

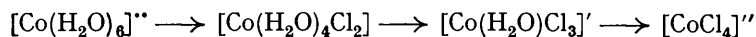
139. *The Absorption Spectrum of Potassium Cobaltous Thiocyanate.*

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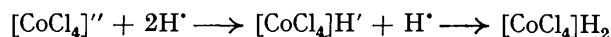
THE general theory has been advanced (Hill and Howell, *Phil. Mag.*, 1924, **48**, 833; see also *Ann. Reports*, 1927, **24**, 288) that the colour of the cobaltous compounds is determined by the number of atoms or groups surrounding the cobalt atom : with six, the colour is red ; with four, it is blue.

The transition from red to blue by addition of hydrochloric acid to aqueous cobalt

chloride solution has been followed by measuring the absorption spectra of a series of solutions containing the same amount of cobalt chloride with increasing concentration of hydrochloric acid (Howell and Jackson, *Proc. Roy. Soc.*, 1933, *A*, **142**, 587). It was shown that the state of the cobalt atom was determined by its environment, *i.e.*, by the relative number of chlorine atoms to water molecules in the solution. The curves for the extinction coefficient against the concentration of hydrochloric acid were discontinuous, and at these discontinuities the relative number of chlorine atoms to water molecules formed a simple ratio. It was thus established that the mechanism of the change is as follows :



For the two principal bands, the extinction coefficient remains constant with further increasing concentration of hydrochloric acid after the formation of the $[\text{CoCl}_4]^{2-}$ complex is complete. For the two auxiliary bands, however, the value continues to increase, more rapidly and reaching a constant value earlier for one band than for the other. This was attributed to depression of ionisation of the complex acid by increasing concentration of hydrogen ion :



These conclusions accord with the changes observed in the absorption spectrum of aqueous solutions of cobalt chloride and hydrochloric acid with change of temperature (Howell and Jackson, *Proc. Roy. Soc.*, 1936, *A*, **155**, 33) and also with changes in other physical properties during the transition from red to blue (Howell, *J.*, 1927, 158; 2039, 2843).

The change from red to blue of aqueous cobalt chloride solution on addition of magnesium chloride (Howell and Jackson, *J.*, 1936, 1268) has also been followed spectroscopically as for hydrochloric acid. The curves for magnesium chloride are precisely similar to those for hydrochloric acid, and the mechanism of the change is exactly the same. With magnesium chloride, however, its solubility at ordinary temperature is not great enough to reach the ratio of chlorine atoms to water molecules requisite for complete conversion into the blue $[\text{CoCl}_4]^{2-}$.

The change in colour from red to blue of aqueous cobalt chloride solution by addition of potassium thiocyanate (due to the formation of potassium cobaltous thiocyanate) has now been examined in a manner exactly analogous to that for the addition of hydrochloric acid or of magnesium chloride. The replacement of water molecules by thiocyanate groups in the complex is determined by their relative numbers in the solution, as is the replacement of water by chlorine, but the course of the change is different in some important particulars.

Many previous investigators have studied the action of potassium thiocyanate on cobalt chloride solution and are agreed that the blue complex $[\text{Co}(\text{CNS})_4]^{2-}$ is produced, but the stages by which its formation proceeds have not previously been elucidated. Many observations on this colour change, as on those of other cobaltous compounds, are invalid because it has been assumed that the changes occurring in solution are complete with the visual change of colour. It will be seen from the absorption curves now given, however, that a very great concentration of potassium thiocyanate is required to bring about complete transformation, and that, in solutions which appear wholly blue to the eye, the change may be very far from complete.

EXPERIMENTAL.

Solutions.—As in the previous investigations with hydrochloric acid and with magnesium chloride, a concentration of 12 g. of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ per l. was employed throughout. Kahlbaum's pure salt, free from iron and nickel, was used.

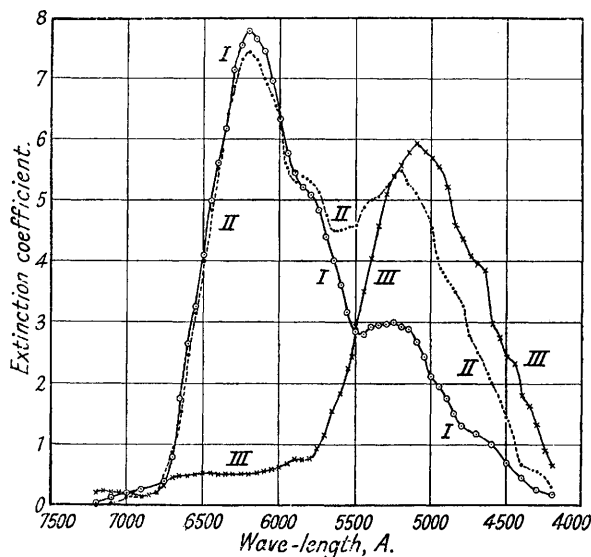
Two stock solutions were prepared, one in pure water and the other in potassium thiocyanate solution containing 960 g. of pure salt per l. A series of intermediate solutions, all containing the same concentration of cobalt but varying amounts of potassium thiocyanate, were prepared by mixing x c.c. of one of the stock solutions and $100-x$ c.c. of the other, both at 18° , and making the mixture up to 100 c.c. with water at 18° . An exactly similar series of solutions was prepared from water and a stock solution of 960 g. of pure thiocyanate only per l., for use as com-

