Electron Transfer Spectra in the Crystals of Hexamminecobalt(III) Salts

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Introduction

The formation of the ion-pairs of hexammine and tris-(ethylenediamine) complex cations of cobalt(III) and chromium(III) with various anions in aqueous solutions and the consequent appearance of a new absorption band in the ultraviolet were first observed by Linhard(1), and the thermodynamical study of the ion-pair formation was spectrophotometrically done by him(1), Evans and Hancollas(2) and Kubota(3); this so-called association band has been attributed to the transfer of an electron from an anion to a complex ion(2,3,4). It will be natural to suppose that in crystals in which a complex ion is closely surrounded by anions, this absorption band will acquire more intensity than in solutions, and indeed Linhard and Weigel(4) suggested in their paper that the deepening in the color of the crystals of hexamminecobalt(III) chloride, bromide and iodide in this order is attributable to the presence of this band. Actually, in 1936, in the study of the absorption spectra of cobalt(III) ammine salt crystals, Kobayashi(5) observed the new absorption band which was absent in solutions. But he attributed it to the transition of an electron from a ligand to the central atom.

On the other hand, studying theoretically the absorption spectra of the first transition metal complexes by the crystalline field ap-

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1) M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944).

2) M. G. Evans and G. H. Hancollas, *Trans. Faraday Soc.*, **49**, 363 (1953).

3) T. Kubota, *J. Chem. Soc. Japan* (*Pure Chem. Sec.*), **75**, 552 (1954).

4) M. Linhard and M. Weigel, *Z. anorg. Chem.*, **266**, 49 (1951).

5) R. Tsuchida and M. Kobayashi, *J. Chem. Soc. Japan* (*Pure Chem. Sec.*), **64**, 1268 (1943); "The Colors and the Structures of Metallic Compounds", Zoshindo Co., Osaka, Japan (1944), p. 180.

proximation, Tanabe and Sugano[6] have recently suggested the possibility of the appearance of the absorption band due to the two-electron jump within a metal ion in the case of nickel(II), cobalt(III) and chromium(III) complexes. Thus, concerning the origin of the new absorption band appearing in crystals, there are three different possibilities, namely, the transitions of electrons of the central atom, a ligand and an anion.

The present study was undertaken for the purpose of confirming the existence of this band in the spectra of various hexamminecobalt(III) salt crystals, as only the chloride was investigated by Kobayashi, and also to determine which of the above mentioned theories is correct.

Experimental

Materials.—Hexamminecobalt(III) salts investigated in the present study are listed in Table I. The chloride was prepared by the air oxidation of the ammonical solution of cobalt(II) chloride and ammonium chloride using activated charcoal as a catalyst according to the method of Bjerrum and McReynolds[7]. The iodide selenate was prepared by the oxidation of the ammoniacal solution of cobalt(II) selenate and ammonium selenate with iodine after Hassel and Bödtker Naess[8]. The others were derived from the chloride by the method described briefly in the table[9-17]. These were, in general, recrystallized from slightly acidic, hot aqueous solutions.

TABLE I

Crystal	Thickness (mm.)	Exposure time (min.)	Wave length of the 2nd band max. (mμ)	Wave length of absorption edge (mμ)	Method for preparation
$[Co(NH_3)_6](ClO_4)_3$	0.058	60	332	254	chloride+$HClO_4$, Ref. 8
$[Co(NH_3)_6]_2(SO_4)_3 5H_2O$	0.076	60	336	265	chloride+H_2SO_4, Ref. 9
$[Co(NH_3)_6]_2(HPO_4)_3 4H_2O$	0.032	30	336	274	chloride+Na_2HPO_4, Ref. 10
$[Co(NH_3)_6]Cl_3$	0.021	30	330	299	Ref. 7
$[Co(NH_3)_6]Br_3$	0.01	30	—	357	chloride+HBr, Ref. 11
$[Co(NH_3)_6]I_3$	0.038	5	—	505	chloride+KI, Ref. 12
$[Co(NH_3)_6]Cl(ClO_4)_2$	0.040	20	331	259	chloride+NH_4ClO_4, Ref. 13
$[Co(NH_3)_6]Cl(SO_4)3H_2O$	0.045	30	334	265	chloride+Na_2SO_4, Ref. 14
$[Co(NH_3)_6]Br(SO_4)$	0.040	30	336	287	bromide+H_2SO_4, Ref. 10
$[Co(NH_3)_6]I(SO_4)$	0.056	30	—	354	sulfate+KI, Ref. 15
$[Co(NH_3)_6]I(SeO_4)$	0.035	30	—	364	Ref. 8
$[Co(NH_3)_6]_2(C_2O_4)_3 4H_2O$	0.041	30	332	292	chloride+$(NH_4)_2C_2O_4$, Ref. 16
$[Co(NH_3)_6](NO_3)_3$	0.048	30	—	—	chloride+HNO_3, Ref. 9
$[Co(NH_3)_6](NO_2)_3$	0.022	30	—	—	chloride+$NaNO_2$, Ref. 17

