# Absorption Spectra of Co-ordination Compounds. I.

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**I. Introduction.** It is already two decades since a number of facts were revealed of absorption spectra of metallic complexes by extensive studies of Y. Shibata⁽¹⁾ and his co-workers, pioneers in the field. Ever since, various hypotheses have been proposed as to the origins of absorption bands of these compounds, but none of those could satisfactorily explain, even qualitatively, the entire empirical facts already known.

According to Shibata,(1)(2) the metallic complexes have generally two selective absorption bands, of which the first lies in the visible region and the second in the near ultra-violet.(3) Some complexes, however, give the third bands in the region of shorter wave-lengths. In more special cases, selective absorption bands due to ligands(4) themselves may superpose on those proper to the co-ordination combination.

The author has recently been studying the third bands of co-ordination compounds and has arrived at some conclusions on the origins of the first and the second band as well as the third. The present paper is an abbreviated summary of the results so far obtained.

**II. The Third Band.** The first systematic study on the third bands was carried out in 1915 by Y. Shibata,(5) who explained the third band of $[Co(NH_3)_4(NO_2)_2{}^{(1)}_{(6)}]X$ as due to the nitro-radicals co-ordinated in trans-position to each other, confirming his theory by several examples such as $[Co(NH_3)_3(NO_2)_3]$, $[Co(NH_3)_2(NO_2)_4]NH_4$, etc.,(6) and further determined the configuration of some compounds by ingenious application of

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

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

(3) In some cases, e.g., $[Ni(NH_3)_6]Cl_2$, $[Co(H_2O)_6]Cl_2$, etc., both the bands are shifted so immensely that the first and the second bands appear in the infra-red and the visible regions. T. Dreisch and W. Trommer, *Z. physik. Chem.*, B, **37** (1937), 37. On the contrary, in other cases, e.g., $[Ir\ en_3]X_3$, $[Rh\ en_3]X_3$, etc., the infra-red and the visible regions are transparent, all the bands being localized in the ultra-violet region. J. L. Lifschitz and E. Rosenbohm, *Z. physik. Chem.*, **97** (1921), 1; *Z. wiss. Phot.*, **19** (1920), 198.

(4) Throughout this article, the word ligand will be used in its original German sense, i.e., an ion or a molecule co-ordinated in a complex radical.

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

(6) Y. Shibata, *J. Coll. Sci., Imp. Univ. Tokyo*, **37** (1916), Art. 8; Y. Shibata and K. Matsuno, *J. Chem. Soc. Japan*, **37** (1916), 160.

his theory on the third band as well as the experiment on the optical resolution of $[\mathrm{Co(NH_3)_2(NO_2)_2C_2O_4}]\mathrm{M}$.(7) During the investigation on the aquotization of $[\mathrm{Co(NH_3)_4Cl_2}\{{}^{(1)}_{(6)}\}]\mathrm{Cl}$, the present author(8) happened to find a third band for this complex, and extending Y. Shibata's theory, assumed that the third band is due to a pair or pairs of negative ligands co-ordinated in trans-positions.(9) A survey of the data available in the literature as well as our measurements of some complexes shows that the extended theory can be applied to all the third bands hitherto found with only one exception of $[\mathrm{Cr(NH_3)_5(NCS)}](\mathrm{NCS})_2$.(10)

All the co-ordination compounds which have or seem to have at least a pair of negative ligands in trans-positions showed the third bands, but none of those deficient of the condition. The third bands confirmed or found in this laboratory are summarized in Table 1.

Table 1.