pensating blanks in the other beam. All concentrations were checked by titration against standard silver nitrate solution, iron alum being used as indicator.

Apparatus.—All measurements were made with the Hilger-Nutting spectrophotometer used in the previous investigations. The same accurately ground glass cells were again employed, and were immersed in the special thermostat already described. The working temperature was $20^{\circ} \pm 0.01^{\circ}$, and readings were taken every 50 Å, from 7200 to 4200 Å.

Results.—The values of the Bunsen extinction coefficient were plotted against the wavelength for each solution. Typical curves for the wholly red (III), a partly blue (II), and a wholly blue solution (I) are given in Fig. 1. It is seen that the curves for the blue form are similar to those obtained with hydrochloric acid and with magnesium chloride, except that they lie further into the region of shorter wave-length and are slightly more extended.

FIG. 1.



- I. Concentration of KCNS : 960 g./l. Scale : as shown.
 II. Concentration of KCNS : 360 g./l. Scale : \times by 0.4.
 III. Concentration of KCNS : 0 g./l. Scale : \times by 0.04.

With hydrochloric acid and with magnesium chloride there were four bands at 6950, 6660, 6260, and 6100 Å. With potassium thiocyanate there are also four. The two principal bands are well defined at 6200 and 5850 Å., but the two subsidiary bands at about 5250 and 4700 Å. overlap the maximum of the absorption band of the red form and are ill-defined, especially in the only partly blue solutions.

The values of the Bunsen extinction coefficient (ϵ) at the two principal band maxima have been read from the curves and are given for each concentration of potassium thiocyanate in Table I (d is the thickness of the layer). They are plotted against the concentration of potassium thiocyanate in Fig. 2. The subsidiary bands, as already indicated, cannot be read accurately; also, the values of the extinction coefficient are low, so that the experimental error becomes appreciable in comparison with the change occurring with increasing concentration. As previously pointed out, the change in the absorption band of the red form cannot be followed because it is so profoundly affected by the overlapping absorption of the much more intense blue form, for which correction would be excessive.

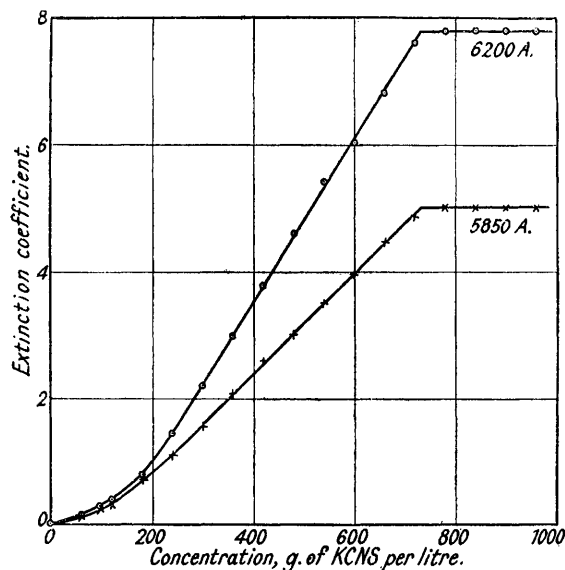
DISCUSSION.

There is one remarkable difference between the curves of the extinction coefficient against concentration for potassium thiocyanate (Fig. 2) and those for hydrochloric acid, in that production of a blue constituent begins at once. The reason for this profound difference will appear below. In other respects the curves for potassium thiocyanate are essentially similar to those for hydrochloric acid. With increasing concentration there is the same

increasingly rapid rise in the extinction coefficient, which merges into a linear relation; this ceases abruptly at a value which remains unchanged with further increasing concentration.