Apparatus and Procedure.—The optical system of the microscope used is shown in Fig. 1, in which A, B, C, I and J are fixed to the body of a usual microscope. As a light source A, a hot cathode hydrogen discharge tube was used except in the case of the iodide in which a tungsten lump was used. A fused quartz lens B of a focal distance 8 cm. was used to parallelize the light from the source. A reflecting condenser[*1]C has the similar abilities with a reflecting objective[*1]I with the exceptions of having some aberrations and providing an iris diaphragm and centering screws. The reflecting objective has the abilities of numerical aperture max. 1.0, magnification 100×, and working distance 1 mm. In addition to the merit of having no color aberration, the reflecting objective has practically neither spherical aberration nor coma by means of making its sur face non spherical[18].

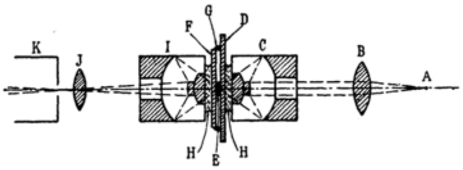

Fig. 1. Optical system (schematic) of the reflecting microscope used for measuring the absorption spectra of microscopic crystals.

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6) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753, 766 (1954).

7) J. Bjerrum and J. P. McReynolds, "Inorganic Syntheses", Vol. II, p. 217.

8) O. Hassel and G. Bödtker Naess, *Z. anorg. Chem.*, **174**, 25 (1928).

9) S. M. Jörgensen, *Z. anorg. Chem.*, **17**, 457 (1898).

10) S. M. Jörgensen, *J. prakt. Chem.*, (2) **35**, 431 (1887).

11) W. Biltz, *Z. anorg. Chem.*, **83**, 178 (1914).

12) E. Fremy, *Ann.* **83**, 290 (1892).

13) H. Alvisi, *Gazz. chim. ital.*, **31**, II, 291 (1901).

14) T. Klobb, *Bull. soc. chim. France*, (3) **25**, 1025 (1901).

15) F. Ephraim and W. Flügel, *Helv. chim. Acta*, **7**, 739 (1924).

16) E. Birk and W. Biltz, *Z. anorg. Chem.*, **153**, 124 (1926).

17) E. Birk. *Z. anorg. Chem.*, **164**, 243 (1927).

*1 Made by Olympus Optical Co, Ltd., Tokyo.

18) S. Miyata, S. Yanagawa and N. Noma, *J. Optical Soc. Am.*, **42**, 431 (1952).

A crystal E is chosen from a sample and its thickness is determined under a travelling microscope. This is placed on a fused quartz slide glass D and is covered with a fused quartz cover glass F and then the latter is sealed with paraffin G to the former. These are brought into the apparatus. As the microscope is a liquid immersion type, the space between C and I is filled with the glycerin water mixture H whose glycerin content is about 90% and the refractivity of which is identical with that of quartz, $n_d=1.458$. Focusing is carried out by inspecting through a glass eyepiece J, which is then removed. The image of the crystal magnified by the microscope is projected on the slit of a Jobin-Yvon medium type quartz spectrograph K and an absorption spectrum is photographed on a dry plate together with a wave length scale, the slit width being fixed at 0.2 mm. throughout this study. A qualitative absorption curve is obtained by tracing the plate photographed with a recording microphotometer. The thicknesses of the crystals used and the time exposed are shown in Table I. As our condenser has the numerical aperture of 1.0, its condensed light falls on the samples, not parallel, but with the angles of max. 43°18′ to the center line. Therefore, the thicknesses shown in the table do not indicate the actual thicknesses of the crystals passed by the light, the true values being a little larger than those reported.

