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The Separation, Identification and Spectra of Chromium(III) Thiocyanate Cationic Complexes

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The species $Cr(H_2O)_6^{+++}$, $Cr(H_2O)_5(SCN)^{++}$ and $Cr(H_2O)_4(SCN)_2^{+}$ have been separated by use of ion-exchange techniques. The complex species have been identified by determination of the (thiocyanate)/(chromium(III)) ratio. The spectra of the three species have been determined.

In many metal–anion complex ion systems, series of complexes M^{+n}, MX^{+n-1}, MX_2^{+n-2}, . . , MX_y^{+n-y} exist. Generally the equilibrium constants for the formation of the complexes are such that it is not possible to have present in a solution at equilibrium predominantly *one* of the intermediate complexes. In case the various equilibria are established slowly, it is possible, at least in principle, to prepare solutions containing single intermediate complexes. Any of the techniques useful in the separation of independent ionic species such as precipitation, extraction, etc., might prove useful. Because the charges on the several complexes vary in a series in which the ligand is an anion, it seems likely that separation may be accomplished by ion exchange techniques.

A system of complex ions in which the equilibria are established very slowly is the chromium(III)–thiocyanate system. This system has been well studied by N. Bjerrum,[1] who demonstrated the existence of the complexes $Cr(SCN)_n(H_2O)_{6-n}^{+3-n}$ (n = 1 to 6, inclusive). In this work the two cationic complexes $Cr(SCN)(H_2O)_5^{++}$ and $Cr(SCN)_2(H_2O)_4^{+}$ and the hydrated ion $Cr(H_2O)_6^{+++}$[2] have been separated by the use of Dowex 50.

Ion-exchange Separation of Cationic Species.—Since the hydrated chromium(III) ion, $Cr(H_2O)_6^{+++}$, as well as the several complexes absorb light at 410 mμ, a convenient means of following the elution is the measurement of the optical density of the eluted solution. An elution curve of the species which had been taken up by a Dowex 50 column in the hydrogen ion form is presented in Fig. 1. These species were removed from a solution of stoichiometric composition 0.05 molar chromium(III) nitrate and 0.15 molar potassium thiocyanate, which had previously been heated at 95° for over three hours. It is seen that there are three distinct peaks in the elution curve; this is expected since three cations $Cr(H_2O)_6^{+++}$, $Cr(H_2O)_5(SCN)^{++}$ and $Cr(H_2O)_4(SCN)_2^{+}$ are known to exist in solutions containing chromium(III) and thiocyanate.

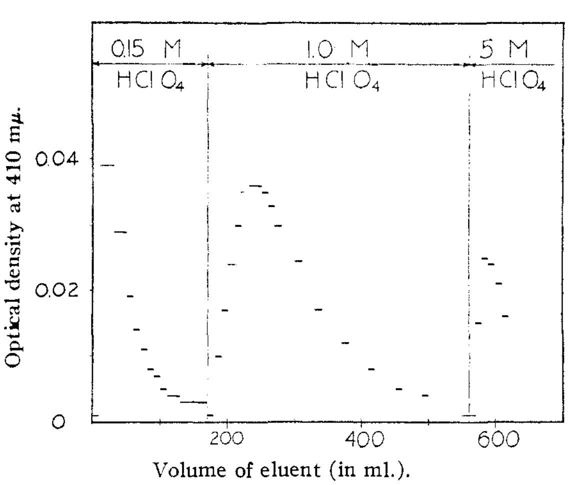

Fig. 1.—Elution of components taken up by Dowex 50 (hydrogen ion form) from solution of composition: 0.05 M $Cr(NO_3)_3$, 0.15 M KSCN (heated at 100° for 3 hours).