For the addition of hydrochloric acid or of magnesium chloride, the slope of the linear portion of the curve is extremely steep. The concentration at the transition from the curved to the linear relation was therefore obtained without appreciable error by projecting the line to strike the axis of concentration. With potassium thiocyanate, however, the linear portion has a very much more gradual slope. This is due to the fact that, over the linear range, with hydrochloric acid or with magnesium chloride, only one remaining molecule of water is being replaced in the complex (by a chlorine atom), whereas with potassium thiocyanate, as will be shown, three molecules of water are being replaced (by

FIG. 2.



thiocyanate groups). The concentration at which the curve first becomes linear is therefore considerably different from that at which the projection of the linear graph strikes the axis of concentration; moreover, the values for the projections of the linear portions of the curves for the two bands differ appreciably from one another. It is therefore necessary to

TABLE I.

<i>d</i> , cm.	KCNS, g./l.	ε at		<i>d</i> , cm.	KCNS, g./l.	ε at		<i>d</i> , cm.	KCNS, g./l.	ε at	
		6200 A.	5850 A.			6200 A.	5850 A.			6200 A.	5850 A.
10.0	0	0.02	0.02	0.5	300	2.19	1.54	0.25	660	6.80	4.44
1.0	60	0.15	0.12	„	360	2.98	2.06	„	720	7.60	4.85
„	96	0.29	0.26	„	420	3.78	2.58	„	780	7.75	5.00
„	120	0.40	0.30	0.25	480	4.60	3.0	„	840	7.75	5.00
„	180	0.78	0.70	„	540	5.40	3.50	„	900	7.75	5.00
0.5	240	1.43	1.10	„	600	6.02	3.95	„	960	7.75	5.00

take directly the concentration at which the curved portion merges into the linear portion. This is found with reasonable accuracy to be 265 g./l. for each curve. The concentration at which the linear relation ceases and the extinction coefficient attains its constant value is very clearly defined at 730 g./l.

The mechanism already postulated to explain the changes occurring on addition of hydrochloric acid or of magnesium chloride to aqueous cobalt chloride solution should also apply to the addition of potassium thiocyanate. The data for the calculation of the numbers of thiocyanate groups and water molecules in solution at the two critical concentrations

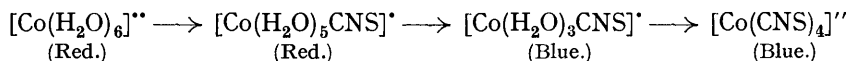
are collected in Table II. It follows that at the beginning of the linear relation there is only one thiocyanate group in the complex. Since the compound is blue, there are only four groups altogether, hence its constitution is $[\text{Co}(\text{H}_2\text{O})_3\text{CNS}]^*$. At the end of the linear relation, the substitution is complete and there are four thiocyanate groups present, yielding $[\text{Co}(\text{CNS})_4]''$.

It has already been pointed out that the mechanism of the initial change on addition of potassium thiocyanate to aqueous cobalt chloride solution is different from that on addition of hydrochloric acid or of magnesium chloride. Now Hantzsch and Shibata (*Z. anorg. Chem.*, 1912, **73**, 309) have shown, from cryoscopic measurements, that in even moderately dilute solution cobalt thiocyanate is only primarily dissociated, yielding the two ions $[\text{Co}(\text{CNS})]^*$ and CNS' . Evidently, therefore, addition of potassium thiocyanate yields immediately the red complex $[\text{Co}(\text{H}_2\text{O})_5\text{CNS}]^*$.

TABLE II.

Critical concns. of KCNS g./l.	0	265	730
Concn. of thiocyanate groups :			
Concn. of CNS, g.-mols./l.	0	2.73	7.52
Concn. of water molecules :			
Wt. of 100 c.c. of solution, g.	100.4	112.7	132.4
" KCNS present, g.	0	26.5	73.0
" CoCl_2 present, g.	0.65	0.65	0.65
" H_2O present, g.	99.8	85.5	58.7
Concn. of H_2O , g.-mols./l.	55.4	47.5	32.6
$[\text{CNS}]/[\text{H}_2\text{O}]$	0	0.0575	0.231
Ratios	0	1	4.02
Ratios of CNS groups in the complexes	0	1	4

Continued addition of potassium thiocyanate does not cause replacement of a second molecule of water by a thiocyanate group, giving a red complex similar to that produced on addition of hydrochloric acid or of magnesium chloride. Instead, two further molecules of water are displaced without introduction of thiocyanate groups, yielding the blue complex $[\text{Co}(\text{H}_2\text{O})_3\text{CNS}]^*$. Still further addition of potassium thiocyanate (over the linear portion of the curve) causes replacement of the three remaining water molecules by thiocyanate groups, yielding the also blue complex $[\text{Co}(\text{CNS})_4]''$. The complete change is therefore as follows :



