Absorption Spectra of Co-ordination Compounds. II.

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A typical metallic complex has generally two absorption bands,(1) of which the first lies in the visible region and the second in the ultra-violet. In case the complex has negative ligands in trans-positions another band is expected, which is here called the third band.(2)(3) Further, in special cases, selective absorption bands due to ligands themselves may be observed.

In Part I(4) of this series, the author discussed on the origins of the first and the second band, concluding that the former is attributed to

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(1) Y. Shibata, *J. Coll. Sci., Imp. Univ. Tokyo*, **37** (1915), Art. 2; Y. Shibata and G. Urbain, *Compt. rend.*, **157** (1913), 593.

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

(3) R. Tsuchida, this Bulletin, **11** (1936), 721; R. Tsuchida and S. Kashimoto, *ibid.*, **11** (1936), 785; R. Tsuchida and M. Kobayashi, *ibid.*, **12** (1937), 83.

(4) R. Tsuchida, *ibid.*, **13** (1938), 388.

electron transitions in an unsaturated transition shell of the central ion and the latter is due to a kind of reversible dissociation of ligands within the complex radical. The present paper deals with the origins of the third and the special bands as well as the relation between the absorption and the stability of the complex radical.

VI. Thermochemical Explanation of the Third Band. In order to explain the second band, it has been postulated in Part I(4) that, when a quantum of the second band is absorbed by a complex radical, one of the co-ordinate links is split open to produce in the original seat of co-ordination an excited ligand, which will recombine in most cases to regenerate the original complex: e.g.,

$$[\mathrm{M\ A_6}]^{n+} + h\nu_2 = [\mathrm{M\ A_5}\{\mathrm{A}\}]^{n+},$$

$$[\mathrm{M\ X_6}]^{n-} + h\nu_2 = [\mathrm{M^+\ X_5}\{\mathrm{X^-}\}]^{n-}, \quad \text{etc.},$$

where $\{\mathrm{A}\}$ and $\{\mathrm{X^-}\}$ denote the excited molecule and ion respectively. Thus the frequency of the second band may be shown by the following relation.

$$S = h\nu_2 = -P + Q + R - \frac{\Phi - \Sigma\Phi_1}{n} \qquad (3),$$

where S = the co-ordination energy, P = the energy of approach, Q = the heat of formation of the complex from the component compounds of first order, R = the energy of activation of the ligand, Φ = the lattice energy of the complex, $\Sigma\Phi_1$ = sum of the lattice energies of the component compounds, and n = the co-ordination number.

For the third band, the author assumes a kind of neutralization between the central ion and one of the co-ordinating anion, in which an excited ionogen is produced in the position of co-ordination: e.g.,

$$[\mathrm{M\ X_6}]^{n-} + h\nu_3 = [\mathrm{M\ X_5}\{\mathrm{X}\}]^{n-}, \quad \text{etc.},$$

where $\{\mathrm{X}\}$ denotes the excited ionogen. It is again assumed that the excited ionogen thus produced by $h\nu_3$ recombines, in most cases, to form the original complex and may be sometimes set free resulting in decomposition or substitution of ligands.

The photochemical neutralization may be treated thermochemically by assuming the following cyclic process. (1) First, the co-ordinate link is broken ($-S$). (2) The excited ion is converted into an ion in normal state ($+R$). (3) Then the ion is taken to infinity ($-P$). (4) The anion is deprived of the electron ($-E$). (5) The electron is given to the central

ion $(+J)$. (6) The ionogen is again brought to the seat of co-ordination and then excited $(-R)$.
Then

$$h\nu_3 = S+P+E+J \qquad (4),$$

where E = the electron affinity of the ligand, and J = the ionization energy of the central ion.

By means of the relation thus derived, several interesting facts may be explained.

(A) *Constancy of* $\nu_3 - \nu_2$. The differences, $\nu_3 - \nu_2$, are nearly equal for a series of similar compounds. The fact is especially remarkable in the nitro-ammine cobaltic series, in which $\nu_3 - \nu_2$ is nearly constant, while $\nu_2 - \nu_1$ varies in considerably wide range. (C.f. Section I.⁽⁴⁾)

We obtain from the relations (2) and (4),

$$h\nu_3 - h\nu_2 = P+E-J\,.$$

Now for nitro-ammine cobaltic compounds, E and J are constant and P also may be regarded as constant, if we neglect the effect of neighbouring ligands. Therefore $\nu_3 - \nu_2$ is constant.