| Complex compound | First band | | Second band | | Third band | | $\nu_2-\nu_1$ | $\nu_3-\nu_2$ |
|---|---|---|---|---|---|---|---|---|
| | $\nu_1(10^{13})$ | $\log\varepsilon$ | $\nu_2(10^{13})$ | $\log\varepsilon$ | $\nu_3(10^{13})$ | $\log\varepsilon$ | | |
| $[\mathrm{Co(NH_3)_4(NO_2)_2}\{{}^{(1)}_{(6)}\}]\mathrm{Cl}$(5)(9) | 67.9 | 2.32 | 87.0 | 3.54 | 119.6 | 4.08 | 19.1 | 32.6 |
| $[\mathrm{Co(NH_3)_3(NO_2)_3}]$(5)(11) | 68.8 | 2.21 | 86.9 | 3.45 | 120.4 | 3.81 | 18.2 | 33.5 |
| $[\mathrm{Co(NH_3)_2(NO_2)_4}]\mathrm{NH_4}$(5)(9) | 69.0 | 2.56 | 85.9 | 3.67 | 119.0 | 3.85 | 16.9 | 33.1 |
| $[\mathrm{Co(NH_3)_3(NO_2)_2Cl}]$(11) | 67.9 | 2.18 | 87.9 | 3.43 | 120.8 | 3.88 | 19.1 | 33.8 |
| $[\mathrm{Co(NH_3)_3(NO_2)_2Br}]$(11) | 66.8 | 2.02 | 87.9 | 3.30 | 120.8 | 3.82 | 21.1 | 32.9 |
| $[\mathrm{Co(NH_3)_2(NO_2)_2C_2O_4}]\mathrm{NH_4}$(12) | 62.5 | 2.18 | 88.0 | 3.53 | 120.2 | 4.57 | 25.5 | 32.2 |
| $[\mathrm{Co(NH_3)_4(NO_2)Cl_2}\{{}^{(1)}_{(6)}\}]\mathrm{Cl}$(9) | 63.2 | 1.87 | 88.8 | 3.13 | 123.0 | 4.07 | 25.6 | 34.2 |
| $[\mathrm{Co(ONO)_6}]\mathrm{Na_3}$(9) | 62.0 | 2.34 | 82.4 | 3.75 | 114.0 | 3.95 | 20.4 | 31.6 |
| $[\mathrm{Co(NH_3)_4Cl_2}\{{}^{(1)}_{(6)}\}]\mathrm{Cl}$(8) | <50 | 1.2 | 63 | 1.4 | 100 | 3.2 | — | 37 |
| $[\mathrm{Co(C_2O_4)_3}]\mathrm{K_3}$(12) | 49.6 | 2.09 | 71.8 | 2.19 | 123.0 | 4.42 | 22.2 | 51.2 |
| $[\mathrm{Fe(CN)_6}]\mathrm{K_3}$(13) | 71.8 | 3.03 | 99.4 | 3.20 | 114.0 | 3.05 | 27.6 | 13.6 |
| $[\mathrm{Pt\,Cl_6}]\mathrm{K_2}$ | 67.0 | 1.58 | 84.0 | 2.58 | 115.6 | 4.11 | 17.0 | 31.6 |
| $[\mathrm{Pt(NH_3)_2Cl_2}\{{}^{(1)}_{(6)}\}]$ | 80.0 | 1.23 | 95.8 | 1.88 | 110.2 | 2.02 | 15.8 | 14.4 |
| $[\mathrm{Hg\,I_4}]\mathrm{K_2}$ (aq. soln. of KI) | — | — | 93.6 | 4.40 | 112.8 | 4.66 | — | 19.2 |
| $\mathrm{KI_3}$(14) (mixed aq. soln. of KI and $\mathrm{I_2}$) | — | — | 84.4 | 4.09 | 104.4 | 4.21 | — | 20.0 |

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(7) Y. Shibata and T. Maruki, *J. Coll. Sci., Imp. Univ. Tokyo*, **41** (1918), Art. 2; *J. Chem. Soc. Japan*, **37** (1916), 1142.

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

(9) R. Tsuchida and S. Kashimoto, this Bulletin, **11** (1936), 785.

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

(11) M. Kobayashi, *J. Chem. Soc. Japan*, **58** (1937), 391.

(12) S. Kashimoto and M. Kobayashi, this Bulletin, **12** (1937), 350.

(13) S. Iimori, *J. Chem. Soc. Japan*, **36** (1915), 171.

(14) R. Tsuchida, this Bulletin, **10** (1935), 37.

From Table 1 it can be pointed out that the differences $\nu_3 - \nu_2$ for cobaltic complexes are about $33 \times 10^{13}$, while the differences $\nu_2 - \nu_1$ show values in a wide range from $17 \times 10^{13}$ to $26 \times 10^{13}$.

The occurrence of the third band is independent of (1) the kind and valency of the central ion, (2) the sort of the ligand in question provided that it is of negative character, (3) the charge of the complex radical, and moreover, (4) the configuration, so long as the trans-pairing condition is fulfilled. It is a remarkable fact that not only the transition elements, but also others such as $Hg^{++}$ and $I^+$ can give rise to the third bands. It is also interesting that a chelate radical so complicated as dimethylglyoxime⁽¹⁵⁾ shows a third band similar to those given by simple ions such as $Cl^-$ and $NO_2^-$. Non-electrolytic complexes, e.g., $[Co(NH_3)_3(NO_2)_3]$, can have the third bands just as complex cations and anions. Complexes of planar structure, e.g., $[Pt(NH_3)_2Cl_2]$, and of linear type, e.g., $I_3^-$, give the third bands as well as those of octahedral configuration. In short, the third band is one of the general characteristics of absorption spectra of co-ordination compounds. According to the author's opinion, as will be discussed later, the third band is theoretically more important than the first which is the origin of the beautiful colour of the complex, and sometimes seems more useful in application even than the second which is the most important feature of the co-ordination compounds.

