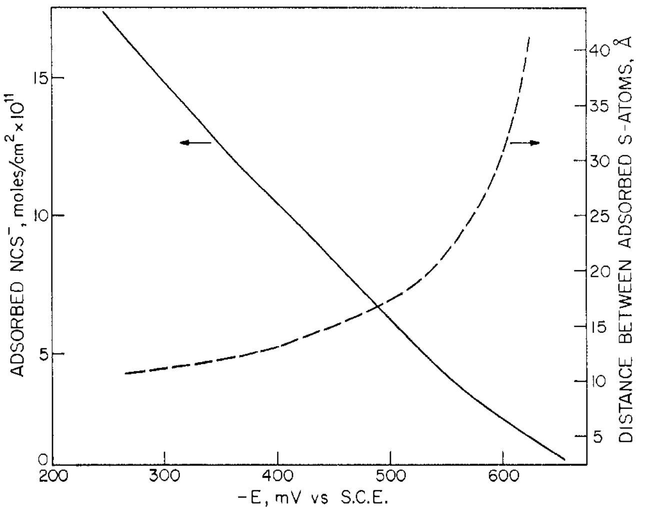

Figure 3.—Potential dependence of thiocyanate ion adsorption and of the distance between sulfur atoms in adsorbed thiocyanate. Adsorption data are from Parsons and Symons[4] for a 25 m*M* NaNCS solution.

The chromium(III)–thiocyanate complexes which result from controlled-potential electrolyses have the spectra of the nitrogen-bonded isomers.[20] The possibility that the sulfur-bonded linkage isomers might be formed initially[28] could not be ruled out in these experiments because of the rapid isomerization of the sulfur-bonded complexes induced by the presence of Cr^{2+}.[29] However, in rapid potential sweep experiments the presence of significant amounts of the sulfur-bonded isomer could have been detected from its characteristically different reduction potential.[30] No evidence for this species was found and we are reasonably confident that the more stable, nitrogen-bonded complexes are the primary products of the electrode reaction.

Larger amounts of $Cr(NCS)_2^+$ and $Cr(NCS)_3$ appear in the reaction products (Table IV) at more positive potentials. This indicates that transition states with two and three bridging ions are favored at more positive potentials. This trend may reflect nothing more than the changes in surface concentration of thiocyanate that changes in the potential produce. Figure 3 shows how the amount of adsorbed thiocyanate and the equilibrium distance between the centers of the sulfur atoms in the adsorbed thiocyanate ions depend upon the electrode potential in a 25 m*M* thiocyanate solution. The

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[28] N. Sutin, *Electrochim. Acta*, **13**, 1175 (1968).

[29] A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 434 (1966).

[30] D. I. Bustin and J. E. Earley, *Inorg. Chem.*, **7**, 1438 (1968)

equilibrium distance between coplanar sulfur atoms in the octahedral complexes *cis*-$Cr(H_2O)_4(NCS)_2^+$ and *cis*-$Cr(H_2O)_3(NCS)_3$ can be calculated to be *ca.* 8–10 Å. Thus, Figure 3 shows that at −500 mV a substantial rearrangement of the adsorbed thiocyanate ions would be required to obtain a double- or triple-ligand bridge, while at −250 mV the adsorbed ions are quite favorably placed for the formation of multiple bridges.

No evidence for multiple-ligand bridging was found during electrooxidation of chromium(II) in halide solutions[2] and it seems likely that this capability may be restricted to thiocyanate and very similar ambidentate ligands which leave a nicely positioned coordination position exposed after forming a strong bond with the mercury surface. In addition, some unusual chemistry appears to be responsible for the stabilization of the multiply bridged transition state and for the remarkably strong adsorption of the chromium(III) products. The cationic $Cr(NCS)_2^+$ ion is adsorbed more strongly on mercury than is free NCS^- ion itself at comparable concentrations in spite of the fact that the mercury surface is positively charged at the potentials involved. For example, at −300 mV where the mercury surface bears a charge of *ca.* $+5\ \mu C/cm^2$, 7.6×10^{-11} mol/cm^2 of $Cr(NCS)_2^+$ is adsorbed from a 0.5 m*M* solution while only 4×10^{-11} mol/cm^2 of NCS^- is adsorbed at the same electrode charge from a 1 m*M* solution.[4] The dependence of the adsorption of $Cr(NCS)_2^+$ upon the electrode potential (and, therefore, surface charge density) shown in Table V is very much smaller than for thiocyanate ion itself,[4] suggesting that purely coulombic forces are not the major factor controlling the adsorption of the complex. The data in Table V make it clear that the adsorption of $Cr(NCS)_3$ is not similar to the "anion-induced" adsorption of white metal cations (Cd^{2+}, Zn^{2+}, In^{3+}) that have been studied in some detail[14,15] because no free thiocyanate ion is required for the adsorption to occur. The fact that rather high concentrations of free thiocyanate are required to alter significantly the adsorption of $Cr(NCS)_3$ (Table VI) shows that thiocyanate ions are able to win out over the complex in the competition for the electrode surface only when the thiocyanate is given the advantage of a much larger activity.

We believe this unusual adsorption behavior of the chromium complexes is understandable in terms of its similarity to the surprisingly strong affinity that several positively charged chromium(III)– and cobalt(III)–thiocyanate complexes display toward mercury(II) cations.[31] For example, Armor and Haim have shown recently[32] that the reaction $Hg^{2+} + CrNCS^{2+} = CrNCSHg^{4+}$ has an equilibrium constant of $10^4\ M^{-1}$. The stability of such highly charged mercury(II) adducts arises in part from an increase in the ligand field stabilization energy produced by an increase in the ligand field at the nitrogen atom when the sulfur–mercury bond is formed.[33] Spectral experiments suggest that the increased ligand field at nitrogen results from an increase in chromium to ligand π bonding when mercury(II) binds to sulfur.[34] In any case, the similarity between a mercury(II) cation and a positively charged mercury metal surface seems close enough to justify the assertion that very similar chemistry is involved in the interaction of both with chromium(III)–thiocyanate complexes.

If this explanation is basically accurate, one is led to expect adsorption on positive mercury surfaces of many nitrogen-bonded transition metal–thiocyanate complexes. The extent of the adsorption is predicted to be greater, the larger the value of the ligand field stabilization energy (LFSE).[35] This prediction is borne out by the systems which have been investigated up to now. Both vanadium(II) and vanadium(III) thiocyanates are adsorbed but the latter (with the larger Δ) much more strongly than the former.[36] Nickel(II) (with a large LFSE) is adsorbed from thiocyanate solutions while manganese(II) (LFSE ≈ 0) is not.[37]

The chemical properties of the mercury electrode clearly play a key role in the electrooxidation of chromium(II) *via* thiocyanate ligand bridges. (The overall process bears much similarity to the oxidation of Cr^{2+} by solid AgSCN which also leads to $CrNCS^{2+}$.[38]) The unusual ability of thiocyanate ion both to bind certain transition metal complexes to mercury surfaces and to catalyze their oxidation or reduction may be exploitable in a number of interesting ways. The possibility of stereoselective electrolytic preparations of metal complexes is apparent from the present work with chromium(II) oxidation. Another possible application, presently under investigation, is the use of metal–thiocyanate complexes, adsorbed on mercury, as sites for the binding and subsequent (possibly catalyzed) electroreduction of suitable ligands.

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