Schwarzschild-Villiger Effect.—Although the reflecting objective is stated to have less Schwarzschild-Villiger (S-V) effect[19] which is very important in microspectrophotometry, than the usual transmission microscope, the stray light entering the objective from the exterior of a sample may still produce a large error in the result obtained. To avoid this, crystals which had larger areas than 0.1 mm.×0.1 mm. were used throughout this study with a few exceptions, considering the image of the light source projected on the crystals was the circle whose diameter was about 0.03 mm. It was proved that the stray light had no effect on the spectra obtained, since the highly absorbed part of the dry plate photographed was perfectly blank after long exposure.

Results

From the smooth microphotometer traces of blanks shown in Fig. 2, it will be apparent that the light source, the optical system and the dry plate give no selective absorption on the spectra obtained, and that our qualitative method is satisfactory for the detection of absorption bands. In the spectra of the perchlorate, the sulfate and the hydrogen phosphate shown in Fig. 3[*2], the second absorption band due to a *d* electron appears clearly, the position of which is about the same in these salts and is almost identical with that in aqueous solutions. There is practically no absorption in the range between the second band and the intense absorption edges[*3] found at shorter wave lengths. It is apparent that these absorption edges are not due to the anions, since these disply no absorption down to 220 mμ[20].

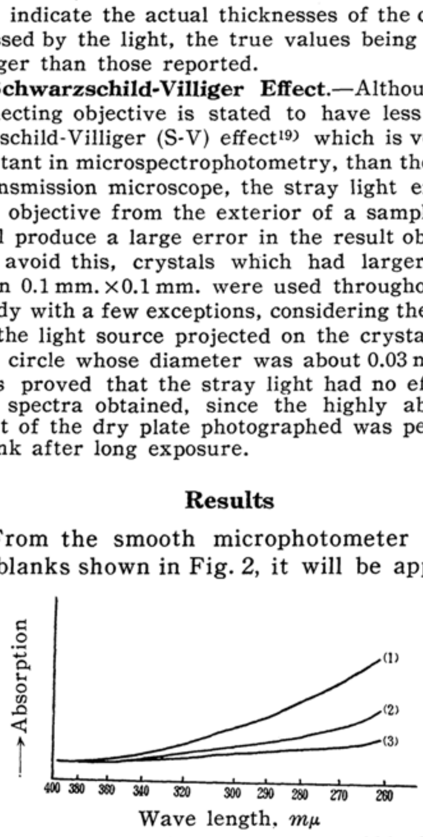

Fig. 2. Microphotometer traces of blanks; exposure time: 10 min. (1), 30 min. (2). 60 min. (3).

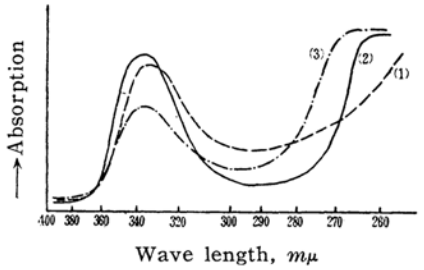

Fig. 3. Absorption spectra of the crystals of hexamminecobalt(III) perchlorate (1), sulfate (2) and hydrogen phosphate (3).