**III. Theories on the Origins of the First and the Second Bands.** The researches on the first and the second bands have been more active than those of the third, and consequently, as to the origins of these bands, there are various theories and hypotheses, which are briefly introduced here chronologically. Luther and Nikolopulos(16) assumed that the chemical linkage between the central metallic atom and the ligand gives rise to the first band. According to Shibata,(2)(10)(17) the first band is probably due to an electron of the central atom and the cause of the second band lies between the central metallic atom and the non-metallic atom of the ligand which combines directly with the former. By Lifschitz,(3) the first band is thought of as due to a group of electrons belonging to the central atom, and the second band is associated with the binding electrons of the co-ordinated group. According to Colmar and Schwartz(18) the first band is attributed partly to the central ion, because of an electronic

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(15) C.f. Table 6.

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

(17) Y. Shibata, "Spectrochemistry," Vol. I, Tokyo (1935).

(18) R. I. Colmar and F. W. Schwartz, *J. Am. Chem. Soc.*, **54** (1932), 3204.

transition, and partly to the internal vibrations of the atoms and ions making up the complex. Joos and Schnetzler(19) found that the absorption spectra of crystalline powder of chromic complexes at low temperatures, consist in several lines, and supported the theory of Deutschbein,(20) who explained the lines of $Cr^{+++}$ as due to the electron transitions $3^4F - 3^2G$, the shift of lines being a kind of the Stark effect of the neighbouring atoms and molecules.

So far, there is no serious unreconcilable contradiction among these theories except that of Luther and Nikolopulos. Mead,(21) however, adopted Pauling's theory(22) and tried to explain both the first and the second band as equally due to energy differences between excited states of the co-ordination electrons. The opinion of Mathieu(23) on the first band is similar to that of Mead: viz., the first band is probably attributed to combination of the transitional energy of the co-ordination electrons and the vibrational energies of the central atom and the ligands. In brief, the matter stands thus. The opinions of various authors may find the point of agreement in attributing the second band to the co-ordination electrons. As to the first band, however, the theories may be divided into two groups: viz., Mead, Mathieu, Luther and Nikolopulos assumed the first band as due to co-ordination electrons, while most of the authors attributed the band to electrons belonging to the central metallic atom.

**IV. The Origin of the First Band.** Before dealing with the origin of the first band, it must be noticed here that the first and the second band could not be attributed to the same cause as was assumed by Mead.(21) Absorption spectra of cobaltic nitro-ammines and related compounds were taken and compared (Table 2).

As is seen from Table 2, the substitution of $NO_2^-$ for $NH_3$ in nitro-ammine series has hypsochromic effect on the first band, while the same substitution has bathochromic effect on the second. If the first and the second band were to arise from causes of the same kind, one and the same substitution would have similar effects on both the bands.

On the other hand, the origin of the first band was attributed, as was stated in the preceding section (III), either to co-ordination electrons or to electrons in the central ion by various authors. It will, however, be highly improbable to attribute the first band to co-ordination electrons,

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(19) G. Joos and K. Schnetzler, *Z. physik. Chem.*, B, **20** (1933), 1.

(20) O. Deutschbein, *Ann. Physik*, **14** (1932), 712.

(21) A. Mead, *Trans. Faraday Soc.*, **30** (1934), 1052.

(22) L. Pauling, *J. Am. Chem. Soc.*, **53** (1931), 1367.

(23) J. P. Mathieu, *Bull. soc. chim.*, [5], **3** (1936), 463.

Table 2.