The results of previous workers are explained by the findings of the present investigation. Rosenheim and Cohn (*Z. anorg. Chem.*, 1901, **27**, 280) from the preparation and properties of double salts, Zawadzki (*Chem. Polski*, 1910, **10**, 49) from the absorption spectra of potassium cobaltous thiocyanate in organic solvents, de Sweemer (*Natuurwetensch. Tijds.*, 1932, **14**, 231; 1933, **15**, 14) from a study of complex metallic thiocyanates, and Hill and Howell (*Phil. Mag.*, 1924, **48**, 833) from a comparison of the absorption spectra of cobalt pigments and solutions, all conclude that the ion $[\text{Co}(\text{CNS})_4]''$ is produced. Hantzsch and Shibata show that the absorption spectrum of cobaltous thiocyanate in 60% potassium thiocyanate solution lies between that of the salt in aqueous solution and in organic solvents. The reason is apparent from our curves, since it is seen that at a concentration of 600 g. of thiocyanate per l., the extinction coefficient is only about three-quarters as great as the constant maximum value.

Bassett's theory that the red colour of cobaltous compounds is due to the electron shift of an unshared electron, and the blue colour to that of an electron shared with another atom, is evidently untenable. He is forced to assume (Bassett and Croucher, J., 1930, 1784) that the "non-ionic complex $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]$ would be pale blue"; our investigations on the addition of hydrochloric acid and of magnesium chloride to aqueous cobalt chloride solution prove conclusively that it is red. Similarly, Bassett is forced to postulate that the complex $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}]^*$ is red; our previous investigations show that this complex does not exist, and it has now been proved further that the corresponding complex

$[\text{Co}(\text{H}_2\text{O})_3\text{CNS}]^*$ is blue. The demonstration of the formation of this positively charged complex also disproves Bassett's dictum that blue cobaltous cations do not exist.

Although the subsidiary bands are incapable of yielding detailed information (see p. 623), it is evident for the band at 5250 Å. that there is little or no increase beyond the point at which the extinction coefficient reaches its constant value for the two principal bands, indicating that the potassium cobaltous thiocyanate is completely or very largely un-ionised when its formation is first complete :



It may be noted that the absorption of the $[\text{Co}(\text{CNS})_4]''$ complex is very much less than that of the $[\text{CoCl}_4]''$ complex. The values of the extinction coefficients at the two principal bands are 7.75 and 5.00 for the former as against 22.0 and 21.6 for the latter at the same temperature (20°).

Further, the values at the two principal bands for $[\text{Co}(\text{CNS})_4]''$ are very different from one another, but for $[\text{CoCl}_4]''$ they are very close; the percentage differences on the lower values are 55% and less than 2% respectively. This suggests a marked difference between the two principal valencies in $[\text{Co}(\text{CNS})_4]''$ and great similarity between those in $[\text{CoCl}_4]''$; and this is in accordance with the facts now established that in the formation of $[\text{Co}(\text{CNS})_4]''$ only one thiocyanate group enters when the complex is red, whereas in the formation of $[\text{CoCl}_4]''$ two chlorine atoms enter practically simultaneously.

SUMMARY.

1. The absorption spectra of a series of aqueous solutions containing a fixed amount of cobalt chloride (12 g. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ per l. as in previous investigations) with increasing concentrations of potassium thiocyanate have been measured at 20° and plotted.

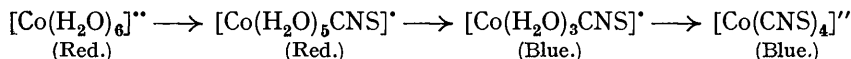
2. The extinction coefficients at the maxima of the two principal bands, 6200 and 5850 Å., have been plotted against the concentration of potassium thiocyanate.

3. The curves are essentially similar to those obtained for addition of hydrochloric acid or of magnesium chloride, except in the important particular that the amount of blue constituent increases rapidly from the beginning.

4. The increase becomes linear at 265 g. of thiocyanate per l. and ceases abruptly at 730 g. per l.; thereafter the extinction coefficient remains constant with increasing concentration of potassium thiocyanate.

5. The ratio of the relative numbers of thiocyanate groups to water molecules in solution at these two critical concentrations is 1 : 4. It follows that these are the relative numbers of thiocyanate groups in the complexes at these two stages.

6. In conformity with the facts that a blue constituent is formed immediately on addition of potassium thiocyanate, and that cobaltous thiocyanate is known to be only primarily ionised, the complete change is :



7. The two subsidiary bands overlap the absorption bands of the red form and are not well defined, but their change with concentration indicates that potassium cobaltous thiocyanate is but little ionised when formation of the complex is first complete :



8. The relative intensities of absorption of the two complexes $[\text{CoCl}_4]''$ and $[\text{Co}(\text{CNS})_4]''$ at the maxima of the two principal bands are discussed.