In the spectra of the halogenides shown in Fig. 4, the edge absorption moves to longer wave lengths in the following order: iodide > bromide > chloride, thus covering

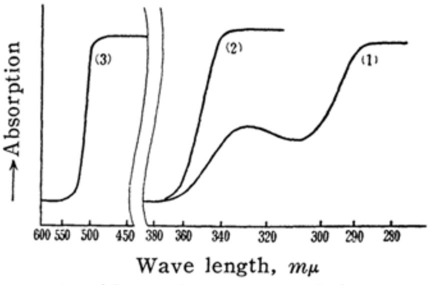

Fig. 4. Absorption spectra of the crystals of hexamminecobalt(III) chloride (1), bromide (2) and iodide (3).

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[19] See for example: H. Naora, *Science*, **114**, 279 (1951); **115**, 248 (1952); *Biochim. Biophys. Acta*, **9**, 582 (1952).

[*2] The flattened upper and lower parts of the spectra indicate the perfect absorption and transmission of light, respectively.

[*3] The term, edge absorption or absorption edge, is used, for convenience, throughout this study to designate our band in question, since it is beyond the ability of our apparatus to determine the stronger part of the spectra using thinner crystals than those used here, because thin crystals usually are attended with smaller sizes, which result in the increase of the S-V effect as stated above. To avoid this, the use of the microscope having much larger magnifying power than the one used here is necessary.

[20] S. Kato, *Sci. Papers Inst. Phys. Research*, Tokyo, **13**, 7 (1950).

perfectly the second band in the bromide and the iodide. This red shift is the feature of the spectra in crystals, as the second band appears clearly in dilute aqueous solution even in the case of the iodide. In the series of the chloride perchlorate, the chloride sulfate, the bromide sulfate, the iodide sulfate and the iodide selenate shown in Fig. 5, the absorption edge behaves like the simple halogenides, but is shifted to a shorter wave length as compared with that of the corresponding halogenide. The absorption spectrum of the oxalate shown in Fig. 6 resembles that of the chloride. Here again, it is apparent that the edge absorption is not attributable to the anion, as it absorbs at a shorter wave length (ca. 270 mμ)[21]. In the spectra of the nitrate and the nitrite shown in the same figure, the absorption bands due to the anions make it impossible for one to determine exactly the positions of the absorption edges.

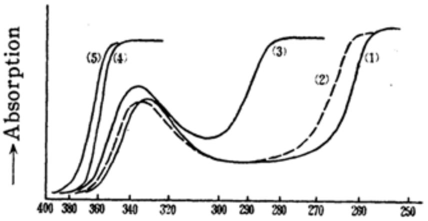

Fig. 5. Absorption spectra of the crystals of hexamminecobalt(III) chloride perchlorate (1), chloride sulfate (2), bromide sulfate (3), iodide sulfate (4) and iodide selenate (5).

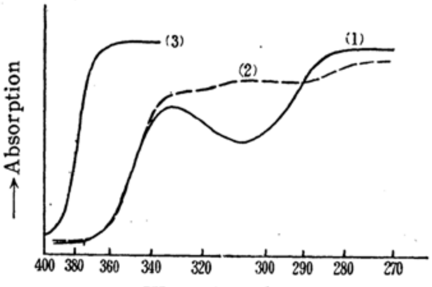

Fig. 6. Absorption spectra of the crystals of hexamminecobalt(III) oxalate (1), nitrate (2) and nitrite (3).

The positions*4 of the absorption edges are listed in Table I. The results obtained are summarized as follows; in the absorption spectra of the crystals of hexamminecobalt (III) salts, there are strong edge absorptions, the positions of which are shifted to longer wave lengths as compared with those in aqueous solutions and are largely affected by anions.

Discussion

Comparison of the Present Results with Kobayashi's.—In the spectrum of the crystal of hexamminecobalt(III) chloride, Kobayashi[5] found the distinct absorption maximum at 282 mμ which had a little lower intensity than that of the second band. In the present study, however, this absorption peak which had been called by Tsuchida and Kobayashi the third band was not found not only in the chloride, but was also absent in the mixed chlorides with the perchlorate or the sulfate, in which the content of the chloride ions was diminished to one-third of the pure chloride. In place of absorption peaks we have obtained absorption edges which indicate the existence of much stronger absorption bands than the second band.