| Complex compound | First band |  | Second band |  | Third band |  | $\nu_2-\nu_1$ | $\nu_3-\nu_2$ |
|---|---|---|---|---|---|---|---|---|
|  | $\nu_1(10^{13})$ | $\log \varepsilon$ | $\nu_2(10^{13})$ | $\log \varepsilon$ | $\nu_3(10^{13})$ | $\log \varepsilon$ |  |  |
| Nitro-ammine complex |  |  |  |  |  |  |  |  |
| $[Co(NH_3)_5NO_2]Cl_2$ | 65.8 | 1.95 | 92.6 | 3.12 |  |  | 26.8 |  |
| $[Co(NH_3)_4(NO_2)_2{}^{(1)}_{(2)}]Cl$ | 65.5 | 1.99 | 91.2 | 3.10 |  |  | 25.7 |  |
| $[Co(NH_3)_4(NO_2)_2{}^{(1)}_{(6)}]Cl$ | 67.9 | 2.32 | 87.0 | 3.54 | 119.6 | 4.08 | 19.1 | 32.6 |
| $[Co(NH_3)_3(NO_2)_3]$ | 68.7 | 2.21 | 86.9 | 3.45 | 120.4 | 3.81 | 18.2 | 33.5 |
| $[Co(NH_3)_2(NO_2)_4]NH_4$ | 69.0 | 2.56 | 85.9 | 3.67 | 119.0 | 3.85 | 16.9 | 33.1 |
| Nitrito-complex |  |  |  |  |  |  |  |  |
| $[Co(ONO)_6]Na_3$ | 62.0 | 2.34 | 82.4 | 3.75 | 114.0 | 3.95 | 20.4 | 31.6 |
| $[Co(NH_3)_5ONO]Cl_2$ | 63.5 | 1.74 | 91.7 | 2.79 |  |  | 28.2 |  |

so long as it has generally been accepted that the second band is due to those electrons.

With the aim of throwing light upon the subject, absorption spectra of $K_2[HgI_4]$ in KI solutions were measured, and two absorption maxima at 321 m$\mu$ ($\nu = 93.6 \times 10^{13}$) and 226 m$\mu$ ($\nu = 113 \times 10^{13}$) were observed.

Now a third band is expected for this compound, because of the negative ligands in trans-positions, and we know from experience that the third band of a co-ordination compound appears usually in the spectral region between $110 \times 10^{13}$ and $120 \times 10^{13}$. Then the band at $113 \times 10^{13}$ may possibly be regarded as the third band and the other at $93.6 \times 10^{13}$, consequently, the second. The co-ordination compound in question, therefore, lacks the first band, which would be impossible if the first band were due to the co-ordination electrons.

Comparing $K_2[Hg\,I_4]$ with other complexes which possess the first bands, we may notice at once the fundamental difference: viz., the central ions of the latter have unsaturated transition shells, while that of the former has not. Now we have come to the conclusion that the first band is attributed to electron transitions in the unsaturated transition shell of the central ion. Then the first band is one of the general characteristics of transition elements.

If we assume that the energy levels of the electron transitions are determined by the ligand co-ordinated in the direction of the transition, the effect of substitution of ligands on the first band will be qualitatively explained. It is now postulated that the electron transitions are depressed by negative fields of the ligands and the stronger the field, the greater the depression.

For the purpose of unitary treatment of the different kinds of ligands, i.e., polar molecules, simple elementary ions, and radical ions, it will be convenient to introduce a quantity *P*, the work which would be done by the system if the ligand were to approach from infinity to the seat of co-ordination. Then a ligand which gives a larger energy of approach would have such negative field that will cause greater depression of the electron transition and consequently give rise to a first band of lower frequency. The greater the charge of the ligand and the larger the polarity and the polarizability as well, the greater will be the energy of approach *P*. Therefore, a simple elementary anion has generally stronger effect than a molecule. Of these anions, those which have larger polarizabilities must bring about larger depression than those which are less polarizable, and molecules which have larger dipole moments must have stronger effect than those of smaller moments. Thus the ligands, no matter whether they may be ions or molecules, could be arranged in the order of their effect on the energy levels. Arranging in the ascending order of *P*, we obtain a spectrochemical series for the first band: viz.,

$$NH_3,\ H_2O,\ F^-,\ Cl^-,\ Br^-,\ I^-.$$

The smaller the value *P*, the weaker the depression and the higher the frequency of the first band. The above series, therefore, shows the descending order of hypsochromic effect of the ligand on the first band. When a ligand is substituted for another which comes behind in the series, the first band is displaced towards the shorter wave-lengths, and, on the contrary, a substitution of a ligand for another ahead of it gives rise to a bathochromic effect. For example, $H_2O$ is bathochromic than $NH_3$, but hypsochromic than $Cl^-$.

In order to verify the hypothesis, a number of complex compounds were prepared and their absorption spectra were taken. The results show that the above series coincides with that obtained from the measurements. For example, the first bands of $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5H_2O]Cl_3$ and $[Co(NH_3)_5Cl]Cl_2$ are $63.6 \times 10^{13}$, $61.6 \times 10^{13}$ and $58.7 \times 10^{13}$ respectively (Table 3).

