Absorption Spectra of Co-ordination Compounds. III. Special Bands of Chromium Complexes.

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It has been established by extensive studies of Y. Shibata⁽¹⁾ and his co-workers that the metallic complex has generally two absorption bands, of which the first appears usually in the visible region and the second in most cases in the ultra-violet. One of the present authors⁽²⁾ has recently come to the conclusion that the first band is attributed to electron transitions in unsaturated transition shells of the central ions and the second band may be explained as due to a kind of incomplete dissociation of the complex radical brought about by irradiation, during which the co-ordinate bond is temporarily broken and the ligand is converted into an excited ion or molecule remaining in general in its seat of co-ordination. Moreover, some complexes may have the third bands⁽³⁾ which are due to negative ligands co-ordinated in trans-positions to each other.⁽⁴⁾ It has been postulated by the present author⁽⁵⁾ that the third band is originated in a kind of neutralization between the central ion and one of the co-ordinated anions, during which the ligand is converted into an ionogen which recombines in most cases to regenerate the original complex.

According to the trans-anion hypothesis, $[Cr(NH_3)_5NCS](NCS)_2$ could not be expected to have a third band, nevertheless it shows three absorption bands in aqueous solutions⁽⁶⁾ as well as in liquid ammonia.⁽⁷⁾ Since rhodanate ion has no absorption band in the spectral regions in question when it is not co-ordinated, Y. Shibata⁽⁸⁾ has explained the extra band of the rhodanato-complex as due to NCS-radical combined to the central metallic atom. Uzumasa, Okuno and Doi⁽⁹⁾ have recently

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(1) Y. Shibata, *J. Coll. Sci., Imp. Univ. Tokyo*, 1915 to 1921; *J. Chem. Soc. Japan*, 1915 to 1922.

(2) R. Tsuchida, this Bulletin, **13** (1938), 388.

(3) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 1243.

(4) R. Tsuchida, this Bulletin, **11** (1936), 721.

(5) R. Tsuchida, this Bulletin, **13** (1938), 436.

(6) Y. Shibata and K. Matsuno, *J. Chem. Soc. Japan*, **39** (1918), 661; Y. Shibata, *J. Coll. Sci., Imp. Univ. Tokyo*, **41** (1918), Art. 6.

(7) H. Shiba and T. Inoue, *J. Chem. Soc. Japan*, **56** (1935), 213.

(8) Y. Shibata, *J. Chem. Soc. Japan*, **35** (1914), 807.

(9) Y. Uzumasa, H. Okuno, and K. Doi, *J. Chem. Soc. Japan*, **59** (1938), 655.

illustrated the hypothesis by absorption bands of a number of rhodanates. Such bands are due to ligands themselves and, therefore, could be attributed neither to transition electrons of the central atom nor to co-ordination electrons of the co-ordination center in question. Being thus unable to be classified as any of the numbered bands, they are described here as special bands.

The present paper deals with some of such special bands taking chromium compounds as examples and also refers to the relation between absorption spectra and chemical properties.

Experimental.

The chromium complexes were prepared as described below and their absorption spectra in aqueous solutions were observed. The molar extinction coefficient ε is given by Beer-Lambert's law: $I = I_0 \times 10^{-\varepsilon cd}$, where c is the concentration in gram-ion per liter and d the thickness of the layer in cm. The absorption curves are given in Tables 1, 2 and 3.

$[Cr(H_2O)_6]Cl_3$ was prepared by the method of Bjerrum.(10) Spectrographic measurements: $c = 0.1$ mol/l. and $d = 15.0$ to 0.30 cm. The measurements were carried out at 20°C., as the complex undergoes tautomeric change at higher temperatures.

$[Cr(NH_3)_6]Cl_3$ was prepared by the method of Christensen(11) from anhydrous chromic chloride and liquid ammonia. Freshly prepared chromic chloride gives better yield of the luteo-salt. Spectrographic measurements: $c = 0.01$ mol/l. and $d = 5.00$ to 1.05 cm.

