Polarographic Studies of Metallic Complexes. II.[1] *Isothiocyanato-ammine and Related Complexes of Chromium (III)*[2]

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There have been few reports on the relation between the half-wave potentials of chromium (III) complexes and their chemical structures, while some studies have been reported for the cobalt(III) complexes by several authors[1,3-6].

The present paper deals with the polarography of isothiocyanato-ammine series of chromium(III) complexes and the related compounds such as [Cr en_3]Cl_3, [Cr $en_2(NCS)_2$]Cl, or [Cr en_2Cl_2]Cl. The main purpose of this study is to examine the relationship between the polarographic stabilities of these complexes and their chemical structures. Furthermore, some examples of polarographic behavior of Reinecke's salt and *cis*-[Cr $en_2(NCS)_2]^+$ will be reported and discussed. These two salts are quite different from the other members of the chromium(III) isothiocyanato-ammine series from the viewpoint of their catalytic influences on the double wave of the oxygen dissolved in solution.

Experimental

Apparatus—A Heyrovsky-Shikata type polarograph, similar to that previously described[1], was employed to take the polarograms. An H-cell with a saturated calomel electrode was used. Two kinds of capillary were employed for measurements. One of them had an *m*-value of 5.828 mg./sec. and a drop time of 4.00 sec./drop and the other had an *m*-value of 33.661 mg./sec. and a drop time of 5.275 sec./drop. These characteristics of capillaries were measured in distilled water at the mercury height of 65 cm. with an open circuit. The cell temperature was maintained at 25±0.1°C by means of a water thermostat. The half-wave potentials were determined from the enlarged polarograms by "plotting method". The potential values were corrected for *iR*-drop by making use of the minimum value of the cell resistance. The reversibilities of the electrode reaction were tested by determining the slopes of $\log i/(i_d-i)$ vs. potential. Slopes of the log-plots indicated irreversible reduction throughout.

Material—The complex compounds studied were prepared by the methods described in literature[7-11] (the references are given in Tables I—II).

Each solution for the electrolysis was made freshly from the dry crystalline chromium(III) complexes before use and polarographic measurements were made as soon as possible after the removal of oxygen. The concentration of the solution was 0.001 F complex ion per litre. In order to remove the dissolved oxygen, a stream of nitrogen, which was purified from oxygen by means of an alkaline solution of pyrogallol, was bubbled through the cell solution for an hour prior to each electrolysis, preventing the evaporation. For the complexes which aquate easily in solution, such as *cis*-[Cr $en_2Cl_2]^+$, nitrogen was bubbled only half an hour and the polarographic runs were completed within ten minutes after the removal of oxygen. No maximum suppressor was used for the purpose of comparing the half-wave potentials of the complexes with one another. The presence of the maximum suppressor causes the lowering of the diffusion current and the shift of the half-wave potential to negative direction. The supporting electrolytes used were 0.1 F potassium chloride and 0.1 F or 1 F potassium thiocyanate.

Results and Discussion

The half-wave potentials of the isothiocyanato-ammine series of chromium(III) complexes are given in Table I. In the neutral and unbuffered solutions of 0.1 F potassium chloride and 0.1 F or 1 F potassium thiocyanate, all the compounds are reduced irreversibly in two steps at the dropping mercury electrode. As is shown in Table I, the half-wave potential

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[2] Presented at the Symposium on Co-ordination Compounds, Nagoya, November 17, 1957.

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TABLE I

HALF-WAVE POTENTIALS OF ISOTHIOCYANATO-AMMINE SERIES OF CHROMIUM(III) COMPLEXES

Complex	SUPPORTING ELECTROLYTE 0.1 F KCl $E_{1/2}$ of 1st Wave	0.1 F KCl $E_{1/2}$ of 2nd Wave	0.1 F KNCS $E_{1/2}$ of 1st Wave	0.1 F KNCS $E_{1/2}$ of 2nd Wave	1 F KNCS $E_{1/2}$ of 1st Wave	1 F KNCS $E_{1/2}$ of 2nd Wave
$[Cr(NH_3)_6]Cl_3$7)	−1.41	−1.65	—	—	—	—
$[Cr(NH_3)_5NCS](NCS)_2$8)	−1.37	−1.65	−1.37	−1.64	−1.38	—*
$[Cr(NH_3)_4(NCS)_2]NCS$9)	−1.34	−1.65	−1.34	−1.65	−1.34	—*
$NH_4[Cr(NH_3)_2(NCS)_4]$10)	−1.31	−1.61	−1.07	—*	−1.23	—*
$K_3[Cr(NCS)_6]$11)	—	—*	−0.74	—*	−0.79	—*

1) The concentration of the complexes: 0.001 F.