The effect of a radical ion on the first band is rather complicated, as it has its own poles which must be modified by neighbouring ions and molecules, and moreover, the effect may also vary according to the way in which it is co-ordinated. For example $NO_2^-$ ion may be co-ordinated either with N or with O, as the case may be. In the former case it is hypsochromic than $NH_3$ and in the latter, bathochromic.(24) The first bands of $[Co(NH_3)_5NO_2]Cl_2$, $[Co(NH_3)_5NH_3]Cl_3$ and $[Co(NH_3)_5ONO]Cl_2$ are 65.8 × $10^{13}$, 63.6 × $10^{13}$ and 63.5 × $10^{13}$ respectively (Table 2).

Being thus unable to decide theoretically, positions of radical ions in the series of *P* have been found from experimental data as follows. In Tables 3, 4 and 5,(25) the complexes have been arranged in the order of frequencies of their first bands.

Table 3.

| Ligand | Complex salt | First band | | Second band | |
|---|---|---|---|---|---|
| | | $\nu_1$ ($10^{13}$) | log ε | $\nu_2$ ($10^{13}$) | log ε |
| $NO_2^-$ | $[Co(NH_3)_5NO_2]Cl_2$ | 65.8 | 1.95 | 92.6 | 3.12 |
| $NH_3$ | $[Cr(NH_3)_5NH_3]Cl_3$ | 65.0 | 1.48 | 86.0 | 1.44 |
| | $[Co(NH_3)_5NH_3]Cl_3$ | 63.6 | 1.66 | 88.8 | 1.57 |
| $ONO^-$ | $[Co(NH_3)_5ONO]Cl_2$ | 63.5 | 1.74 | 91.7 | 2.79 |
| $H_2O$ | $[Co(NH_3)_5H_2O]Cl_3$ | 61.6 | 1.62 | 87.5 | 1.62 |
| $NCS^-$ | $[Cr(NH_3)_5NCS](NCS)_2$ | 61.6 | 1.82 | (83) | 1.67 |
| | $[Co(NH_3)_5NCS]Cl_2$ | 60.2 | 2.14 | (84) | 2.60 |
| $NO_3^-$ | $[Co(NH_3)_5NO_3](NO_3)_2$ | 60.2 | 1.74 | (83) | 1.8 |
| $SO_4^=$ | $[Co(NH_3)_5SO_4]I$ | 60.0 | 1.70 | 85.5 | 2.76 |
| $OH^-$ | $[Co(NH_3)_5OH](NO_3)_2$ | 59.8 | 1.82 | (82) | 1.9 |
| $C_2O_4^=$ | $[Co(NH_3)_5C_2O_4]Br$ | 59.2 | 1.87 | — | — |
| $CO_3^=$ | $[Co(NH_3)_5CO_3]NO_3$ | 59.0 | 1.84 | (82) | 1.9 |
| $S_2O_3^=$ | $[Co(NH_3)_5S_2O_3]Cl$ | 58.2 | 1.76 | (79) | 2.15 |
| $Cl^-$ | $[Cr(NH_3)_5Cl]Cl_2$ | 58.7 | 1.53 | 80.0 | 1.54 |
| | $[Co(NH_3)_5Cl]Cl_2$ | 57.5 | 1.64 | 82.8 | 1.66 |
| $CrO_4^=$ | $[Co(NH_3)_5CrO_4]NO_3$ | 55.6 | 2.14 | 78.4 | 3.54 |
| $Br^-$ | $[Co(NH_3)_5Br]Br_2$ | 55.4 | 1.68 | (81) | 2.8 |

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(24) As will be seen in Table 2, successive substitution of $NO_2$ for $NH_3$ in the nitroammine series, causes gradual shift of the first band towards the shorter wave-lengths, but the first band of Fischer's salt, $K_3Co(NO_2)_6$, has by far the longest wave-length, betraying that it is hexanitritocobaltiate, $[Co(ONO)_6]K_3$, instead of hexanitrocobaltiate, $[Co(NO_2)_6]K_3$. R. Tsuchida, *J. Chem. Soc. Japan*, **59** (1938), 731.

(25) The absorption curves of the complexes in these tables as well as others will soon be published.