$[Cr(NH_3)_5Cl]Cl_2$ was partly prepared by the method of Christensen(11) and partly by our own. By introducing anhydrous chromic chloride in liquid ammonia the purpureo-salt and the luteo-complex are simultaneously produced, but of freshly prepared chromic chloride most portion is converted into the hexammine complex. The present authors heated hydrated chromic nitrate $Cr(NO_3)_3 \cdot 9H_2O$ with liquid ammonia at about 50°C. for a few hours in an autoclave. Excess of ammonia was evaporated and the residue was then treated with hydrochloric acid. Crude pentammine salt thus obtained was purified as usual. Spectrographic Measurements: $c = 0.005$ mol/l. and $d = 15.0$ to 1.05 cm.

$[Cr(NH_3)_5NCS](NCS)_2$. Werner and Halban(12) reported that they were unable to prepare the rhodanato-complex in crystalline form

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(10) N. Bjerrum, *Z. physik. Chem.*, **59** (1907), 340.

(11) O. T. Christensen, *Z. anorg. Chem.*, **4** (1893), 229.

(12) A. Werner and J. v. Halban, *Ber.*, **39** (1906), 2669.

and it was still impure after second recrystallization. The colour according to the same authors is reddish brown to orange and their analysis gave 18.27% Cr for the theoretical value of 16.7% Cr.

The present authors prepared the salt by the same method and obtained it in two different crystalline forms after repeated recrystallization: yellowish pink crystalline powder and brownish red pyramidal crystals of about 1 mm. in length. The two forms are usually obtained as mixtures in various proportions according to conditions in recrystallization, and consequently the colour may be sometimes reddish brown and sometimes orange as has been described by Werner and Halban. Rapid precipitation from hot solutions gives yellowish pink form and slow crystallization from cold solutions the brownish red form. The chromium contents of the two forms were found to be 16.3% and 15.9% respectively, corresponding to theoretical values of 16.7% as $Cr(NCS)_3{\cdot}5NH_3$ and 15.8% as $Cr(NCS)_3{\cdot}5NH_3{\cdot}H_2O$. The absorption of both the forms was measured. Spectrographic measurements: $c = 0.002$ mol/l. and $d = 15.0$ to 0.08 cm. The absorption curves thus obtained were identical, showing that the water molecule in the reddish brown form is merely the water of crystallization outside the complex radical.

$[Cr(NH_3)_2(NCS)_4]NH_4{\cdot}H_2O$ was prepared by the method of Christensen.(13) Spectrographic measurements: $c = 0.001$ mol/l. and $d = 15.0$ to 0.04 cm.

$[Cr(NCS)_6]K_3{\cdot}4H_2O$ was prepared by the method of Roesler.(14) Spectrographic measurements: $c = 0.001$ mol/l. and $d = 15.0$ to 0.04 cm.

$[Co(NH_3)_5CrO_4]Cl$ was prepared by the method of Briggs.(15) Spectrographic measurements: $c = 0.001$ mol/l. and $d = 5.00$ to 0.02 cm.

K_2CrO_4. Spectrographic conditions: $c = 0.010$ and 0.002 mol/l. and $d = 1.05$ to 0.02 cm.

Discussion of the Results.

(1) Special Bands of Rhodanato-complexes. Whereas $[Cr(H_2O)_6]Cl_3$, $[Cr(NH_3)_6]Cl_3$ and $[Cr(NH_3)_5Cl]Cl_2$ have two bands each, the first and the second, $[Cr(NH_3)_5NCS](NCS)_2$ has three and $[Cr(NH_3)_2(NCS)_4]NH_4$ and $[Cr(NCS)_6]K_3$ have four bands each, just as could be expected from the author's hypotheses.(2)(5)

As is clear from Fig. 1 and Table 1, substitution of NCS^- for NH_3 is bathochromic and at the same time hyperchromic for the first and the second band. Then the same substitution must be bathochromic also for

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(13) O. T. Christensen, *J. prakt. Chem.*, **45** (1892), 216.