2) The characteristics of capillaries used: $\begin{cases} m = 5.828 \text{ mg./sec.} \\ t = 4.00 \text{ sec./drop.} \end{cases}$

3) * Maximum wave

4) Applied potential: V. vs. S.C.E.

5) Temperature: 25°C

TABLE II.

HALF-WAVE POTENTIALS OF THE CHROMIUM(III) COMPLEXES

Complex	$E_{1/2}$ of 1st Wave	$E_{1/2}$ of Aquated Complexes	$E_{1/2}$ of 2nd Wave
$[Cr(NH_3)_6]Cl_3$7)	−1.41	No wave	—*
$[Cr\,en_3]Cl_3\cdot 3.5\,H_2O$14)	−1.38	No wave	—*
trans-$[Cr\,en_2(NCS)_2]Cl$15)	−1.00	−1.30	—*
cis-$[Cr\,en_2(NCS)_2]Cl$14)	−0.96	−1.30	—*
cis-$[Cr\,en_2Cl_2]Cl$15)	−0.76	−1.28	—*

(V. vs. S.C.E.).

Supporting electrolyte: 0.1 F KCl.

Characteristics of capillaries used: $\begin{cases} m = 33.661 \text{ mg./sec.} \\ t = 5.275 \text{ sec./drop.} \end{cases}$

*Maximum wave.

of the first wave shifts to the direction of the more positive potential when the ammonia molecules of $[Cr(NH_3)_6]^{3+}$ are replaced by isothiocyanate ligands. While the half-wave potential of the second wave is always in close proximity to that of $[Cr(OH_2)_6]^{2+}$ ion ($E_{1/2} = -1.63$ V. vs. S.C.E. in 1 F potassium sulfate solution)12). Judging from these facts the first wave apparently represents the reduction of chromium(III) complexes to chromium (II) state, and the second represents the reduction to metallic state.

The height of the second wave is significantly greater than twice that of the first wave. The ratio of the wave heights increases with the decreasing concentration of the chromium(III) complexes. Therefore, the second wave is likely to include the "hydrolysis current" which was thoroughly studied by J. J. Lingane and R. L. Pecsok13). Thus the hydrogen ion from the hydrolysis of the complexes may contribute to the second diffusion current.

In the supporting electrolyte of 1 F potassium thiocyanate the second wave of these chromium(III) complexes have the maxima, which can not be suppressed in the presence of the high concentration of the usual surface active agents such as gelatin, methyl red, Triton-X 100* or Tween-80**.

The process of the reduction of $[Cr(NH_3)_6]^{3+}$ is considered as follows:

$$[Cr(NH_3)_6]^{3+} + e^- \rightarrow [Cr(NH_3)_6]^{2+}$$
$$[Cr(NH_3)_6]^{2+} + 6H_2O \rightarrow [Cr(OH_2)_6]^{2+} + 6NH_3$$
$$[Cr(OH_2)_6]^{2+} + 2e^- \rightarrow Cr + 6H_2O.$$

Similar mechanisms are applicable to the other chromium(III) complexes here studied. Table II shows the half-wave potentials of some chromium(III) complexes other than the isothiocyanato-ammine series.

For the complexes of $[Cr\,en_2X_2]^+$ type it is expected that they are easily aquated in solution. In fact, these complexes gave rise to the two distinct polarographic waves for the reduction step of chromium

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* Alkylated aryl polyether alcohol (Rohm & Haas Co. in U. S. A.).

** Polyoxyethylene sorbitan mono-oleate(Atlas Powder Co. in U. S. A.).

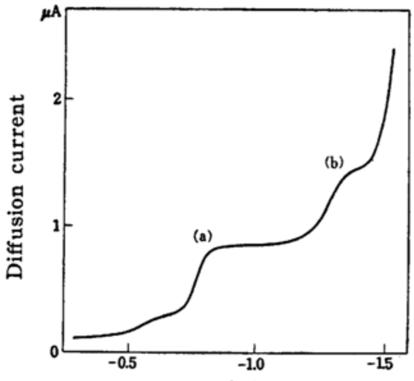

Fig. 1. The polarogram of cis-[Cr en_2Cl_2]Cl in 0.1 F KCl.
The concentration of the complex: 0.001 F.
a) The reduction wave of cis-[Cr en_2Cl_2]$^+$ to Cr(II) state.
b) The reduction wave of the aquated Cr(III) complexes to Cr(II) state.

