Spectroscopic Investigations of the Interaction Between Simple Salt Anions and Transition Metal Cations. Part I. The Absorption Spectra of Hexammine Cobalt (III) and Chromium (III) Complexes in Aqueous Solutions of Salts of Weak Acid

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The solubility of the luteo complex in various concentrated aqueous salt solutions varies to a large extent with the kinds of salt. The present author assumed that this fact has a close relation to the formation of "zweischalige" complexes resulting from the association of anions around complex cations. On the association between complex cations and halogen ions, Linhard[1] reported the spectroscopic investigations and, especially in the case of the iodide, he succeeded in obtaining the equilibrium constants from his analysis of the absorption band appearing newly in association. The present author expected that such "association bands" would appear not only in the iodide solution, but also in other salt solutions. He confirmed this expectation by measuring absorption spectra and also obtained some knowledge on the association by analysing the results.

Experimental

The complexes used were $[Co(NH_3)_6]Cl_3$, $[Co\ en_3]Cl_3$, $[Cr(NH_3)_6]Cl_3$ and $[Cr\ en_3]Cl_3$, and the salts used were KNCS, Na_2SO_3, $Na_2S_2O_3$ and Na_2CO_3. Each salt was dissolved to make solutions of 1, 0.1, 0.01 mol./l. concentrations. In each solution, the complex was dissolved to 0.005 mol./l. concentration. This solution of the complex was used in the absorption measurement. In order to cancel the absorption due to the unassociated free anions, the corresponding salt solution was used as a standard for the measurement. The measurement of absorption was made using a quartz spectrograph by the rotating sector method. As internal change of the complex may be possible during measurement, the whole procedure was completed in 20 minutes after the preparation of the complex solution. The measurement was done at room temperature between 18–20°C.

Results

The experimental results are shown in Fig. 1–10. In these figures full lines 1, 2, 3 correspond to the absorption curves for 1, 0.1, 0.01 mol./l. salt solutions respectively, one broken line 4 to that of the complex itself, and the other broken line 5 to that of the corresponding monoacidopentammine complex having the same anion as the salt solution in its complex radical.

In the Cr complex, the end absorption lies in the far ultraviolet region. Consequently, if the absorption band due to association should appear at the same position as in the Co complex, we could easily find its maximum exactly, and from such values we could calculate an exact value of the degree of association. But the experimental result did not fulfil this expectation. The association band

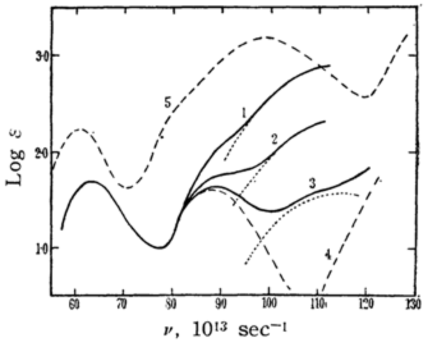

Fig. 1. $[Co(NH_3)_6]Cl_3$ in KNCS solutions

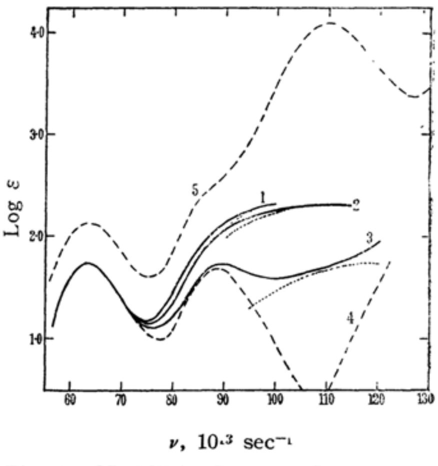

Fig. 2. $[Co(NH_3)_6]Cl_3$ in Na_2SO_3 solutions.

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[1] M. Linhard, *Z. Elektrochem.*, 50, 224 (1944), M. Linhard and M. Weigel, *Z. anorg. u. allgen. Chem.*, 266, 49 (1951).

appeared farther in the ultraviolet than in the Co complex and its maximum position could not be ascertained. However, in this case the similar characteristics of the association were also recognized.

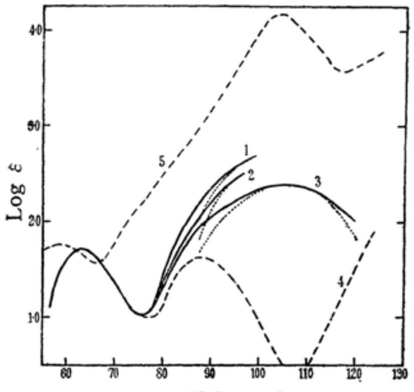

Fig. 3. [Co(NH$_3$)$_6$] Cl$_3$ in Na$_2$S$_2$O$_3$ solutions.