This discrepancy will be interpreted by considering the S-V effect in the apparatus used by Kobayashi, in which the condenser having small magnifying power and the transmission microscope, which are both apt to produce stray light, are employed Since the stray light increases as the wave length becomes shorter, it is expected that the sum of the light really transmitted and the stray light may produce a spurious maximum at a given wave length. It should also be pointed out that the error due to the S-V effect gets greater as the optical density of a sample becomes larger, and according to Naora[19], in some extreme cases, a sample having the transmittance of 1% indicated the erroneous value of 20%.

The above statement will also apply to the spectra of other cobalt(III) ammine in which Kobayashi found either no absorption bands or weak ones in crystals, even in the case where complexes showed strong absorption in aqueous solutions. In fact, the discrepancy has been found recently in the crystals of dinitrotetramminecobalt(III) salts investigated by Faust and Quagliano[22]. In place of only one broad weak band reported by Kobayashi, they obtained the strong absorption bands corresponding to those in aqueous solutions using a potassium bromide disk method.

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[21] H. Ley and B. Arends, *Z. physik. Chem.*, **B17**, 177 (1932).

*4 These were obtained by subtracting a corresponding blank curve from each absorption spectrum, and taking, for convenience, the wave length of the edge absorption which had the same intensity as that of the maximum of the second band. Where the latter was unknown, it was calculated from another salt assuming Lambert's law to be valid.

[22] J. P. Faust and J. V. Quagliano, *J. Am. Chem. Soc.*, **76**, 5346 (1954).

Origin of the Edge Absorption.— The dependence of the edge absorption on anions is understood only by considering the strong interaction between a complex ion and an anion in a crystal. We shall first consider the possibility of interpreting the edge absorption by the transitions of the electrons within a complex ion.

According to Tanabe and Sugano[6], a possible transition responsible for the third band in cobalt(III) complexes is a two-electron excitation, $(d\varepsilon^6)^1A_1 \rightarrow (d\varepsilon^4 d\gamma^2)^1F_2$. The degree of the energy change in the upper level, $^1F_2$, by the change in a crystalline field is, though a little larger, not so different from those in the levels, $(d\varepsilon^5 d\gamma)^1F_1$ and $(d\varepsilon^5 d\gamma)^1F_2$, which are responsible for the first and the second bands, respectively, in so far as we assume that, even in crystals, the field acting on the cobalt ion is of cubic symmetry as a first approximation. Therefore, the fact that the edge absorption is remarkably affected by anions, in contrast to the almost unchanged second band, suggests that the former is not due to the above transition. Moreover, the intensity criterion made by Tanabe and Sugano that as the mixing with another configuration may be small, the third band must have a much lower intensity than those of the first two bands, makes the two-electron jump hypothesis more inadequate for the origin of the edge absorption. Further evidence substantiating the above conclusion will be given in the last section of the discussion.

Tsuchida and Kobayashi[5] proposed the idea that the ammonias in ammine complexes dissociated into amino radicals and protons as a result of the hydrogen bonds with anions, and that the transition of the electron of the amino radical thus formed to the central atom was the very one responsible for the third band in crystals. Actually, in the crystals of metal complexes the possibility of hydrogen bonding is very large. For example, we can find it in trinitrotriamminecobalt(III) and chlorodinitrotriamminecobalt(III) for which the hydrogen bonds between ammonias of one molecule and oxygens of the others were suggested by Tanito et al.[23], and in dichlorotetrammineplatinum(IV) chloride and chloropentammineplatinum(IV) chloride monohydrate in which the hydrogen bonds between nitrogens and anionic chlorines were found by Bokij et al.[24]. On the other hand, the partially dissociated character of strongly hydrogen bonded NH and OH groups, which results in the formation of non-bonding electrons, has recently been shown by Tsuboi[25]. The effect of an anion on the electron of the hydrogen bonded NH bond will be larger than on d electrons and largely determined by the hydrogen bonding power or the electro-negativity of the anion. Therefore if the edge absorption were due to the electron of the dissociated ammonia, it should shift to longer wave lengths and increase its intensity in the following order: chloride>bromide>iodide, since the approach of the anion will facilitate the transition and increase its probability. As the order in the shifts is contrary to the results obtained, the dissociation hypothesis must be abandoned.