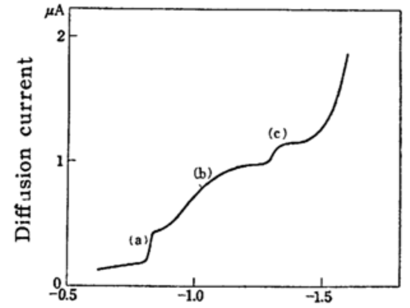

Fig. 2. The polarogram of cis-[Cr $en_2(NCS)_2$]Cl in 0.1 F KCl.
The concentration of the complex: 0.001 F.
a) The oxygen wave. (It was impossible to diminish the wave.)
b) The reduction wave of cis-[Cr $en_2(NCS)_2$]$^+$ to Cr(II) state.
c) The reduction wave of the aquated Cr(III) complexes to Cr(II) state.

(III)→chromium(II). Figs. 1 and 2 show the typical polarograms. This double wave is thought to be due to an aquation of the complexes. In the process of the aquation one or two of the coordinated negative radicals are replaced by water molecules, resulting in an equilibrium mixture of the aquated and the originial species. For instance,

$$trans\text{-}[\mathrm{Cr\ en_2(NCS)_2}]^+ + \mathrm{H_2O} \rightarrow trans\text{-}[\mathrm{Cr\ en_2(OH_2)NCS}]^{2+} + \mathrm{NCS^-},$$

$$trans\text{-}[\mathrm{Cr\ en_2(OH_2)NCS}]^{2+} + \mathrm{H_2O} \rightarrow trans\text{-}[\mathrm{Cr\ en_2(OH_2)_2}]^{3+} + \mathrm{NCS^-}.$$

Thus the first wave of the double wave represents the reduction of the original complex and the second that of the aquated species. This postulate is advanced for the following reason. For the *cis* and *trans* isomer of [Cr $en_2(NCS)_2$]$^+$, the half-wave potentials of the second of the double wave have the same values of −1.30 V. vs. S. C. E. within the experimental errors.

The diffusion current of the second waves increased with time. This evidently owes to the formation of the aquo-complexes. For instance, forty minutes after the preparation of the solution, the height of the second wave of [Cr en_2Cl_2]$^+$ is approximately three times as high as that of the second waye of *cis*- or *trans*-[Cr $en_2(NCS)_2$]$^+$. This means that *cis*-[Cr en_2Cl_2]$^+$ aquates more rapidly than *cis*- or *trans*-[Cr $en_2(NCS)_2$]$^+$.

For the benefit of comparing the half-wave potentials of the first wave with

TABLE III
THE HALF-WAVE POTENTIAL OF THE FIRST WAVE OF THE RELATED COMPLEXES OF Cr(III) AND Co(III)[a,1)]

Cr(III) Complex	$E_{1/2}$
[Cr$(NH_3)_6$]$^{3+}$	−1.41
[Cr en_3]$^{3+}$	−1.38
[Cr$(NH_3)_4(NCS)_2$]$^+$	−1.34
cis-[Cr $en_2(NCS)_2$]$^+$	−0.94
trans-[Cr $en_2(NCS)_2$]$^+$	−1.00
Co(III) Complex[b)]	$E_{1/2}$
[Co$(NH_3)_6$]$^{3+}$	−0.24
[Co en_3]$^{3+}$	−0.43

(V. vs. S.C.E.)

a) The supporting electrolyte: 0.1 F KCl.
b) The experimental conditions are almost the same as for the Cr(III) complexes except the temperature and the characteristics of the capillaries.

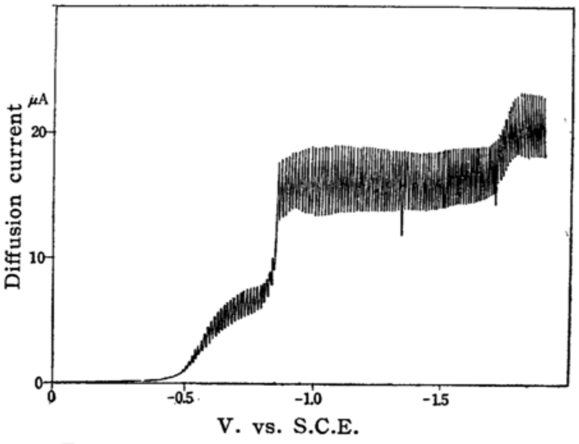

Fig. 3. The polarogram of the double wave of oxygen in the presence of 0.001 F NH_4[Cr$(NH_3)_2(NCS)_4$] and 0.1 F KCl.