The identities of the species eluted by 0.15 and 1.0 molar perchloric acid have been investigated by determination of the ratio of thiocyanate to chromium(III). In three separate experiments, analyses of the 0.15 molar perchloric acid eluent gave values of the ratio (thiocyanate)/(chromium(III)) of 2.04, 2.08 (average of three successive portions of eluent) and 1.98 (average of three successive portions of eluent). These values are within experimental error of 2.00; this indicates that the first species eluted is $Cr(H_2O)_4(SCN)_2^{+}$. Five successive portions of 1.0 molar perchloric acid eluent gave values of the ratio (thiocyanate)/(chromium(III)) of 1.01, 1.01, 1.01, 1.00 and 1.00. Thus the species eluted by 1 molar perchloric acid is $Cr(H_2O)_5(SCN)^{++}$. The species which is not effectively eluted by 1.0 molar perchloric acid, but which is by perchloric acid more concentrated than 1.5 molar, is the ion of charge +3, $Cr(H_2O)_6^{+++}$. This was demonstrated by determining the extinction coefficient of the chromium species eluted by 2.0 molar perchloric acid. In measurements on four successive portions of eluent at 5 wave lengths, the average difference between the observed ϵ and that determined for $Cr(H_2O)_6^{+++}$ was 5%.

If a single absorbing species is present in the eluent coming from the column, ϵ, the molar extinction coefficient ($\epsilon = (\log I_0/I)/(Cr^{III})l$, where (Cr^{III}) is the molar concentration of chromium(III) and l is the cell length in cm.), should be a constant in successive portions of eluent. In two different experiments the absorption of three successive aliquots of the 0.15 molar perchloric acid eluent was determined at 410 and 570 mμ. In the first of these experiments the values of ϵ at 410 mμ were found to be 54, 52 and 51, while in the second experiment the value was found to be 52 in each portion. At 570 mμ the values of ϵ were found to be 53, 52 and 51 in one experiment and 51, 52 and 52 in the other. In another experiment five successive portions of 1.0 molar perchloric acid eluent were found to have optical densities corresponding to ϵ values at 410 mμ of 33.6, 33.9, 33.9, 33.3 and 33.1 and at 570 mμ of 31.3, 31.5, 31.9, 31.4 and 31.2. These data confirm that

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[1] N. Bjerrum, *Z. anorg. allgem. Chem.*, **119**, 179 (1921).

[2] J. P. Hunt and Henry Taube, *J. Chem. Phys.*, **18**, 757 (1950).

single species are present in each of these elution peaks.

Absorption Spectra of Chromium(III) Thiocyanate Species.—Complete spectra of the hydrated chromium(III) ion and the two cationic complexes over the wave length range 340 to 700 mμ are presented in Fig. 2. At all of the wave lengths studied the complex ions absorb more strongly than does the hydrated chromium(III) ion; this is particularly pronounced in the near ultraviolet region. The positions of the maxima shift only very slightly in going from the spectrum of the hydrated ion to the spectra of the complexes. This is in contrast to the behavior in other chromium(III)-complex ion systems, such as the chloride system, in which marked shifts of the position of these two maxima have been observed.

Experimental

Solutions.—All solutions were prepared using reagent grade chemicals without further purification. Doubly distilled water was used.

Spectrophotometric Studies.—A Beckman DU quartz spectrophotometer was used in all spectral studies. One-cm. cells were used.

Analytical Procedures.—In determining the ratio of thiocyanate to chromium(III) in the portions of eluent, the complex ion was first decomposed by treatment with sodium hydroxide solution. Chromium hydroxide or chromite ion and thiocyanate ion were formed. The aliquot to be used for chromium analysis was treated with 30% hydrogen peroxide while still alkaline, the excess hydrogen peroxide was allowed to decompose, the solution was diluted and its absorption at several wave lengths in the region 400–500 mμ was determined. The extinction coefficients for chromate ion had been determined independently. The aliquot for thiocyanate analysis was acidified with perchloric acid after the treatment with base and then was divided into two portions. To one was added a definite amount of iron(III) nitrate solution and its absorption at 402, 460 and 490 mμ was determined *versus* a blank made by dilution of the portion to which no iron(III) had been added. Blank experiments involving varying known amounts of thiocyanate with the same concentrations of iron(III) and hydrogen ion had been run previously.

Some of the solutions used in the determination of the extinction coefficients of the several species were analyzed for chromium(III) by the procedure just outlined. In the case of some other solutions, the absorption at wave lengths at which the ϵ values were already established was used to determine the concentration.