(B) *Estimation of the third ionization potential of cobalt.* Assuming the distance between the central ion and the negative charge of the nitro-radical of $[Co(NH_3)_2(NO_2)_4]Ag$⁽⁵⁾ as 2.5 Å, we may roughly estimate the value P.

$$P = 27.4\times10^{12}\ \text{ergs} = 17.5\ \text{e.v.}$$

$$h\nu_3 - h\nu_2 = 33h\times10^{13} = 2.16\times10^{12}\ \text{ergs} = 1.4\ \text{e.v.}$$

Hence $$J = P+E-(h\nu_3 - h\nu_2) = 20\ \text{e.v.}$$

This value of J seems too small for the third ionization of cobalt. The deviation might probably be attributed to the neglection of the polarization.

(C) *Third bands of non-metallic complexes.* Triiodide ion may be regarded as a non-metallic complex, of which the center and the ligands are all iodine ions, positive and negative. Then it should have a second band, while it should lack the first, the central ion being of an inert gas configuration. (Cf. Section IV.⁽⁴⁾) According to Mooney⁽⁶⁾ the complex ion has a linear structure, and if we extend the hypothesis on the third band⁽⁴⁾ to this non-metallic complex, here again a third band is expected.

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(5) A. F. Wells, *Z. Krist.*, **95** (1936), 74.

(6) R. C. L. Mooney, *Z. Krist.*, **90** (1935), 143.

In fact, triiodide ion has two bands at 94×10^{13} and 113×10^{13}, which may possibly be regarded as the second and the third band respectively. (Cf. Section II.(4)) Allsopp(7) postulated that the twin bands have the origin in the simultaneous production during irradiation of iodine atoms in the normal and in the excited, metastable state. According to our hypothesis, however, the third band is due to a neutralization, in which iodine atoms in the normal and in the excited state are produced simultaneously just as was assumed by Allsopp. Absorption of the light energy corresponding to the second band produces an excited metastable ion.

(D) *The absorption bands of alkali halides.* Hilsch and Pohl(8) studied the absorption bands of crystals of alkali halides and explained the band of the longest wave-length as related to a neutralization of adjacent ions, e.g.,

$$\mathrm{Na}^+ + \mathrm{Cl}^- + h\nu = \mathrm{Na} + \mathrm{Cl}\ .$$

The energy was expressed by

$$h\nu = \Phi + E - J\ ,$$

where Φ = the lattice energy, J = the ionization energy of the alkali atom, and E = the electron affinity of the halogen atom. Born(9) modified the formula, by postulating "Lochenergie".

In order to extend the results of absorption spectra of co-ordination compounds, the author assumes further that the co-ordinate covalene may be considered as to consist of two parts, i.e., electro-valence and covalence, and these, in turn, may be explained as extreme cases of co-ordinate covalence: the electro-valence is an extreme case of co-ordinate covalence, in which the covalent linkage is so weak as may be neglected, and the covalence, the opposite extreme case, in which it lacks the electrostatic part. Then all the chemical linkages might be regarded as co-ordinate combination and consequently the results obtained for co-ordination compounds may be widely applied to various compounds.

Now sodium chloride, for example, should lack the first and the second band, because it has neither unsaturated transition shell nor co-ordinate bonds. In crystalline form, however, six chlorine ions are situated around a sodium ion, just as in a sexa-coördinated complex, every two of the former making a pair in trans-position to each other, and therefore a third band may be expected. Thus the band of the longest wave-length

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(7) C. B. Allsopp, *Proc. Roy. Soc.* (London), A **158** (1937), 167.

(8) R. Hilsch and R. W. Pohl, *Z. Physik*, **59** (1928), 812.

(9) M. Born, *Z. Physik*, **79** (1932), 62.

in the ultra-violet region could be regarded as the third band and the relation (4) may be applied.

$$h\nu_3 = S+P+E-J\ .$$

Now P in this case is the work to bring Na^+ and Cl^- to infinity, i.e., the lattice energy Φ. And if we assume $S=0$, the relation is reduced to

$$h\nu_3 = \Phi+E-J\ .$$

This is identical with the equation of Hilsch and Pohl, the latter being a special case of the relation (4).