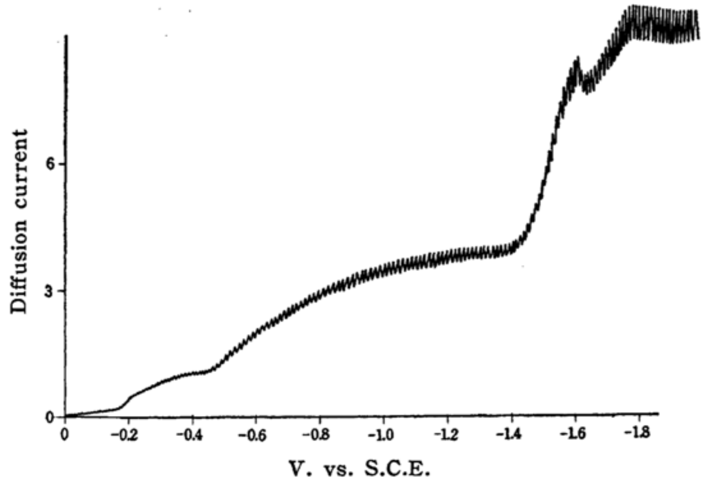

Fig. 4. The polarogram of 0.001 F $K_3[Cr(NCS)_6]$ in 0.1 F KCl. This polarogram was taken immediately after bubbling nitrogen through the solution for an hour.

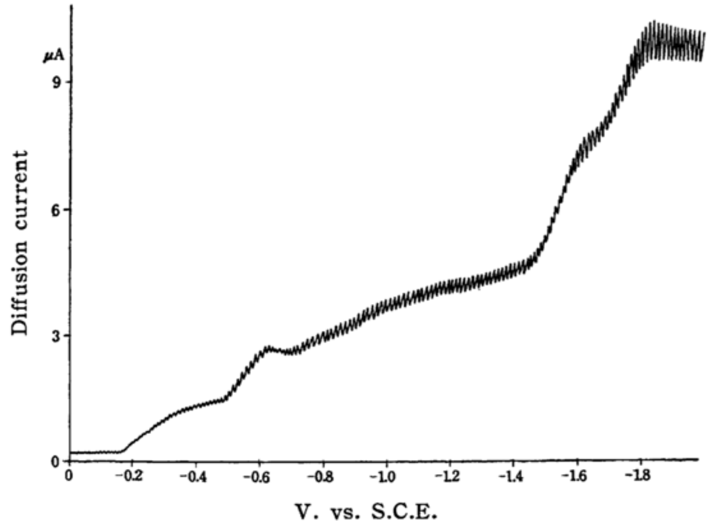

Fig. 5. The polarogram of 0.001 F $K_3[Cr(NCS)_6]$ in 0.1 F KCl. This polarogram was taken ten minutes after the polarographic run of Fig. 5 being completed. It was impossible to determine the half-wave potential of $K_3[Cr(NCS)_6]$ in 0.1 F KCl owing to the interference of the double wave of oxygen.

one another, a part of the data is picked up again here in Table III.

From the comparison of the half-wave potentials for the reduction step of chromium(III)→chromium(II) in the Tables I, II and III, it was found that the polarographic stabilities of the chromium(III) complexes increase in the following order of the ligands:

$$Cl^- < NCS^- < en < NH_3$$

In this series it should be noted that the order of ethylenediamine and ammonia is quite contrary to the order of these ligands for cobalt(III) complexes.

The fact that the *trans* isomer of $[Cr\ en_2(NCS)_2]^+$ has a slightly more negative half-wave potential than that of the corresponding *cis* isomer agrees with the results obtained by Holtzclaw et al.[3] in the several pairs of *cis* and *trans* isomers of cobalt(III) complexes.

The Peculiar Polarographic Behaviors of *cis*-$[Cr\ en_2(NCS)_2]Cl$ and Reinecke's Salt, $NH_4[Cr(NH_3)_2(NCS)_4]H\cdot{}_2O$. In the presence of 0.001 F $NH_4[Cr(NH_3)_2(NCS)_4]$ in 0.1 F potassium chloride solution, the first wave of oxygen dissolved in the solution shifted to the direction of negative potential and the wave forms of both the first and the second of the oxygen double wave were extraordinarily modified. Fig. 3 shows the typical polarogram of the dissolved oxygen in the presence of Reinecke's salt. This polarogram was taken after bubbling oxygen into the solution for an hour. It seemed that the limiting current of the oxygen wave depends upon the concentration of oxygen dissolved in the solution. In open air the current value changed from 0.95μA at 25°C after expelling the dissolved oxygen to 8.10μA after saturating oxygen at 25°C. The half-wave potential of the first wave is -0.50 V. (vs. S.C.E.) and that of the second is -0.85 V. (vs. S.C.E) for the solution saturated with oxygen in the air (25°C).