Ion-exchange Separations.—An ion-exchange column of one cm. diameter and fifteen to twenty cm. length containing Dowex 50 in the hydrogen ion form was used in separating the chromium(III) species. The column was operated at room temperature with a flow rate of approximately 2–3 cc. per minute. Before the elution procedure shown in Fig. 1 was adopted, numerous experiments were performed to determine optimum concentration conditions for elution of the several species. It was found that while 200 ml. of 1 *M* perchloric acid did not elute appreciable quantities of $Cr(H_2O)_6{}^{+++}$, 25 ml. of 1.5 *M* perchloric acid did elute some $Cr(H_2O)_6{}^{+++}$. It was found that no chromium(III) species was eluted by 0.15 *M* perchloric acid from a column on which only $Cr(H_2O)_6{}^{+++}$ and $Cr(H_2O)_5SCN^{++}$ were present.

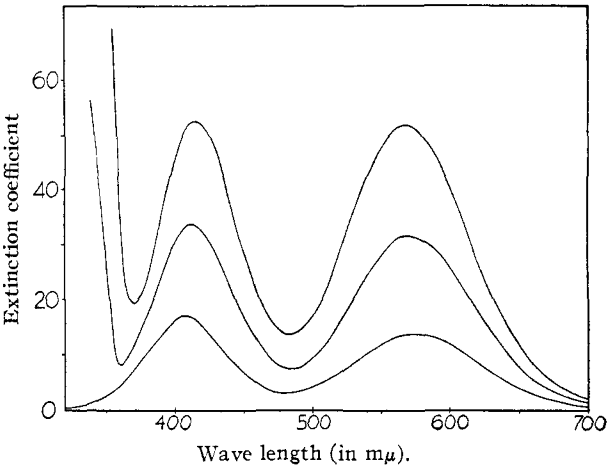

Fig. 2.—Spectra of chromium(III) species: upper curve, $Cr(H_2O)_4(SCN)_2{}^+$ (may be mixture of isomers) in 0.15 *M* $HClO_4$; middle curve, $Cr(H_2O)_5(SCN)^{++}$ in 1 *M* $HClO_4$; lower curve, $Cr(H_2O)_6{}^{+++}$ in 2 *M* $HClO_4$.

Discussion

The ion-exchange technique appears to be well suited for separating complex ions of different charge. In systems in which equilibrium is slowly established, such as the chromium(III)-thiocyanate system, it is thus possible to prepare solutions containing single intermediate species; this cannot be done in any system in which the corresponding equilibria are established rapidly.

Since the cation of charge +1 is effectively eluted by 0.15 molar perchloric acid, it is clear that the concentration of other univalent ions in a mixture must be lower than approximately 0.15 molar if all of the $Cr(H_2O)_4(SCN)_2{}^+$ is to be taken up by the resin. It is likely that some of this complex, as well as the neutral and anionic species, passed directly through the Dowex 50 column in the experiment presented in Fig. 1.

It is seen that the ions are eluted in the order of their charges, the ion of lowest charge being most easily eluted. This is consistent with trends in ion exchange resin affinities observed for simple ions.[3] Many interesting facets of the question of the relative affinities of complex ions for the ion exchange resin phase are as yet uninvestigated. Complexes of the same charge, such as those of an aquo-ammine series or the geometric isomers which exist in some systems, may also be separable using an ion-exchange technique. Presumably, these separations would be more difficult than the separations realized here, but with longer columns and properly chosen eluting agents such separations should be possible.

The species $Cr(H_2O)_4(SCN)_2{}^+$ exists in two isomeric forms. It has not been demonstrated whether we are dealing here with one of the two isomers or a mixture. Thus the spectrum of $Cr(H_2O)_4(SCN)_2{}^+$ which is presented may not be that of a single species but may be a weighted average of the spectra of the *cis* and *trans* forms of this ion.

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[3] G. E. Boyd, J. Schubert and A. W. Adamson, THIS JOURNAL, **69**, 2818 (1947).