(E) *Absorption spectra of various compounds of first order.* From the viewpoint suggested in (D), various binary compounds of the type M_mX_n, usually understood as compounds of first order, may be recognized as co-ordination compounds. A few examples are given here. Anhydrous chromic chloride may be regarded as a polynuclear complex compound. As is clear from its crystal structure,(10) every chromic ion is surrounded octahedrally by six chlorine ions and the entire crystal is of a layer lattice, each layer being built up of such octahedra having chlorine ions in common. Now, according to the author's opinion, the compound should have the first, the second and the third band.

It has already been stated that mercuric chloride could be regarded as a co-ordination compound, the second and the third band being expected. (Cf. Section V.(4)) As was discussed in (D), only the third band is expected for sodium chloride in crystalline state. Extending the idea on the opposite side, the author expects that stannic bromide, etc., should have the second and the third band.

In connection with this problem, the interesting research of the Joffés(11) must be referred to. They measured electrical conductivity of single crystals of cuprous oxide irradiating them with monochromatic lights. The spectrum of conductivity gives three maxima at 590 mμ, 420 mμ and 270 mμ, showing a curve quite similar to that of an absorption spectrum of a typical complex compound which has a third band. The crystal structure(12) shows that oxygen atoms are co-ordinated in trans-positions to each other referring to a copper atom, and this is the very structure for which a third band may be expected.

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(10) N. Wooster, *Z. Krist.*, **74** (1930), 363.

(11) A. W. Joffé and A. T. Joffé, *Physik. Z. Sowjetunion*, **11** (1937), 241.

(12) P. Niggli, *Z. Krist.*, **57** (1922), 253.

VII. Extension of Trans-Pairing Hypotheses. It has long been known that the ligands co-ordinated in trans-position to each other are in special relation. The phenomenon of geometrical isomery is too well known. Drew, Cox and others⁽¹³⁾ have shown that the four linkings to the ammonia molecules of tetrammine platinic salts are differentiated into two equivalent pairs which function independently, a closer relationship existing between the members of a pair than exists between either member of one pair and either member of the other. Cox and Preston⁽¹⁴⁾ extended the theory. H. Sueda⁽¹⁵⁾ assumed that the absorption spectra of complex compounds could be expressed as the sum of the characteristic absorption caused by the radicals situated at the trans-position, and analyzed second bands of various complex salts. Y. Shibata⁽²⁾ explained the third bands of nitro-ammine cobaltic compounds by his trans-dinitro-theory. And the present author⁽³⁾ extended Shibata's theory, explaining the third band as due to a pair or pairs of negative ligands in trans-positions.

As has been shown in the preceding section, it must be postulated in order to explain the third band that it has its origin in a kind of neutralization between the central cation and a ligand anion, but the postulate does not imply that the ligand must have another anion in its trans-position. The author should like to explain this point conventionally by the following hypothesis. In the process of the neutralization the electron must be transferred from the ligand to the central ion, during which the latter would undergo a great polarization, and this polarization in turn would cause in the ligand in trans-position further polarization of such a degree that anions only could correspond to it. In case there is a neutral ligand in the trans-position, it would resist the polarization and accordingly the neutralization would be prevented.

If we assume that the trans-pairing is due to polarization through the central ion as above, all the third bands could be explained. (Cf. Section II.⁽⁴⁾) Whereas in octahedral or square configuration the pair of ligands in trans-position only can have opposite co-ordination directions referred to the central ion, in tetrahedral configuration, however, any two ligands can have opposite components of co-ordination directions. Then another possibility of the third band must be admitted: viz., the third bands may be expected for tetrahedral molecules and ions such as SnI_4, $CrO_4^=$, etc., though they have no ligands in trans-positions. Thus

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(13) H. D. K. Drew, F. W. Pinkard, W. Wardlaw, and E. G. Cox, *J. Chem. Soc.*, **1932**, 1004.

(14) E. G. Cox and G. H. Preston, *ibid.*, **1933**, 542.

(15) H. Sueda, *J. Chem. Soc. Japan*, **56** (1936), 406, 542.

the trans-diacido-hypothesis for octahedral and square configurations should be modified in its application to compounds of tetrahedral configuration.

