

Studies on the Thiocyanates of Chromium

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1. The object of the studies, the results of which I am going to summarize here, has been to find satisfactory numerical expressions for the complex formation between two ions, which have a strong tendency to form complexes. With a view hereto a comprehensive examination has been made of the complexes formed by the ion Cr^{+++} and the ion CNS^- , and after having determined the composition and the properties of the complex groups formed, it has been possible to achieve the main object of the work by studying the chemical equilibrium in solutions of thiocyanates of chromium.

2. *Composition of the complexes.* With the ion CNS^- the atom of trivalent chromium forms six different complex groups, the formulae of which can be derived from that of the hexaquo-chromic ion by substituting the six molecules of water successively by thiocyanate ions.

$\text{Cr}(\text{H}_2\text{O})_6^{+++}$	hexaquo-chromic ion,
$\text{Cr}(\text{CNS})(\text{H}_2\text{O})_5^{++}$	thiocyanato-pentaquo-chromic ion,
$\text{Cr}(\text{CNS})_2(\text{H}_2\text{O})_4^+$	dithiocyanato-tetraquo-chromic ion
$\text{Cr}(\text{CNS})_3(\text{H}_2\text{O})_3$	trithiocyanato-triaquo-chrome,
$\text{Cr}(\text{CNS})_4(\text{H}_2\text{O})_2^-$	tetrathiocyanato-diaquo-chromiate ion,
$\text{Cr}(\text{CNS})_5(\text{H}_2\text{O})^{--}$	pentathiocyanato-monaquo-chromiate ion,
$\text{Cr}(\text{CNS})_6^{---}$	hexathiocyanato-chromiate ion.

The complexes with one or two thiocyanato groups are cations forming salts with various acids. Trithiocyanato-triaquo-chrome is undissociated, it is a non-electrolyte. The complexes with four or more thiocyanato groups are anions which form salts with various metals.

3. *Preparation and analysis of the complexes.* It has been ascertained that the *monothiocyanato* and *dithiocyanato complexes* exist in solution, but it has not been possible to find acids suitable for separating the complexes and thus obtaining

them in the form of solids, and consequently their content of water has not been determined experimentally. They are insoluble in ether.

Trithiocyanato-triaquo-chrome has been prepared in crystalline form. The crystals were, however, not completely pure. In solution the complex has been obtained in a much purer form. The low electric conductivity of this substance shows that it is not dissociated into ions. For a 0.1 M solution of the crystals at 0° C μ has been found to be 3.87 (μ = the molecular conductivity); for purified solutions of a strength of 0.015 M at 9° C μ has been found to be 0.61. It should be noticed that trivalent electrolytes in the corresponding condition will exhibit a molecular conductivity between 250 and 300. After dehydration in vacuum above calcium chloride at ordinary temperature the highly hygroscopic crystals only retained 3.2–3.6 molecules of water; it is thus probable that the trithiocyanato complex contains 3 molecules of constitutional water. This complex is easily soluble in ether, by evaporation of the ether solution a residue is obtained which, when heated with water, releases more ether.

The *tetrathiocyanato complex* has been isolated in the form of a dilute solution of the free acid, from which it is possible by neutralisation to prepare the corresponding salts. Neither the acid nor any of the salts have been prepared in the solid state. It has, however, been possible to ascertain that salts of quinine or strychnine precipitate the complex, and that, when a great quantity of a quinoline salt is added, it will precipitate a quinoline salt of the complex in the form of an oil. Tetrathiocyanato-chromiate acid is soluble in ether; in that respect it does not resemble its salts.

From the *pentathiocyanato complex* an insoluble quinoline salt has been obtained. It appears in the form of beautiful crystals; and from the quinoline salt it has been possible to prepare solutions which contained the sodium salt and the free acid. An analysis of the quinoline salt has given the result that it contains two molecules of water, one of which is so closely attached that it is not lost in dry air at ordinary temperature. From this we can conclude that the pentathiocyanato complex, as expected, contains one molecule of constitutional water. Pentathiocyanato-chromiate acid is soluble in ether, while its salts are insoluble.