Table 4.

| Ligand | Complex compound | First band | | Second band | |
|---|---|---|---|---|---|
| | | $\nu_1$ ($10^{13}$) | log $\varepsilon$ | $\nu_2$ ($10^{13}$) | log $\varepsilon$ |
| $NO_2^-$ | $[Co(NH_3)_4(NO_2)_2{}^{(1)}_{(6)}]Cl$ | 67.9 | 2.32 | 87.0 | 3.54 |
| | $[Co(NH_3)_4(NO_2)_2{}^{(1)}_{(2)}]Cl$ | 65.5 | 1.99 | 91.2 | 3.10 |
| $NH_3$ | $[Cr(NH_3)_4(NH_3)_2]Cl_3$ | 65.0 | 1.48 | 86.0 | 1.44 |
| | $[Co(NH_3)_4(NH_3)_2]Cl_3$ | 63.6 | 1.66 | 88.8 | 1.57 |
| $H_2O$ | $[Co(NH_3)_4(H_2O)_2]Cl_3$ | 60.0 | 1.40 | 84.0 | 1.48 |
| $C_2O_4^{=}$ | $[Co(NH_3)_4C_2O_4]Br$ | 58.8 | 1.78 | 84.0 | 1.88 |
| $CO_3^{=}$ | $[Co(NH_3)_4CO_3]Br$ | 57.2 | 2.02 | 82.6 | 2.03 |
| $Cl^-$ | $[Co(NH_3)_4Cl_2{}^{(1)}_{(6)}]Cl$ | $<50$ | 1.2 | 63 | 1.4 |

Table 5.

| Ligand | Complex compound | First band | | Second band | |
|---|---|---|---|---|---|
| | | $\nu_1$ ($10^{13}$) | log $\varepsilon$ | $\nu_2$ ($10^{13}$) | log $\varepsilon$ |
| en | [Co *en*$_3$]Br$_3$ | 65.2 | 1.83 | 90.0 | 1.77 |
| $NH_3$ | $[Cr(NH_3)_6]Cl_3$ | 65.0 | 1.48 | 86.0 | 1.44 |
| | $[Co(NH_3)_6]Cl_3$ | 63.6 | 1.66 | 88.8 | 1.57 |
| $ONO^-$ | $[Co(ONO)_6]Na_3$ | 62.0 | 2.34 | 82.4 | 3.75 |
| $NCS^-$ | $[Cr(NCS)_6]K_3$ | 53.1 | 2.08 | 70.8 | 2.00 |
| $H_2O$ | $[Cr(H_2O)_6]Cl_3$ | 52.5 | 1.02 | 73.6 | 1.20 |
| $C_2O_4^{=}$ | $[Co(C_2O_4)_3]K_3$ | 49.6 | 2.09 | 71.0 | 2.19 |

From Table 3, we obtain, experimentally, the spectrochemical series for the first band: viz.,

$$NO_2^-,\ NH_3,\ ONO^-,\ H_2O,\ NCS^-,\ NO_3^-,\ SO_4^{=},\ OH^-,$$
$$C_2O_4^{=},\ CO_3^{=},\ S_2O_3^{=},\ Cl^-,\ CrO_4^{=},\ Br^-.$$

Also from Table 4:

$$NO_2^-,\ NH_3,\ H_2O,\ C_2O_4^{=},\ CO_3^{=},\ Cl^-.$$

From Table 5:

$$en,\ NH_3,\ ONO^-,\ NCS^-,\ H_2O,\ C_2O_4^{=}.$$

All these series as well as the theoretical one above coincide with one another, and all the experimental rules by various authors(8) (16) (18) (21) (26)

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(26) T. Uemura and H. Sueda, this Bulletin, **10** (1935), 267.

about the shifts of bands by substitutions of ligands may be included in the series.

The first band is expected to be more or less additive, as a complex may contain more than two kinds of ligands which have different *P*-values. The complexes which co-ordinate only one kind of ligand should naturally have narrower, symmetrical first bands than those which have ligands of different kinds, and among the latter, those which have ligands situated far apart in the spectrochemical series should have broader and less symmetrical first bands and sometimes these bands may be analysed into two or more components. For example $[Co(NH_3)_5Cl]Cl_2$ has broader and less symmetrical first band than $[Co(NH_3)_5NO_2]Cl_2$ or $[Co(NH_3)_5H_2O]Cl_3$ and may be analysed into the principal first band at about $57 \times 10^{13}$ and an auxiliary first band at about $62 \times 10^{13}$. Mathieu,(23) Ernsberger and Brode(27) have tried to analyse the first bands into components.

**V. Thermochemical Treatment of the Second Band.** So long as the origin of the second band is concerned, opinions of various authors seem to find the point of agreement in attributing the second band to the co-ordination electrons. Whereas some of the co-ordination compounds lack the first bands and most of them the third, they never fail to give the second bands. This fact betrays the relation between the co-ordinate linkage and the second band. Another evidence is photochemical behaviour of co-ordination compounds. For example, $K_3[Co(C_2O_4)_3]$ is decomposed most readily by rays of the second band(28) and hydrolysis of $[Co(NH_3)_5C_2O_4]_2SO_4$ is accelerated most effectively by rays corresponding to its second band.(29) These and other photochemical changes show that the second band has direct relation to the formation and decomposition of the co-ordination compound: in other words, the co-ordination linkage is directly affected by the rays of the second band.