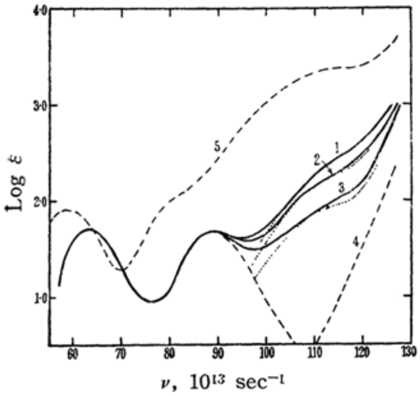

Fig. 4. [Co(NH$_3$)$_6$] Cl$_3$ in Na$_2$CO$_3$ solutions.

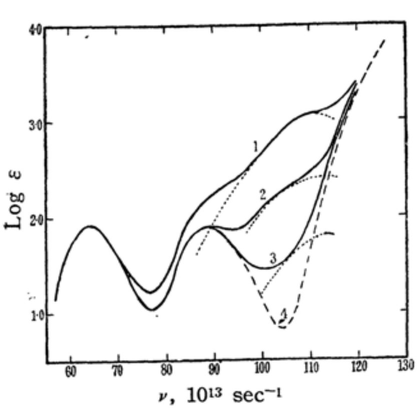

Fig. 5. [Co en$_3$] Cl$_3$ in KNCS solutions.

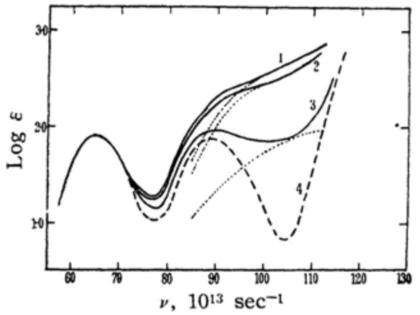

Fig. 6. [Co en$_3$] Cl$_3$ in Na$_2$SO$_3$ solutions.

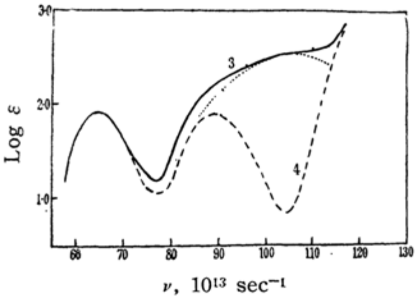

Fig. 7. [Co en$_3$] Cl$_3$ in a Na$_2$S$_2$O$_3$ solution.

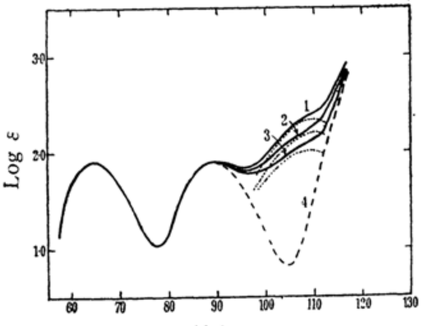

Fig. 8. [Co en$_3$] Cl$_3$ in Na$_2$CO$_3$ solutions.

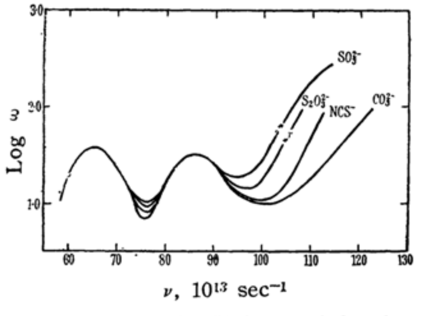

Fig. 9. [Cr(NH$_3$)$_6$] Cl$_3$ in 1 mol./l. salt solutions.

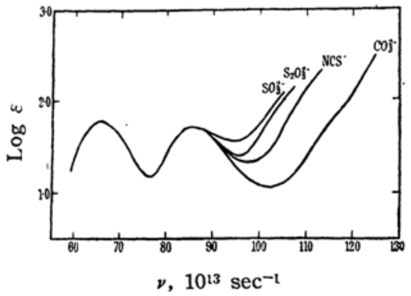

Fig. 10. [Cr en_3] Cl_3 in 1 mol./l. salt solutions.

The inspection of these figures shows the following facts.

(1) As expected, in every case there exists in the ultraviolet a new broad band probably due to the association between anions and complex cations.