VIII. Special Bands. We have seen that all the compounds which show the third bands have negative ligands co-ordinated in trans-positions and vice versa. The only exception in the literature is $[Cr(NH_3)_5(NCS)](NCS)_2$ which gives three bands in spite that it has only one negative ligand in co-ordination. Y. Shibata(16) proved that the special band is due to NCS radical itself when co-ordinated to any central metallic atom.

Then $[Co(NH_3)_5(NCS)]Cl_2$, $[Cr(NH_3)_2(NCS)_4]NH_4$ and $[Cr(NCS)_6]K_3$ should have the special bands. The author prepared these compounds as well as $[Cr(NH_3)_5(NCS)](NCS)_2$ and measured their absorption. The results are given in Table 6.

Table 6.

Complex compound	1st bd.		2nd bd.		Special bd.		3rd bd.		$\nu_s-\nu_2$	$\nu_3-\nu_2$
	$\nu_1(10^{13})$	$\log\varepsilon$	$\nu_2(10^{13})$	$\log\varepsilon$	$\nu_s(10^{13})$	$\log\varepsilon$	$\nu_3(10^{13})$	$\log\varepsilon$		
$[Co(NH_3)_5(NCS)]Cl_2$	60.2	2.14	(84)	2.60	98.0	3.20	—	—	14	
$[Cr(NH_3)_5(NCS)](NCS)_2$	61.5	1.82	(83)	1.67	100.4	3.56	—	—	17	
$[Cr(NH_3)_2(NCS)_4]NH_4$	57.5	1.95	(75)	1.75	99.6	4.17	(113)	3.9	25	38
$[Cr(NCS)_6]K_3$	53.1	2.08	70.8	2.00	98.6	4.40	(108)	4.3	28	37
$[Co\ dg_2'\ Cl\ NH_3]$(17)	63.8	1.75	86.0	3.08	(101)	3.7	121.8	4.50	15	36
$[Co\ dg_2'\ Cl\ py]$(18)	65.5	2.24	89.0	3.39	(102)	3.7	121.5	4.35	13	33

The special band of $[Cr(NH_3)_5NCS](NCS)_2$ is at $\nu = 100.4 \times 10^{13}$. $[Cr(NH_3)_2(NCS)_4]NH_4$ and $[Cr(NCS)_6]K_3$ give similar bands whose frequencies are 99.6×10^{13} and 98.6×10^{13} respectively. Whereas each of the first, the second and the third band of $[Cr(NCS)_6]K_3$ has a larger frequency than that of the corresponding band of $[Cr(NH_3)_2(NCS)_4]NH_4$, the position of the special band of the former is nearly the same as that of the latter. In these isorhodanato-complexes we may notice a peculiar group of atoms, $M \leftarrow N = C<$, to which the special bands may be attributed. In $[Co\ dg_2'\ Cl\ NH_3]$ and $[Co\ dg_2'\ Cl\ py]$, the same group may

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(16) Y. Shibata, *J. Chem. Soc. Japan*, **35** (1914), 807; *J. Coll. Sci., Imp. Univ. Tokyo*, **41** (1918), Art. 6.

(17) R. Tsuchida and M. Kobayashi, this Bulletin, **12** (1937), 83.

(18) S. Kashimoto and M. Kobayashi, *ibid.*, **12** (1937), 350.

again be found and accordingly similar special bands should be expected. In fact these dimethylglyoxime-complexes show four bands each, of which those at about 100×10^{13} may be regarded as the special bands. Moreover, salicylaldehyde-ethylenediamine-cobalt which was recently reported by T. Tsumaki⁽¹⁹⁾ has also a special band similar to those mentioned above and it may probably be due to the same origin.

We have seen that the spectra of a co-ordination compound consists of the first, the second, and the third band as well as special bands. The author, however, does not mean that a numbered band, say the third, is actually the third or there are at least three bands. For example, the third band of $[\mathrm{Hg\,I_4}]\mathrm{K_2}$ is actually the second and that of rock salt, the first. Moreover, the third band of $[\mathrm{Co}\,dg_2'\,\mathrm{Cl\,NH_3}]$ is really the fourth, special band due to $\mathrm{M} \leftarrow \mathrm{N} = \mathrm{C} <$ being the third numbered from the long-wave side.