In order to explain these facts, it is now postulated that when a quantum of the second band is absorbed by a complex radical, one of the co-ordination links is split open and an excited ligand is produced in the original seat of co-ordination, e.g.,

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

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(27) M. L. Ernsberger and W. R. Brode, *J. Am. Chem. Soc.*, **56** (1934), 1842.

(28) I. Vranek, *Z. Elektrochem.*, **23** (1917), 336; F. M. Jaeger, *Rec. trav. chim.*, **38** (1919), 249.

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

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

where {A} and {X} denote the excited molecule and ion respectively.

It is postulated here that the excited ligand thus produced by $h\nu_2$, recombine in most cases to form the original complex. It may sometimes be set free or sometimes be replaced by other ion or molecule, as the case may be, resulting in decomposition and substitution respectively. In case of recombination, the energy $S$ is set free, which may be defined as co-ordination energy.

The relation of $S$ to other energies may be shown by assuming the following cyclic process. (1) First the salt, say $MX_3$, whose lattice energy is $\Phi_1$, is separated into its constituent ions. (2) The ligands are brought to the positions of co-ordination. (3) And the next step is to excite the ligands till they are ready to enter into the co-ordination linkage with the central ion. (4) Then the combination takes place, setting the energy $S$ free. (5) The last process is to form the complex crystal, whose lattice energy is $\Phi$. The energy of approach in the process (2) is the same as $P$ in the preceding section (IV), and that of excitation in the process (3) may be represented by $R$. Let $Q$ be the heat of formation of the complex crystal from the component compounds of first order per one co-ordination, then

$$\mathrm{M\ X_3}+n\mathrm{A}=[\mathrm{M\ A}_n]\,\mathrm{X_3}+nQ\,,$$

and

$$Q=P-R+S+\frac{\Phi-\Phi_1}{n} \qquad \text{(1a)},$$

where $n$ is the co-ordination number.

When the ligands are negative ions,

$$\mathrm{M\ X_3}+(n-3)\,\mathrm{K\ X}=[\mathrm{M\ X}_n]\,\mathrm{K}_{n-3}\,,$$

and

$$Q=P-R+S+\frac{\Phi-\Sigma\Phi_1}{n} \qquad \text{(1b)},$$

where $\Sigma\Phi_1$ denotes the sum of the lattice energies of the compounds of first order.

Let $Q'$ be the heat of formation of the complex radical from the central ion and the ligands, (1a) and (1b) will be equally reduced to

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

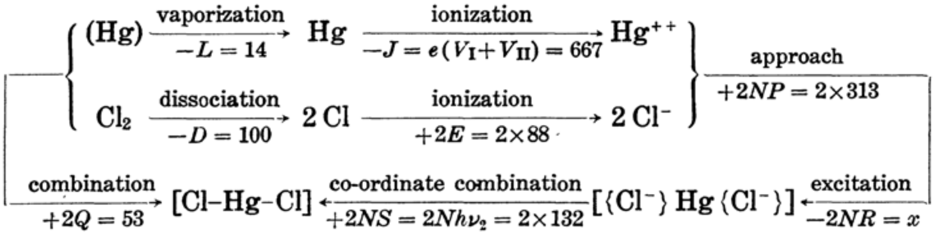
It must be noticed here that the process (4) is the reverse reaction of the photochemical process by $h\nu_2$ mentioned above.

Hence

$$S = h\nu_2 \qquad (2).$$

Therefore, $S$ may be found spectroscopically and $Q$ and $\Phi$'s may also be determined experimentally. The value $P$ could be calculated if the polarized state of the ligand in the position of co-ordination were exactly known. At present, however, we should be contented with approximate computation from its polarizability or dipole moment. And in special cases, $R$ might be estimated. A few example of computing $R$ are as follows.