(14) J. Roesler, *Ann.*, **141** (1867), 185.

(15) S. H. C. Briggs, *J. Chem. Soc.*, **115** (1919), 70.

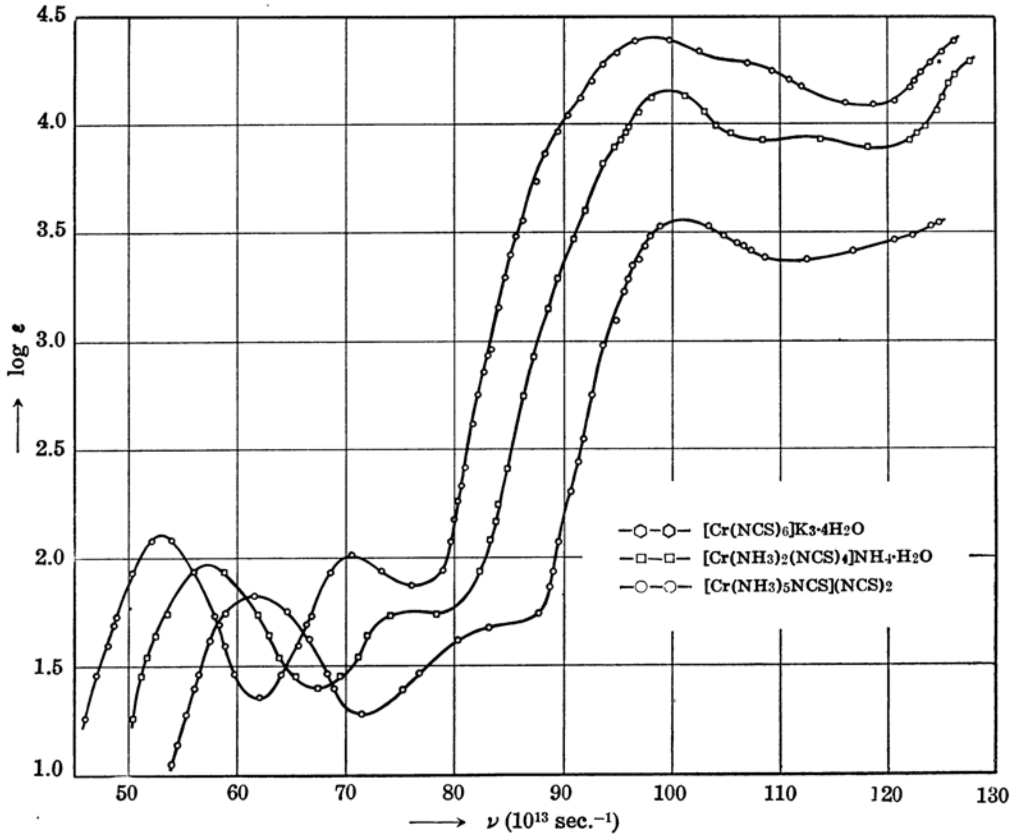

Fig. 1.

Table 1.

Complex compounds	1st bd.		2nd bd.		Special bd.		3rd bd.	
	$\nu_1(10^{13})$	log ε	$\nu_2(10^{13})$	log ε	$\nu_s(10^{13})$	log ε	$\nu_3(10^{13})$	log ε
$[Cr(NH_3)_5NCS](NCS)_2$	61.5	1.82	(83)	1.67	100.4	3.56		
$[Cr(NH_3)_2(NCS)_4]NH_4$	57.5	1.95	(75)	1.75	99.6	4.17	(113)	3.9
$[Cr(NCS)_6]K_3$	53.1	2.08	70.8	2.00	98.6	4.40	(108)	4.3
$[Co(NH_3)_5NCS]Cl_2$ (16)	60.2	2.14	(84)	2.60	98.0	3.20		
$[Co\ dg'_2\ NH_3Cl]$ (17)	63.8	1.75	86.0	3.08	(101)	3.7	121.8	4.50
$[Co\ dg'_2\ py\ Cl]$ (18)	65.5	2.24	89.0	3.39	(102)	3.7	121.5	4.35

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(16) R. Tsuchida, *J. Chem. Soc. Japan*, **59** (1938), 592.