Besides the absorption bands hitherto discussed, every co-ordination compound has the so-called end absorption, which is the superposition of special bands due to less effective ligands and their parts. By investigating shorter wave-lengths, we must naturally meet such bands. The special bands given in Table 6 are some of those which have comparatively longer wave-lengths.

As was discussed in Section I,⁽⁴⁾ all the chemical combinations may be regarded as co-ordinate linkages or the extreme cases. The entire absorption spectrum of a compound may possibly be treated as a kind of superposition of co-ordination spectra of parts of the compound. For example, the spectrum of $[\mathrm{Co(NH_3)_5CrO_4}]\mathrm{Cl}$ may be analysed into spectra mainly of sexa-coördinate absorption unit, of which the center is Co and a quadri-coördinate unit whose center is Cr. These absorption units may be denoted as $[\mathrm{Co(NH_3)_5O}-]$ and $[\mathrm{Cr\,O_3O}-]$ for the sake of convenience. The former should have two bands, the first and the second, and the latter also two bands, the second and the third. Measurements show that the absorption bands due to $[\mathrm{Cr\,O_3O}-]$ are slightly shifted towards the longer wave-lengths compared with those of $\mathrm{CrO_4^=}$ alone: viz., the second band of the former is at 78×10^{13} and that of the latter, at 81×10^{13}. The first band of $[\mathrm{Co(NH_3)_5O}-]$ is at 56×10^{13}, but the second is covered by the strongly absorbing second band of $[\mathrm{Cr\,O_3O}-]$. The bands of $[\mathrm{Cr\,O_3O}-]$ in this case may therefore, be called special bands of $[\mathrm{Co(NH_3)_5CrO_4}]\mathrm{Cl}$.

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(19) T. Tsumaki, this Bulletin, **13** (1938), 252; *J. Chem. Soc. Japan*, **58** (1937), 1288.

IX. Stability of Co-ordination Compounds. There has been neither fixed definition nor generally accepted measure as to the stability of co-ordination compounds. The stability in solution must of course depend upon the nature of the solvent. The photochemical stability as was studied by Schwarz(20) could not be applied to compounds which do not undergo photochemical change.

Ephraim and his co-workers(21) have studied thermal decomposition of solid ammine complexes, but his definition of stability is applicable only to those complexes which are built up by Werner's auxiliary valences. In short, there is no definition of stability which would cover the entire field of co-ordination compounds. In order to establish such a definition, it is necessary to choose as the measure a property which is quite common to all co-ordination compounds. For this purpose spectroscopic data would give a fine measure. Luther and Nikolopulos(22) assumed that the first band is due to the linkage between the central atom and the ligand, and the strength of the linkage could be judged from the colour of the compound. In other words, they adopted the first band as the measure of stability. This hypothesis implies that the shorter the wave-length of the first band, the greater is the stability. According to this hypothesis, $[Co(NH_3)_5(NO_2)]Cl_2$, the most stable complex among the nitro-ammines, should have a first band of shorter wave-length than any other member of the series, but, as a matter of fact, the first band has lower frequency than those of less stable compounds such as $[Co(NH_3)_3(NO_2)_3]$ and $[Co(NH_3)_2(NO_2)_4]NH_4$. (Cf. Table 2.(4)) Moreover, the order of actual stability seems almost reverse to that of the frequency of the first band for the nitro-ammine cobaltic series. Thus the band could not be the true measure of stability, nevertheless it may be taken as a rough measure by the reason which will be shown later.

On the contrary, the frequency of the second band is precisely in the order of actual stability. In the nitro-ammine series, for example, $[Co(NH_3)_5(NO_2)]Cl_2$ has the highest frequency and $[Co(NH_3)_2(NO_2)_4]NH_4$ the lowest, the other members(23) being intermediate. Thus the second band may be adopted as the measure of stability, and consequently S may serve for the same purpose. From the

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(20) R. Schwarz and K. Tede, *Ber.*, **60** (1927), 65, 69; R. Schwarz and H. Weiss, *ibid.*, **58** (1925), 746.

(21) F. Ephraim, *Ber.*, **45** (1912), 1322; **46** (1913), 3103, 3742; **47** (1914), 1828; **48** (1915), 41, 624, 629, 638, 1770, 2007; **49** (1916), 529; **50** (1917), 1069, 1088; **51** (1918), 130, 644, 706; **52** (1919), 236, 941; *Z. physik. Chem.*, **81** (1912), 513, 539; **83** (1913), 196.