(A) Mercuric chloride. This compound may be regarded as a co-ordination compound, as will be discussed in Part II(30) of this paper, and consequently the rules of absorption spectra so far obtained may be applied. As the molecule is of linear configuration,(31) a third band is expected (section II), nevertheless it will lack the first band (section IV). Therefore, the band of the longest wave-length, i.e., 205 m$\mu$,(32) should be regarded as the second. The data necessary to calculate $R$ are as follows. Latent heat of vaporization of mercury: $L = 13.8$ Cal. Ionization potentials: $V_{\mathrm{I}} = 10.38$ volts, $V_{\mathrm{II}} = 18.67$ volts. Heat of dissociation of chlorine: $D = 100$ Cal. Electron affinity of chlorine: $E = 88$ Cal. Polarizability of chlorine ion: $\alpha = 3.05 \times 10^{-24}$ e.s.u. Lattice energy of mercuric chloride: neglected. The second band: $\nu_2 = 146 \times 10^{13}\mathrm{sec}^{-1}$ ($\lambda_2 = 205$ m$\mu$). Heat of formation of mercuric chloride: $2Q = 53.2$ Cal. Distance between Hg and Cl in the molecule: $d = 2.25$ Å.



From the cyclic process $R$ may be found: viz., $NR = 116$ Cal.

(B) $[\mathrm{Ni(NH_3)_6}]\mathrm{Cl_2}$ and $[\mathrm{Ni(H_2O)_6}]\mathrm{Cl_2}$. The first bands of these compounds lie in the infra-red regions and the second bands are those whose maxima are at 568 m$\mu$ and 718 m$\mu$ respectively.

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(30) It will be soon published.

(31) H. Braekken and W. Scholten, *Z. Krist.*, **89** (1934), 448.

(32) H. Fromherz and K. Lih, *Z. physik. Chem.*, A, **167** (1933), 103.

| Complex salt | $6NQ$ | $\lambda_2$ | $\nu_2\,(10^{13})$ | $Nh\nu_2\,(=NS)$ | $NR$ |
|---|---|---|---|---|---|
| $[Ni(NH_3)_6]Cl_2$ | 86.4 Cal. | 568 mμ | 52.8 | 47.5 Cal. | $37.1+N\left(\frac{\Phi-\Phi_1}{6}+P\right)$ Cal. |
| $[Ni(H_2O)_6]Cl_2$ | 20.3 ,, | 718 ,, | 41.8 | 37.6 ,, | $34.2+\left(\frac{\Phi'-\Phi_1}{6}+P'\right)$ ,, |

The lattice energy of $NiCl_2$, $\Phi_1$ and the polarizability of $H_2O$ being unknown, the values $NR$ could not be calculated, but it may be assumed that $\Phi \simeq \Phi'$ and $P \simeq P'$. Hence the energies of excitation of $NH_3$ and $H_2O$ in the ammine and the aquo-salt are nearly the same, in spite of the great difference between their heats of formation.

## Summary.

(1) The origins of absorption bands of co-ordination compounds have been discussed.

(2) The first band is attributed to electron transitions in the unsaturated transition shell of the central ion. The band, therefore, appears only when the central ion is of a transition element.

(3) The shift of the first band by substitution of ligands may be explained by postulating that the electron transitions are more or less depressed by the negative field of the ligand, which may conveniently be represented by $P$, the energy of approach of the ligand, i.e., the work done by the ligand if it were to approach from infinity to the seat of co-ordination. The ascending order of $P$, i.e., the sequence of hypsochromic effect, is theoretically

$$NH_3,\ H_2O,\ F^-,\ Cl^-,\ Br^-,\ I^-.$$

The empirically obtained order of hypsochromic effect on the first band is

$$NO_2^-,\ NH_3,\ ONO^-,\ H_2O,\ NCS^-,\ NO_3^-,\ SO_4^{=},$$
$$OH^-,\ C_2O_4^{=},\ CO_3^{=},\ S_2O_3^{=},\ Cl^-, CrO_4^{=},\ Br^-.$$

All the experimental rules so far obtained of the shifts of the first bands by substitutions of ligands may be explained by the hypothesis.

(4) The first band is more or less additive. The complexes which have ligands situated far apart in the spectrochemical series have broader and less symmetrical first bands than those which contain only one kind of ligands.

(5) The second band may be attributed to the co-ordination electrons, and is, therefore, the most general characteristic which a co-ordination compound should possess. Postulating that by absorption of a quantum $h\nu_2$ ($\nu_2$ = frequency of the second band) the co-ordinate linkage is broken to produce an excited metastable ligand in the original seat of co-ordination, the following relations have been derived:

$$Q = P - R + S + \frac{\Phi - \Sigma\Phi_1}{n},$$

and

$$S = h\nu_2,$$

where $Q$ = heat of formation per co-ordination, $R$ = activation energy, $S$ = co-ordination energy, $\Phi$ = lattice energy of the co-ordination compound, $\Phi_1$'s = lattice energies of the component compounds of first order, and $n$ = co-ordination number.

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