(2) The first band proper to the complex always has a constant maximum, irrespective of kind and concentration of the salt solution, that is, it coincides with that of the complex itself in its position and height. The second band also has a constant maximum, coinciding with that of the complex itself in its position and height within the experimental errors. In some cases, however, where a new broad band covers them more or less completely, their maximum positions cannot be recognized.

TABLE I

THE MAXIMA OF THE FIRST AND SECOND BANDS

	First Bands		Second Bands	
	$\nu \cdot 10^{13}$sec.$^{-1}$	log ε	$\nu \cdot 10^{13}$sec.$^{-1}$	log ε
$[Co(NH_3)_6]Cl_3$	63.5	1.70	88.5	1.63
$[Co\ en_3]Cl_3$	65.5	1.92	89.5	1.89
$[Cr(NH_3)_6]Cl_3$	65.0	1.60	86.0	1.52
$[Cr\ en_3]Cl_3$	66.0	1.78	86.0	1.75

Discussion

Separation of "Association Bands".—As the association band appears in every case as a very broad band spreading between the second and the end absorption, the recognition of its maximum position and height is very difficult. But as mentioned above, the first and second bands of the complex in salt solutions are the same as those of the complex itself, so it may be justified as an approximation to assume that absorption due to the association, remains when the absorption of the complex itself is subtracted from the whole absorption of the complex in the salt solution. On this assumption, the absorption curves were calculated, and were drawn in the figures with the dotted lines affixed to the corresponding full lines. By these calculations the association band is separated from the second band distinctly and, at the same time, from the end absorption.

TABLE II

THE PROBABLE MAXIMUM POSITIONS OF THE ASSOCIATION BANDS IN THE Co COMPLEXES

(Faequency 10^{13}sec^{-1}. units)

NCS^-: 115, SO_3^{2-}: 110, $S_2O_3^{2-}$: 105, CO_3^{2-}: ca.115

But as the end absorption is affected easily by the experimental conditions, there is almost no meaning in discussing the difference of such calculated maximum positions. Thus except in the case of $S_2O_3^{2-}$, where the maximum lies far from the end absorption, we can derive no more than a generalisation that there exist maxima at about 115∼110× 10^{13}sec^{-1}. In each figure the absorption curve of the corresponding monoacidopentammine complex is drawn by the broken line 5 for comparison. Comparing this with it, we can easily find that the maximum position of the association band, in the cases of SO_3^{2-}, $S_2O_3^{2-}$ and CO_3^{2-}, is almost identical with the special band of the corresponding monoacido complex. In contrast to this, in the case of NCS^-, the two maxima do not coincide in their position, and the maximum of the association band lies much farther in the shorter wave-lengths compared with the special band of the corresponding monoacido complex. Here it should be noted that the maximum positions of the association bands are almost identical in the cases both of the ammonia complexes and the ethylenediamine complexes.

Equilibrium of Association.—In order to treat the equilibrium of association from the value of the optical density, it is assumed that though there exist several kinds of association products i.e. those having 1, 2, 3, etc. anions per one complex cation, their absorptions appear as that of the same deformed anions. Accordingly, their optical densities are determined only by the number of the anions associating around the complex cations. Linhard assumed that in the association between complex cations and halogen ions, the association products in a concentrated KI solution exist in electrically neutral ion-pairs. Under this assumption he succeeded in the calculation of the equilibrium constants. In his case the association bands were so sharply separated that the use of the optical densities at their maximum position was possible. In the present case, the association bands are so broad and, in addition, no maximum positions are available in most cases, that the calculation of the equilibrium constants after Lihard's method will produce greater errors. Besides, the solubility of the complex in the salt solutions is very large in the present case. This fact makes a marked contrast to the case of the alkali iodide solution in which the solubility of the complex is exceedingly small. Thus the author considered that it was not proper to assume the association product as an electrically neutral ion-pair, and that it should be regarded as a " zweischalige " complex containing excessive anions, e.g. $[Co(NH_3)_6](NCS)_{4-6}$, $[Co\,en_3](SO_3)_{2-3}$ etc.

On the basis of the above consideration, the author must be content with the rough estimation of the degree of association. Here the degree of association is defined as follows: The " zweischalige " complex in a 1 mol./l. salt solution is regarded as saturated with anions and taken as a standard. (This assumption does not hold in the association of NCS^-. From the inspection of the curves of the association bands in the 1, 0.1 and 0.01 mol./l. NCS^- solutions, we can presume that the complex is not yet saturated even in the 1 mol./l. solution. (See Fig. 1 and Fig. 5.) The degree of association in a 0.1 or 0.01 mol./l. salt solution is obtained as the ratio of the optical densities of the association band of the solution to that of the corresponding 1 mol./l. solution. As the optical densities the author used those at frequencies as near as possible to the maximum position. The calculated results are shown in Table III.