The explanation of the far ultraviolet intense edge absorption of the hexamminecobalt(III) ion in aqueous solutions ($\log\varepsilon = 4$) by the transition of the bonding electron of a Co-N bond proposed by Linhard[1] is interesting because of the facts that our band in question also absorbs strongly, and that the transition of bonding electrons usually produces intense absorptions. However, it is easy to show that if the edge absorption in crystals were due to the red shift of the one in aqueous solution, it should shift to longer wave lengths in the following order: bromide sulfate> iodide sulfate>iodide selenate>iodide>perchlorate, since the potential energy of an hexamminecobalt(III) ion in a crystal, $A'''e^2/r_\alpha$, increases in this order (see Table II). Here again, this order is inconsistent with our results. Therefore, all the possible transitions within the complex ion stated above are inadequate to account for the edge absorption.

Secondly, we must consider the possibility of the red shift of the absorption band due to an anion which was taken up by Linhard[1] in an early stage and by Yoneda[26] recently to explain the association band in solutions. In oxy-acidic anions, sulfate, hydrogen phosphate, perchlorate, oxalate, nitrate and nitrite ions, there are the non-bonding electrons which were shown, in some cases, to be rather strongly affected by an outer field. For example, according to Schaumann[27], the weak band of nitrate ion in aqueous solutions at 302 mμ with $\varepsilon = 7$ which is said to arise from an $n \rightarrow \pi$ transition[28,29], suffers in the crystal a large shift in its position, the

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[23] Y. Tanito, Y. Saito and H. Kuroya, This Bulletin, 25, 188 (1952); 26, 420 (1953).

[24] G. B. Bokij and M. A. Poraj-Koshits, *Doklady Akad. Nauk S.S.S.R.*, 64, 337 (1949); G.B. Bokij and L.A. Popova, ibid., 67, 73 (1949).

[25] M. Tsuboi, This Bulletin, 25, 385 (1952).

[26] H. Yoneda, This Bulletin, 28, 125 (1955).

[27] H. Schaumann, *Z. Physik*, 76, 106 (1932).

[28] H. McConnell, *J. Chem. Phys.*, 20, 700 (1952).

[29] W.G. Trawick and W.H. Eberhardt, ibid., 22, 1462 (1954).

values of which are 304 mμ for potassium nitrate, 291 mμ for sodium nitrate and 278 mμ for barium nitrate. Another example is the weak band of sodium nitrite at 350 mμ which is said to arise from the transition of the non-bonding electron of nitrogen to an antibonding orbital[29]. It was shown that the crystal of silver nitrite lacked this band on account of probable existence of the weak covalent binding between the nitrogen and the silver[29]. But, the present measurements on the crystals of hexamminecobalt(III) nitrate and nitrite suggest that the shift of the absorption band of the anions due to the complex ion is not sufficiently large to explain the remarkable shift of the edge absorption. The same is also observed in the absorption bands of chromate and permanganate ions which are both said to arise from $n \rightarrow \pi$ transitions[30] and are almost equal in aqueous solution and in mixed crystals[31].

Although we can not draw any definite conclusion as to whether the red shift of the absorption band of an anion can explain the edge absorption from the above discussion, the situation is simpler in the halogendies than in the oxy-acidic salts, as will be seen in the following paragraphs.

Absorption spectra of alkali halogenides in gaseous molecules, aqueous solution and crystals were studied extensively by many workers[32], and the results showed that there was no evidence of the transition within an anion and the absorption spectra were due to the transfer of an electron from an anion to a cation or water. That this is also true in our crystals containing halogen ion is shown by the following consideration: if the edge absorption of the iodide sulfate and the iodide were the absorption band of the iodide ion perturbed by a crystalline field, the former should be more bathochromic than the latter, since the potential energy of the iodide ion in the crystals, $A'e^2/r_\alpha$, is larger in the iodide sulfate than in the iodide as is seen from Table II. As this is contrary to the experimental results, the possibility of the red shift of the absorption band of an anion must be excluded at least in the halogenides and the edge absorption must be interpreted by the transfer of an electron from an anion to the complex ion, as in the association band in aqueous solution.