(17) R. Tsuchida and M. Kobayashi, this Bulletin, **12** (1937), 83. The symbol *dg′* denotes a dimethylglyoxime residue behaving as a monobasic acid.

(18) S. Kashimoto and M. Kobayashi, this Bulletin, **12** (1937), 350. The symbol *py* denotes a pyridine molecule.

the third band, so long as the following relation⁽⁵⁾ should exist between the second and the third band.

$$h\nu_3 - h\nu_2 = P + E - J = \text{constant}.$$

For $[Cr(NH_3)_2(NCS)_4]NH_4$ and $[Cr(NCS)_6]K_3$, therefore, the third bands are those of the shortest wave-lengths. The band at about 100×10^{13} sec.$^{-1}$ which remains almost unaffected by the substitution is the special band due to $Cr \leftarrow N{=}C$.

It is interesting to notice that the ε-value of the special band is approximately proportional to the number of NCS-radicals in the co-ordination. This fact shows that the special band is additive and the additivity in turn suggests that the absorption centers of the special band in a complex radical are fairly independent with one another, which could not be the case for the other numbered bands.

Table 2.

Rhodanato-complexes	$\nu_s(10^{13}$sec.$^{-1})$	log ε	ε	Ratio
$[Cr(NH_3)_5NCS](NCS)_2$	100.4	3.56	36×10^2	1
$[Cr(NH_3)_2(NCS)_4]NH_4$	99.6	4.17	15×10^3	4
$[Cr(NCS)_6]K_3$	98.6	4.40	25×10^3	6.6

Whereas the second band of $[Cr(NCS)_6]K_3$ is isolated from the special band, those of $[Cr(NH_3)_2(NCS)_4]NH_4$ and $[Cr(NH_3)_5NCS](NCS)_2$, however, are partly superposed by their special bands. Further the second band of $[Co(NH_3)_5NCS]Cl_2$⁽¹⁶⁾ is inexplicit, being almost entirely covered by its special band, which is due to the origin similar to that in the cases of rhodanato-chromic complexes. It has been shown by Shibata⁽¹⁹⁾ that $[Co(NCS)_4]K_2$ has also a special band of similar origin. A peculiar group which may be represented by $M \leftarrow N{=}C$ is the common feature of all the above-mentioned complexes which have the special bands. Thus the special bands of $[Co\, dg_2'\, NH_3\, Cl]$⁽¹⁷⁾ and $[Co\, dg_2'\, py\, Cl]$⁽¹⁸⁾ might also be explained as due to the same group of $M \leftarrow N{=}C$. In Table 1 are summarized the complexes which have the special bands due to $M \leftarrow N{=}C$, where M is a metallic ion of any valency and of any kind, perhaps including hydrogen ion as in free thiocyanic acid.

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(19) Y. Shibata, *J. Chem. Soc. Japan*, **35** (1915), 807; A. Hantzsch and Y. Shibata, *Z. anorg. Chem.*, **73** (1912), 309.

(2) Special Bands of Chromato-pentammine Cobaltic Salt. Being due to the unsaturated transition shell of the central ion, the first band(2) is expected for all the tervalent chromium complexes. For chromate ion, however, the first band could not be expected, as it has an electronic configuration similar to that of sulphate ion. The second and the third band are expected from the consideration given in the preceding paper(5) and are found at 81×10^{13} sec.$^{-1}$ and 110×10^{13} sec.$^{-1}$ respectively. The absorption curve is given in Fig. 2.