(22) R. Luther and A. Nikolopulos, *Z. physik. Chem.*, **82** (1913), 361.

(23) It has already(4) been discussed that $[Co(ONO)_6]M_3$ does not belong to this series.

practical point of view alone, it is far advantageous to take the second band as the measure, because all the co-ordination compounds have the second bands whereas some of them lack the first as was shown in Part I.⁽⁴⁾

Substitution of NO_2^- for NH_3 in nitro-ammine complexes, gives rise to an instabilization of the complexes, or in other words, NH_3 is more hypsochromic than NO_2^-. The order of hypsochromic effect on the second band may be easily found for various ligands. In Tables 7 and 8, pentammine and tetrammine cobaltic complexes are arranged in the order of frequency of their second bands, i.e., the order of stability.

Table 7.

Ligand	Complex	ν_2 (10^{13})	log ε
NO_2^-	$[Co(NH_3)_5NO_2]Cl_2$	92.6	3.12
ONO^-	$[Co(NH_3)_5ONO]Cl_2$	91.7	2.79
H_2O	$[Co(NH_3)_5H_2O]Cl_3$	87.5	1.62
NCS^-	$[Co(NH_3)_5NCS]Cl_2$	(84)	2.60
OH^-	$[Co(NH_3)_5OH](NO_3)_2$	(84)	1.9
NO_3^-	$[Co(NH_3)_5NO_3](NO_3)_2$	(83)	1.8
Cl^-	$[Co(NH_3)_5Cl]Cl_2$	82.8	1.66
$CO_3^=$	$[Co(NH_3)_5CO_3]NO_3$	(82)	1.8
Br^-	$[Co(NH_3)_5Br]Br_2$	(81)	2.8

Table 8.

Ligand	Complex	ν_2 (10^{13})	log ε
NO_2^-	$[Co(NH_3)_4(NO_2)_2{}^{(1)}_{(2)}]Cl$	91.2	3.10
H_2O	$[Co(NH_3)_4(H_2O)_2{}^{(1)}_{(2)}]Cl_3$	84.0	1.48
$C_2O_4^=$	$[Co(NH_3)_4C_2O_4]Br$	84.0	1.88
$CO_3^=$	$[Co(NH_3)_4CO_3]Br$	82.6	2.03

From Table 7, we can find the hypsochromic order of ligands, i.e., the spectrochemical series for the second band:

$$NH_3,\ NO_2^-,\ ONO^-,\ H_2O,\ NCS^-,\ OH^-,\ NO_3^-,\ Cl^-,\ CO_3^=,\ Br^-.$$

It will be noticed that the series almost coincides with that of the first band. (Cf. Section IV.⁽⁴⁾) This fact may easily explained by the following consideration. We have seen in Section V,⁽⁴⁾

$$S = -P + Q' + R \qquad (1').$$

The smaller the value P, the greater will be the value S if Q' and R remain nearly equal. Thus the theoretical consideration for the first band given in Section IV⁽⁴⁾ will also hold approximately for the second band. For example P for H_2O is smaller than that for Cl, but greater than that for NH_3. The ligand H_2O, therefore, forms more stable co-ordinate combination than Cl, but less stable linkage than NH_3.

From the same consideration it follows that the first and the second bands will be displaced side by side by a substitution, so long as Q' and R for the compounds remain nearly constant. In such cases we may be able to compare approximately the stability of these compounds by the position of the first bands, as has been proposed by Luther and Nikolopulos.⁽²²⁾ The first bands, however, fail sometimes to be the measure, as we have seen in the case of nitro-ammine cobaltic compounds. The first band is merely an approximate measure of stability after all.

In Table 9, symmetrical complex salts of iron, chromium and cobalt are shown all together in the order of the frequencies of the second bands. Here again it coincides with the order of actual stability, showing that the second band is the absolute measure of stability which covers the entire field of co-ordination compounds.

Table 9.