The *hexathiocyanato complex* is already known, as it constitutes the radical of the well-known complex double-salts of the type $R_3Cr(CNS)_6$. Of this series two new insoluble salts have been prepared: the salts of pyridine and quinoline. Analysis of the quinoline salt shows that it contains one molecule of water; but by dehydration in dry air at ordinary temperature this salt readily loses this molecule of water. As it might be expected, the hexathiocyanato-chromiates thus do not contain constitutional water. By treating a strongly acid solution of a hexathiocyanato-chromiate in water with ether, three liquid layers are obtained: at the bottom a rather acid, slightly coloured, aqueous layer, in the centre a

thin, highly coloured layer, consisting of a concentrated solution of hexathio-cyanato-chromiate acid in ether, and at the top a thicker, slightly coloured ethereal layer. The behaviour of the complex chromicthiocyanic acid towards ether is thus similar to that of phospho- and silico-tungstic acid.

4. In *aqueous solution* the chromicthiocyanate complexes are of a reddish-violet colour. An increase in the content of thiocyanate has the effect of making the colour slightly more reddish, and at the same time the intensity of the colour is increased considerably. In *ethereal solution* the trithiocyanato-chrome complex assumes a greenish colour, and tetrathiocyanato-chromiate acid is of an almost pure green colour. On the other hand, pentathiocyanato-chromiate acid and hexathiocyanato-chromiate acid have almost the same colour in ethereal solution as they have in aqueous solution.

5. The *partition coefficient* for ether and water of the complexes soluble in ether has at ordinary temperature approximately the following values:

$\text{Cr}(\text{CNS})_3(\text{H}_2\text{O})_3$	$\text{H}[\text{Cr}(\text{CNS})_4(\text{H}_2\text{O})_2]$	$\text{H}_2[\text{Cr}(\text{CNS})_5(\text{H}_2\text{O})]$	$\text{H}_3[\text{Cr}(\text{CNS})_6]$
about 3.6	about 9.4	about 4	about 0.3
(3.3 — 4.7)			

Velocity constants of the decomposition of thiocyanato-chromic complexes at ordinary temperature (16°–18° C)

	In acidified water	In water ⁶⁾	In 0.25 M solution of CH_3COONa	In 0.035 M solution of NaHCO_3	In 0.01 M solution of NaOH	In ether
$\text{Cr}(\text{CNS})(\text{H}_2\text{O})_5^{++}$		0.0000054 ⁷⁾			large	
$\text{Cr}(\text{CNS})_2(\text{H}_2\text{O})_4^+$			0.0035		large	<0.000007
$\text{Cr}(\text{CNS})_3(\text{H}_2\text{O})_3$	<0.00004	0.00002	0.00025 ³⁾		large	<0.00003
$\text{Cr}(\text{CNS})_4(\text{H}_2\text{O})_2^-$	<0.00004	0.00004		0.013 ⁴⁾	large	0.005 ⁴⁾
$\text{Cr}(\text{CNS})_5(\text{H}_2\text{O})^{--}$	<0.00014 ⁵⁾	0.00014 ¹⁾			large	
$\text{Cr}(\text{CNS})_6^{---}$	0.00041	0.00050 ²⁾			0.00060	large

1) In the dark. ($C_H = 0.73 \cdot 10^{-3}$).

2) In the dark. In diffuse daylight: 0.0017–0.0064.

3) A little acetic acid has been added to the solution so as to make the solution 0.002 M with regard to acetic acid.

4) In the dark.

5) In the dark. In diffuse daylight: 0.002.

6) Due to hydrolysis the solutions were slightly acid. Probable values of C_H : about 10^{-3} to 10^{-5} .

7) at 25° C.

For the acids, the partition coefficient is defined by the expression:

$$K = \frac{a}{b \cdot C_H^n}$$

where a is the molar concentration of the acid in the ethereal layer, b the molar concentration of the complex in the aqueous layer, and n the basicity of the acid.

The tri- and tetrathiocyanato complexes have partition coefficients which vary slightly according to the method of preparation. This seems to indicate that the preparations used represent different mixtures of two isomers. In fact *Werner's theory* implies the existence of these complexes in two stereoisomeric forms.

6. The *stability* of the various complexes has been measured by measuring the quantity of CNS-ions formed by the decomposition of the complexes. This measurement has been performed colorimetrically by means of the colour which the solutions assume when ferric nitrate is added. The above table contains the velocity constants of the decomposition of the complexes. In case the velocity constant is low, it will be a direct measurement of the relative amount of complex decomposed in unit of time, i.e., in this case, in one minute.

It appears from the above table that in *aqueous solution* the stability of the hexathiocyanato-chromiate complex is almost independent of the reaction of the solution — whether it is acid, neutral or basic. As regards the other complexes they are more stable in acid solution than the hexathiocyanato complex, and their stability increases with decreasing content of thiocyanate in the complex. In basic solution, on the other hand, the other complexes are less stable than the hexa-complex, and their stability decreases with decreasing content of thiocyanate in the complex.