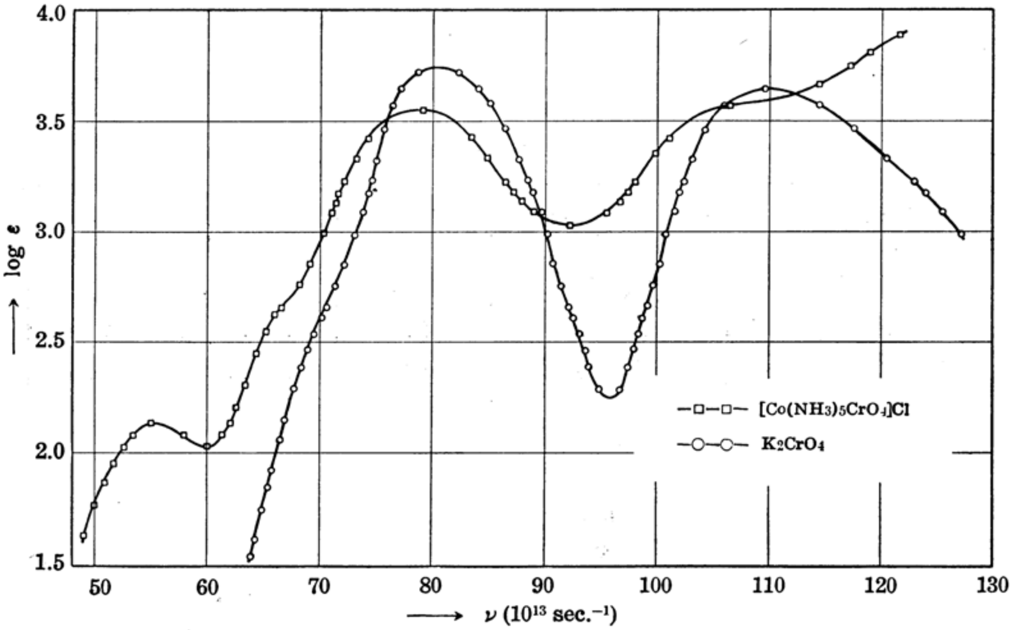

Fig. 2.

The absorption spectrum of $[Co(NH_3)_5CrO_4]Cl$ may be analysed into spectra mainly due to a sexa-coördinate absorption unit whose center is Co and a quadri-coördinate unit whose center is Cr. These absorption units may be denoted as $[(NH_3)_5Co{-}O{-}]$ and $[{-}O{-}CrO_3]$ for the sake of convenience. These two units are combined with each other having one oxygen atom in common. The former should have two bands, the first and the second, and the latter also two bands, the second and the third. As can be seen from Fig. 2, the absorption bands due to $[{-}O{-}CrO_3]$ are slightly shifted towards the longer wave-lengths compared with those of free $CrO_4^{=}$ alone and the extinction coefficients at the absorption maxima of the former are considerably smaller than those of the latter: in other words, formation of co-ordinate linkage between Co^{+++} and $CrO_4^{=}$ has a bathochromic and a hypochromic effect upon the absorption bands of CrO_4^-. The first band of $[(NH_3)_5Co–O–]$ is at 55.6×10^{13} sec.$^{-1}$, but the second band is completely covered by the strongly absorbing second band of $[–O–CrO_3]$.

The bands of $[–O–CrO_3]$ in this case may be regarded as special bands of $[Co(NH_3)_5CrO_4]Cl$, if we take Co as the center of the entire complex. If we take Cr as the center, the bands of $[(NH_3)_5Co–O–]$ may be regarded as special bands as well. The special band, therefore, is relative to the absorption unit in question, and is essentially a numbered band of some other absorption unit.

We may notice that there are two kinds of special bands: viz., the bands which may be observed in the ligands themselves even when they are not combined in co-ordination and those which appear only when the ligands are co-ordinated. The special bands of the first kind may be represented by $[Co(NH_3)_5CrO_4]X$ and those of the second kind may be illustrated by $[Cr(NH_3)_5NCS]X_2$, etc.