Linkage	Complex salt	ν_2 (10^{13})	$\log \varepsilon$
$Fe^{+++}-CN^-$	$[Fe(CN)_6]K_3$	99.4	3.20
$Co^{+++}-en$	$[Co\ en_3]Br_3$	90.0	1.77
$Co^{+++}-NH_3$	$[Co(NH_3)_6]Cl_3$	88.8	1.57
$Cr^{+++}-NH_3$	$[Cr(NH_3)_6]Cl_3$	86.0	1.44
$Co^{+++}-ONO^-$	$[Co(ONO)_6]Na_3$	82.4	3.75
$Cr^{+++}-H_2O$	$[Cr(H_2O)_6]Cl_3$	73.6	1.20
$Co^{+++}-C_2O_4^{=}$	$[Co(C_2O_4)_3]K_3$	71.0	2.19
$Cr^{+++}-NCS^-$	$[Cr(NCS)_6]K_3$	70.8	2.00

The stability may sometimes be roughly compared without spectroscopic data. By dint of the relation (1′), we may be able to compare the stability of co-ordination compounds, of which *Q*'s and *R*'s are nearly equal. For example, the heats of formation(24) of $[\mathrm{Co(NH_3)_4Cl_2}{}_{\substack{(1)\\(6)}}]$ Cl and $[\mathrm{Co(NH_3)_4Cl_2}{}_{\substack{(1)\\(2)}}]$Cl are 215 and 214 Cal. respectively, which may be regarded as equal, and *R*, i.e., the activation energy for $\mathrm{Cl^-}$ to combine with $\mathrm{Co^{+++}}$ may also be assumed as equal for this pair of isomers. Then we obtain from (1′) $S = -P +$ constant. If we neglect the polarization of $\mathrm{Cl^-}$, the energy of approach, P, may be roughly calculated for the cis-form and the trans-isomer.

$$P_{\mathrm{trans}} - P_{\mathrm{cis}} = -\frac{e^2}{r}\left(\frac{1}{2} - \frac{1}{\sqrt{2}}\right) > 0\ ,$$

where r denotes the distance between the central ion and the ligand.

Hence $\qquad P_{\mathrm{cis}} < P_{\mathrm{trans}}\ .$

Therefore $\qquad S_{\mathrm{cis}} > S_{\mathrm{trans}}\ .$

The cis-compound should, therefore, be more stable than its trans-isomer. Another example of geometrical isomery may be found in Table 2,(4) in which ν_2's of $[\mathrm{Co(NH_3)_4(NO_2)_2}{}_{\substack{(1)\\(2)}}]$Cl and $[\mathrm{Co(NH_3)_4(NO_2)_2}{}_{\substack{(1)\\(6)}}]$Cl are 91.2×10^{13} and 87.0×10^{13} respectively, the former thus being more stable.

In photochemical decomposition of $[\mathrm{Co(NH_3)_4(NO_2)_2}]$Cl, however, the trans-form has been proved(20) to be more stable than the cis-isomer. This fact seems at first sight to contradict with the above conclusion, nevertheless this apparent discrepancy may be easily overcome by the following consideration.

When a complex radical absorbs $h\nu_2$, the co-ordinate link is split open and an excited ligand will be produced at the seat of co-ordination, as was shown in Section V.(4) Such excited state of a ligand may be reached otherwise, viz., by making the ligand approach to the central ion from infinity $(-P)$ and then giving it the energy of activation $(+R)$. The excited ligand which has the energy $(R-P)$, may either combine with the central ion to regenerate the original complex or leave the position of co-ordination resulting in decomposition or substitution. In other words, there may be assumed an intermediate metastable state prior to the formation or the destruction of the linkage.

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(24) T. C. J. Ovenston and H. Terry, *J. Chem. Soc.*, **1936**, 1660.

$$[\mathrm{M\ A_5B}]+h\nu_2(=S) \rightleftarrows [\mathrm{M\ A_5\{B\}}] \rightleftarrows [\mathrm{M\ A_5}]+B+(R-P)\ ,$$

where {B} represents the excited ligand.

The greater the value S, the greater the stability of the complex in thermal reactions. During irradiation with $h\nu_2(=S)$, however, the energy of the intermediate excited state will sway the stability. The greater the energy $R-P$, the intermediate state will be the more readily decomposed. The stability in photochemical reaction, therefore, depends on the value $P-R$. We have seen above that

$$P_{\mathrm{cis}} < P_{\mathrm{trans}}\ .$$

Hence $$(P-R)_{\mathrm{trans}} > (P-R)_{\mathrm{cis}}\ .$$

Thus the trans-form is more stable in photochemical change than its cis-isomer.