In *ethereal solution* the trithiocyanato complex is fairly stable, but the stability of the complexes in ethereal solution decreases rapidly with increasing content of thiocyanate, and hexathiocyanato-chromiate acid decomposes almost instantaneously in ethereal solution.

The thiocyanato-chromic complexes are rather *photosensitive*. In diffuse daylight the decomposition of hexa- and penta-complexes proceeds more than ten times faster than in the dark.

7. *Explanation of the decomposing effect of hydroxyl ions.* It seems probable that if the hydroxyl ion decomposes the thiocyanato-chromic complexes, it is because it facilitates the formation of instable hydroxo-compounds. These compounds are formed when in the hydrated ions the water molecules are replaced by, or rather transformed into, hydroxyl radicals. The hexathiocyanato complex is the only one which cannot form hydroxyl derivatives, consequently the decomposition of this complex is not influenced by hydroxyl ions.

8. A method for *quantitative analysis* of the six different thiocyanato-chromic complexes has been evolved. Firstly the hexa- and pentacomplexes are precipitated in the form of *quinoline salts*, and the respective amounts of the two complexes contained in the precipitate are established by quantitative determination of chromium and thiocyanate. The filtrate from the precipitate contains the other complexes. The tri- and tetra-complexes are separated from this liquid by systematic *extraction with ether*, and this ether extraction in itself enables us to separate the tri- and tetra-complexes, the respective quantities being determined by a subsequent determination of the chromium. Finally the amounts of chromium and thiocyanate complexes which remain in the mother liquor from the ether extractions are determined by titration. When these determinations are performed, we only require to know the amount of hexaquo-complex to be able to calculate the amounts of mono- and di-thiocyanato complexes. To obtain this value hexaquo-complex is precipitated *in the form of alum* by means of acid potassium sulphate and alcohol.

9. The thiocyanato-chromic complexes which we have referred to here are formed slowly in solutions containing hexaquo-chromic ions and thiocyanate ions. The *velocity* with which this formation takes place has not been subjected to a systematic study. It may, however, be observed that in aqueous solution the chemical equilibrium of these complexes will be attained at 100° C in about half an hour, at 50° C in 1-2 days, while at ordinary temperature the equilibrium will probably be reached only in the course of some years.

For the formation of the monothiocyanato-chromic complex the velocity constant in aqueous solution has been found to be 0.0018 at 25° C and 0.13 at 50° C.

10. *The chemical equilibrium* which exists between the different complexes and the thiocyanate ion in aqueous solution has been determined for 10 different solutions at 50° C.

These experiments have given the following mean values:

$$\begin{array}{lll} K_{\text{CrCNS}} = 328; & K_{\text{Cr(CNS)}_2} = 17.5; & K_{\text{Cr(CNS)}_3} = 4.56; \\ K_{\text{Cr(CNS)}_4} = 1.93; & K_{\text{Cr(CNS)}_5} = 0.81; & K_{\text{Cr(CNS)}_6} = 0.41; \end{array}$$

$$K_{\text{Cr(CNS)}_n} = \frac{C_{\text{Cr(CNS)}_n}}{C_{\text{Cr(CNS)}_{n-1}} \cdot C_{\text{CNS}}}$$

The six values stated above represent a quantitative measurement of the tendency to form complexes which the chromium thiocyanates have at 50° C. As the number of complexes formed is six, it is evident that this tendency cannot be expressed by a single figure.