(3) Stability and Absorption Spectra of Chromic Complexes. All the co-ordination compounds which contain tervalent chromium ions should

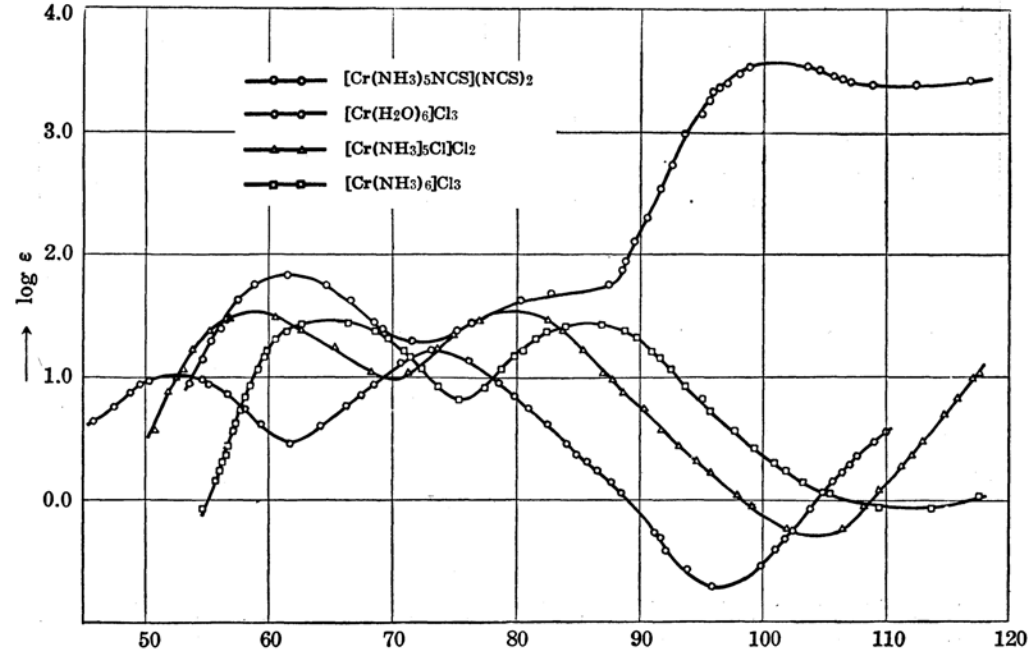

Fig. 3.

have the first and the second bands, the latter giving the measure of stability.(5) From the chromic complexes in Figs. 1 and 3, we may be able to find the spectrochemical series of ligands. Thus the hypsochromic order of ligands for the second bands of chromic complexes is NH_3, NCS^-, Cl^-. (Table 3). The hypsochromic order is from Table 4 NH_3, H_2O, NCS^-. Combining both series, we obtain NH_3, H_2O, NCS^-, Cl^-.

Table 3.

Chromic complexes	1st bd.		2nd bd.		Special bd.	
	$\nu_1(10^{13})$	log ε	$\nu_2(10^{13})$	log ε	$\nu_s(10^{13})$	log ε
$[Cr(NH_3)_5NH_3]Cl_3$	65.0	1.48	86.0	1.44		
$[Cr(NH_3)_5NCS](NCS)_2$	61.6	1.82	(83)	1.67	100.4	3.56
$[Cr(NH_3)_5Cl]Cl_2$	58.7	1.53	80.0	1.54		

Table 4.

Chromic complexes	1st bd.		2nd bd.		Special bd.		3rd bd.	
	$\nu_1(10^{13})$	log ε	$\nu_2(10^{13})$	log ε	$\nu_s(10^{13})$	log ε	$\nu_3(10^{13})$	log ε
$[Cr(NH_3)_6]Cl_3$	65.0	1.48	86.0	1.44				
$[Cr(H_2O)_6]Cl_3$	52.5	1.02	73.6	1.20				
$[Cr(NCS)_6]K_3$	53.1	2.08	70.8	2.00	98.6	4.40	(108)	4.3

As was discussed in the previous paper,(5) the spectrochemical series shows the order of the stability of the co-ordinate link between the central ion and the ligand. The above series indicates that chloro-pentammine and rhodanato-pentammine chromic salts are rather unstable in aqueous solutions. The absorption measurements of these complexes, therefore, were carried out with great precaution against the photo-chemical aquotization, using the solutions as fresh as possible by frequent preparations during the measurements.