X. Substitution of Ligands. Experience shows that the substitution of ligands which proceeds naturally occurs in the direction in which the value S increases, i.e., the second band is shifted towards the shorter wave-lengths.(25) In other words, the substitution reaction takes place so as to produce more stable substitution products. For example, $[Co(NH_3)_4Cl_2{}^{(1)}_{(6)}]Cl$ in aqueous solution changes step by step into $[Co(NH_3)_4(H_2O)_2{}^{(1)}_{(2)}]Cl_3$, the second band of the latter as well as those of the intermediate compounds showing the corresponding hypsochromic shifts from that of the initial compound.

This rule may be advantageously applied to judge the stability of complex compounds in solution. Whereas ligands which have larger S-values than H_2O, will form complexes stable in aqueous solution, complexes which contain ligands of smaller S-value than H_2O will be unstable in aqueous solution and aquotization will then take place. For example, the second bands of $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5H_2O]Cl_3$ and $[Co(NH_3)_5Cl]Cl_2$ are respectively at 88.8×10^{13}, 87.5×10^{13} and 82.8×10^{13}. The luteo-salt is, therefore, very stable in aqueous solution, while the purpureo-salt changes gradually into the roseo-salt. The preparation of the purpureo-salt by adding hydrochloric acid to aqueous solution of the roseo-salt depends upon the fact that the former has much smaller solubility than the latter. It is the question of solubility and not of stability.

Extending the above consideration, we may now be able to discuss the possibility of methods of preparation of complex compounds. It is

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

possible to prepare by substitution reaction a complex compound whose S is larger than that of the material. The greater the difference in S, the easier the preparation. For example, the substitution of NH_3 for Cl^- should be much easier than that of NH_3 for H_2O.

Anhydrous chromic chloride $CrCl_3$ may be regarded as a polynuclear complex compound as was pointed out in Section VI. By simply keeping this salt in liquid ammonia, $[Cr(NH_3)_6]Cl_3$ is easily produced, but it is rather difficult to obtain the latter from $[Cr(H_2O)_6]Cl_3$ and liquid ammonia. These empirical rules and the hypothesis might be widely applied in explaining various chemical reactions as well as finding methods of preparation of co-ordination compounds. For this purpose the spectrochemical series for the second band given in Section IX may be of considerable service.

Summary.

(1) The absorption spectra of co-ordination compounds consist of the first, the second and the third bands as well as those due to ligands themselves. Some of the compounds may lack the first, the third, or both the bands, but none of them the second.

(2) Postulating that by absorption of a quantum $h\nu_3$ ($\nu_3 =$ the frequency of the third band) a kind of neutralization takes place between the central ion and one of the co-ordinated anion to produce an excited ionogen in the original seat of co-ordination, the following relation has been derived.

$$h\nu_3 = S+P+E-J\,,$$

where $E =$ electron affinity of the anion, $J =$ ionization energy of the central ion, $S =$ co-ordination energy, and $P =$ work of approach of the anion.

The ultra-violet absorption band of solid alkali halide has been explained as a special case of the third band.

(3) Besides the numbered bands, a co-ordination compound has generally some more bands due to ligands themselves. Examples of these special bands are given. The end absorption has also been explained.

(4) The co-ordination energy, $S(=h\nu_2)$, may be taken as the measure of stability of the co-ordination compound. The order of hypsochromic effect of ligands on the second band gives the order of strength of the co-ordinate linkages between the central ion and the ligands. The order of stability has been determined experimentally.

$$NH_3,\ NO_2^-,\ ONO^-,\ H_2O,\ NCS^-,\ OH^-,\ NO_3^-,\ Cl^-,\ CO_3^=,\ Br^-.$$

(5) Whereas the stability of co-ordination compounds may be defined by S as a rule, the photochemical stability, however, should be given by $P - R$, R being the activation energy. Both the stabilities were compared with illustrations.

(6) The substitution of ligands which proceeds naturally, takes place in the direction, in which the value S increases, or in other words, the second band is displaced towards the shorter wave-lengths. This rule and the spectrochemical series in (4) give the means of explaining as well as finding methods of preparation of various co-ordination compounds.

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