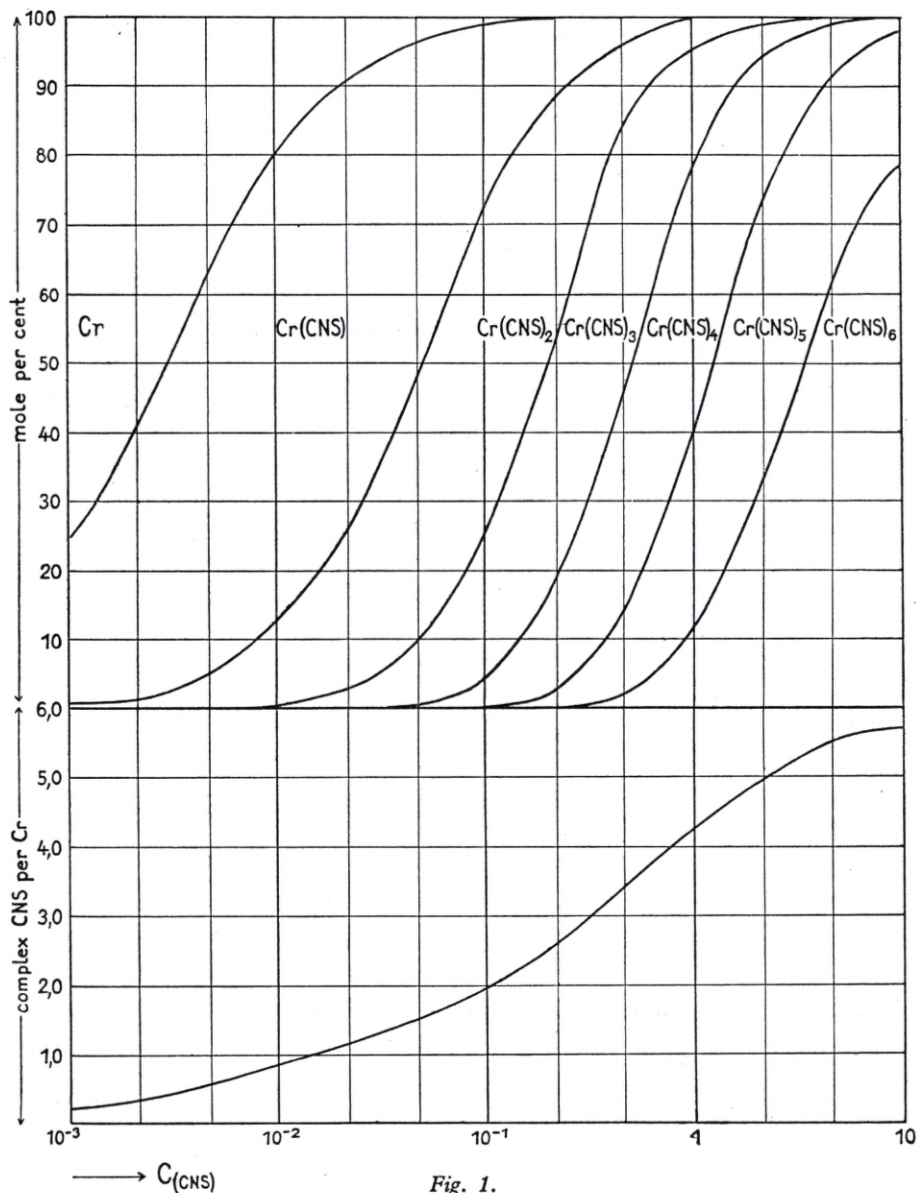


Fig. 1.

Measurements of conductivity have confirmed the results obtained by the chemical analysis of the solutions of chromium thiocyanates.

11. *The affinity* between the thiocyanate ion and the chromium atom in solutions, the molarity of which is 1 as regards all the substances can be calculated from the equilibrium constants and will be as follows:

For the first	thiocyanato group	3710 cal.
- - second	—	1840 -
- - third	—	970 -
- - fourth	—	420 -
- - fifth	—	-130 -
- - sixth	—	-570 -

The calculation has been performed by means of the formula $A = RT \log_e K$.

An increase of the temperature will produce a slight decrease in the tendency exhibited by chromium to form complexes with the thiocyanate ion.

12. The figure shows the variation of the amounts of the different complexes with the concentration of the thiocyanate ion. Along the axis of abscissa the concentration of the thiocyanate ion has been plotted in logarithmic scale. In the upper part of the diagram the sections of the ordinates delimited by the curves represent the molecular percentages of the various complexes, the areas contained within the curves each corresponding to the complex stated in that area. The curve in the lower part of the diagram indicates the correlation between the concentration of the thiocyanate ion (C_{CNS}) and the number (n) of complexly bound thiocyanato groups per atom of chromium.

Calculation of the state of equilibrium in a solution with known concentrations of chromium and thiocyanate.

If a and b denote the total concentrations as regards chromium and thiocyanate respectively, we have

$$C_{\text{CNS}} + n \cdot a = b.$$

When taken together with the curve (C_{CNS}, n) of the diagram, this equation enables us by the method of trial and error to find the value of C_{CNS} ; next we can, from the curves of the upper part of the diagram, find the molecular percentages of the various complexes.