It is interesting to notice that the above series for chromic complexes is coincident with the spectrochemical series for cobaltic complexes,(5) i.e., NH_3, NO_2^-, ONO^-, H_2O, NCS^-, OH^-, NO_3^-, Cl^-, $CO_3^=$, Br^-. We may, therefore, be able to discuss chemical properties of chromic complexes by dint of the spectrochemical series of cobaltic complexes, which have been far more thoroughly investigated than the former.

(4) Applications of the Spectrochemical Series in Preparation. Some of the chemical reactions used in preparing chromic complexes may be easily explained by the spectrochemical series. For example, Christensen's method⁽¹¹⁾ of preparing $[Cr(NH_3)_6]Cl_3$ and $[Cr(NH_3)_5Cl]Cl_2$ may be mentioned, in which anhydrous chromic chloride is simply kept in contact with liquid ammonia. Anhydrous chromic chloride may be regarded as a polynuclear complex compound, in which chromium atoms are surrounded by six chlorine atoms octahedrally just as in other chromic complexes. Then the rule⁽⁵⁾ for substitutions in complex radicals may be applied to this compound: viz., the chlorine ions in complexes can be easily displaced by ammonia molecules, as Cl^- is far behind NH_3 in the spectrochemical series. The substitution takes place so readily that it proceeds rapidly even at the temperatures of liquid ammonia. Anhydrous chromic chloride when it is freshly prepared is almost entirely converted into the luteo-salt. The method of Christensen is, therefore, highly recommended for preparation of the luteo-salt, but it is rather inconvenient for preparing the purpureo-salt, especially when chromic chloride is too fresh. In short, the substitution of NH_3 for Cl^- in liquid ammonia is too rapid for preparing the purpureo-salt. Another method of preparing $[Cr(NH_3)_5Cl]Cl_2$ is based on the same principle. As NH_3 is ahead of H_2O in the series, $[Cr(H_2O)_6](NO_3)_3$ should be converted into $[Cr(NH_3)_6](NO_3)_3$ in liquid ammonia. It is evident from the positions of the ligands in the series that the substitution of NH_3 for H_2O is more difficult than for Cl^-: the latter is too rapid and the former is rather too slow for preparing $[Cr(NH_3)_5Cl]Cl_2$. The present authors, therefore, raised the temperature of liquid ammonia to about 50°C. in order to facilitate the dissociation of $Co\text{–}OH_2$ bonds.

Summary.

(1) Absorption spectra of several chromic complexes were measured and it was found that the spectrochemical series is coincident with that for cobaltic complexes.

(2) From the spectrochemical series was discussed the stability of the chromic complexes and some of the methods of preparation were explained.

(3) All the chromic complexes have the first and the second bands. $[Cr(NH_3)_5NCS](NCS)_2$ has another band in addition, which is due to the group $M \leftarrow N=C$ (M= a metal-ion of any kind and valency). $[Cr(NH_3)_2(NCS)_4]NH_4$ and $[Cr(NCS)_6]K_3$ have four bands each, the first, the second, the special and the third. The special bands are due to

the same origin as that of $[Cr(NH_3)_5NCS]X_2$ and the third bands are attributed to trans-pairing of the anions.

(4) Chromate ion, a quadri-coördinate complex, has not the first band, but the second and the third, as could be expected from the author's hypotheses.

(5) Absorption spectra of polynuclear compounds may be analysed into those of component complex radicals. For example $[Co(NH_3)_5CrO_4]Cl$ has three bands, of which one is the first band of the sexa-coördinate cobaltic complex and the other two are mainly the second and the third band of quadri-coördinate chromate radical. The second band of the former is almost entirely covered by the second band of the latter.

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