The results of calculation are rather satisfactory, considering the accuracy of the experiment and the roughness of the calculation procedure. It is very suggestive to find that a more voluminous trisethylenediamine complex shows almost the same degree of association as that of a less voluminous hexaammonia complex. As already noted, the maximum positions of the association bands in the two complexes are almost identical to each other. These facts suggest that the main origin of the association lies not in the mere electrostatic attraction but in some localized force acting between the anion and the complex radical. As one of the probable origins of such localized force we may consider the hydrogen bridge between the NH_2 radical and the anion. But as the appearence of the marked association band cannot be explained merely by the hydrogen bridge, the main origin of the association should be searched for in the special interaction between the anion and the central metal ion of the complex radical.

Origin of the Association Band.—According to the present author's opinion, the appearence of the association band may be considered as occurring in the following way.

An anion in an aqueous solution forms with water molecules the hydrogen bridge. In this state it has an absorption maximum at about 2000Å, corresponding to the energy difference of the ground and excited states of the anion concerned. But when the complex is dissolved, the anion enters into the special field of the complex and associates with it. In this case it is quite natural for the anion to alter its electronic states and

TABLE III

DEGREES OF ASSOCIATION

$\nu\cdot10^{13}sec^{-1}$.	1 mol./l soln.		0.1 mol./l soln.			0.01 mol./soln.		
	Opt.	Dens.	Opt.	Dens.	Degr. As.	Opt.	Dens.	Degr. As.
$[Co(NH_3)_6]Cl_3$					(%)			(%)
SO_3^{2-}: 100	211		174		82.5	29		11.3
95	178		141		79.2	20		11.2
				mean	81		mean	11
$S_2O_3^{2-}$: 95	327		282		75.8	145		38.9
90	190		133		70.0	75		39.5
				mean	73		mean	39
CO_3^{2-}: 115	282		200		71.0	89		31.2
110	182		139		76.5	72		39.6
				mean	74		mean	35
$[Co\,en_3]Cl_3$								
SO_3^{2-}: 105	473		376		79.5	71		15
100	355		282		79.5	56		15.8
				mean	80		mean	15
CO_3^{2-}: 110	214		160		74.8	99		46.3
107.5	207		143		69.1	100		48.3
				mean	72		mean	47

In the case of $[Co\,en_3]Cl_3$, the thiosulphate solutions of 0.1 and 1 mol./l. concentrations cannot dissolve the complex to make a 0.005 mol./l. complex solution.

as a result the energy difference between the ground and excited states is diminished. This diminishing effect appears as the bathochromic shift of the absorption band. When an anion enters into the complex radical, that is, it contacts with the central metal ion to form an acidopentammine complex, this tendency is strengthened and in general induces a more bathochromic special band. This interpretation is exceedingly probable, when the absorption curves of NCS^-, $[Co(NH_3)_6](NCS)_n$ and $[Co(NH_3)_5NCS]^{2+}$ are compared with each other. In the Cr complex the same tendency is observed. But in the Co complex and the bivalent anions SO_3^{2-}, $S_2O_3^{2-}$ and CO_3^{2-}, the association bands and the special bands of the corresponding monoacido complexes have almost the same maximum positions. In these cases the anions are greatly affected in their electronic states and are considered to have almost the same state with as of the anions of the monoacido complex. This interpretation suggests that even in the association product, the anion comes very near to the central metal ion owing to the strong attraction, and forms a structure like that of the hepta-coordinated complex. However, it is not yet decided from the present data, whether such strong interaction is originated merely from the strong electrostatic attraction between the bivalent anions and the trivalent cations. In connection with this, it is interesting to notice the fact that the cation of a typical element can produce neither association nor special band with anions. For example, an aluminum cation forms the rhodanato complex in a concentrated rhodanate solution, but even in a very concentrated rhodanate solution, we can find no special band in the ordinary measurable regions. From this fact we may conclude that the deforming power of the transition metal ion is not merely due to its strong positive field, but chiefly originated in its special electronic state, namely in its *d*-electron configuration. The great difference of the maximum positions of the association bands between Co and Cr complexes is explained by the difference of their electronic configurations.

Conclusion

The association of anions NCS^-, SO_3^{2-}, $S_2O_3^{2-}$ and CO_3^{2-} around hexa-ammonia and trisethylenediamine Co and Cr complexes was studied by the spectroscopic method. As the results, the following facts were revealed:

1) The association bands of the ammonia complex have almost the same maximum positions as those of the ethylenediamine complex.

2) The degrees of association in the ammonia complex are almost identical with those in the ethylenediamine complex.

From these facts the main origin of the association was discussed.

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