Hexaisothiocyanato chromium(III) complex, $[Cr(NCS)_6]^{3-}$, also shows such kinds of polarographic behavior, though slightly. In the solution of 0.1 F potassium chloride the half-wave potential of the first wave of $[Cr(NCS)_6]^{3-}$ is near to that of the second wave of oxygen double wave and the two waves overlap with each other (Figs. 4 and 5).

No catalytic effects on the double wave of oxygen have been found in the other members of the isothiocyanato-ammine series of chromium(III) complexes. Fig. 6 shows the typical polarogam of the dissolved oxygen in the presence of 0.001 F *cis*-$[Cr\,en_2(NCS)_2]Cl$ and of 0.1 F potassium chloride. The first wave of the oxygen double wave has a maximum and the second has the same wave-form and the same half-wave potential (-0.85 V. vs. S.C.E.) as in the case of the Reinecke's salt. The corresponding *trans* isomer, *trans*-$[Cr\,en_2(NCS)_2]Cl$, has never shown the catalytic effects on the oxygen waves.

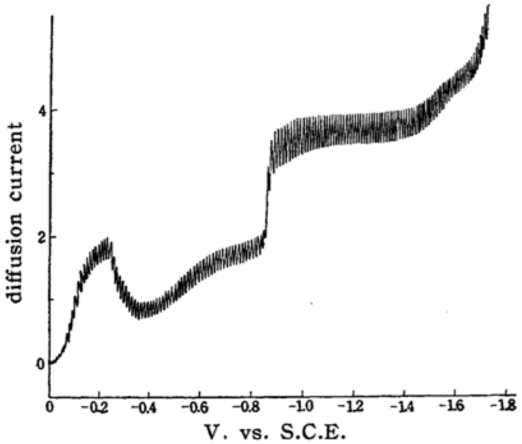

Fig. 6. The polarogram of the double wave of oxygen in the presence of 0.001 F *cis*-$[Cr\,en_2(NCS)_2]Cl$ and 0.1 F KCl.

It should be noted here that all the complexes which show the catalytic effects on the double wave of oxygen have two isothiocyanate ligands on *cis* positions in the coordinated sphere. Therefore, the fact that $[Cr(NH_3)_4(NCS)_2]^+$ did not show such polarographic behavior might be considered as a proof for the *trans* structure of the ion.

Summary

1. In neutral and unbuffered solution of 0.1 F potassium chloride, 0.1 F potassium thiocyanate, or 1 F potassium thiocyanate, the complex ion, $[Cr(NH_3)_n(NCS)_{6-n}]^{n-3}$ and $[Cr\,en_3]^{3+}$ were all reduced irreversibly in two steps at the dropping mercury electrode. The first diffusion current corresponds to the reduction, chromium(III) →chromium(II), and the second to the reduction, chromium(II)→chromium(0).

2. In the solution of 0.1 F potassium chloride, the polarograms of $[Cr\,en_2X_2]^+$ type complexes show three waves. Each of the first two waves, corresponding to a gain of one electron, represents the reduction of chromium(III) to chromium(II) and the last wave, corresponding to a gain of two electrons, represents the reduction to the metallic state. As regards the first two waves, the former wave represents the reduction of the original chromium(III) complexes to chromium(II) state and the latter represents the reduction of the aquated chromium(III) complexes to chromium(II) state.

3. In agreement with the results obtained for cobalt(III) complexes by Holtzclaw et al., the *trans* isomer of $[Cr\,en_2(NCS)_2]^+$ has a little more negative half-wave potential than the corresponding *cis*-form.

4. The polarographic stabilities of chromium(III) complexes increase in the following order of the ligands:

$$Cl^- < NCS^- < en < NH_3$$

5. The catalytic effects on the double wave of oxygen have been found for $[Cr(NH_3)_2(NCS)_4]^-$, $[Cr(NCS)_6]^{3-}$, or *cis*-$[Cr\,en_2(NCS)_2]^+$. Such special polarographic behavior was not found in the other chromium(III) complexes.

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