Such an electron transfer is also expected in the oxy-acidic anions, since the far ultraviolet intense absorption bands of nitrate, nitrite, chlorate ions etc. have been attributed to the transfer of an electron from an anion to its hydration sphere[33], although the alternative interpretation which assigned $\pi \rightarrow \pi$ transitions to them also exists[29].

Calculations of the Differences Between the Wave Lengths of the Absorption Edges by the Energy Cycle Method.—If the edge absorption is an electron transfer spectrum, it should correspond to the first absorption band of ionic crystals due to an exciton, the wave length of which can be calculated by the energy cycle method as is usually performed. We shall do this below to the bands of the iodide, the iodide selenate, the iodide sulfate and the bromide sulfate.

We perform the following cycle[34,35,36].

1) Remove a halogen ion[*5] from a crystal; the work necessary is $A'e^2/r_\alpha$, where A' is the crystal potential constant at the lattice point of the halogen ion and r_α the lattice constant of the crystal.

2) Remove an electron from the halogen ion; the work necessary is E, the electron affinity of the corresponding halogen atom.

3) Replace the halogen atom; the work necessary is zero.

4) Remove a neighbouring hexamminecobalt(III) ion from the crystal; the work necessary is $(A'''-B)e^2/r_\alpha$, where A''' is the crystal potential constant at the lattice point of the hexamminecobalt(III) ion and B the potential constant at that point due to a neighbouring halogen ion.

5) Add the electron to the hexamminecobalt(III) ion; the work necessary is $-I$, where I is the ionization potential of an hexamminecobalt(II) ion.

6) Replace the hexamminecobalt(II) ion; the work necessary is $-2(A'''-B)e^2/3r_\alpha$.

7) The movement of the electron from the halogen ion to the hexamminecobalt(III) ion will polarize the surrounding medium; the polarization energy is denoted by $-\omega$.

8) It will also polarize the halogen atom and the hexamminecobalt(II) ion; we denote the polarization energy of the former by $-\Omega_X$ and that of the latter, plus the decrease in the energy due to the dipole formed in the latter, by $-\Omega_L$.

Adding the contributions of covalent binding, the van der Waals force and hydrogen bonding designated by ΔU, the total energy $h\nu$ of an edge absorption is thus given by

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[30] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

[31] J. Teltow, *Z. physik. Chem.*, **B43**, 198 (1939).

[32] E. Rabinowitch, *Revs. Modern Phys.*, **14**, 112 (1942).

[33] H.L. Friedman, *J. Chem. Phys.*, **21**, 319 (1953); see also Ref. 32.

[34] W. Klemm, *Z. Physik*, 82, 529 (1933).

[35] N.F. Mott, *Trans. Faraday Soc.*, **34**, 500 (1938).

[36] Y. Uehara, *J. Chem. Soc. Japan(Pure Chem. Sec.)*, **63**, 597 (1942).

$$h\nu=\psi+E-I-\omega-\Omega_X-\Omega_L+\Delta U, \qquad (1)$$

where $\psi=A'e^2/r_\alpha+(A'''-B)e^2/3r_\alpha$.

Unfortunately, even the approximate calculations of $h\nu$'s are impossible for the reason that the values of I and ΔU are unknown, and also the estimations of ω and Ω_L are impossible since the estimation of the former requires the unknown polarizabilities of hexaminecobalt(III) and sulfate or selenate ions and that of the latter requires the unknown polarizability of hexamminecobalt(II) ion, according to the method of Klemm[34].

Thus, we must content ourselves only with calculating the differences of the $h\nu$'s between those salts. Taking into account the fact that the sum of ω and Ω_L are a few eV in alkali halogenides, the differences between the halogenides of a same cation being much smaller[34,36], the values of Ω_X are less than 0.1 e.V. in our crystals[*6], and the values of ΔU are also a few eV, even in the silver halogenides[37] which have considerable covalent character, we neglect these terms in Eq. 1, which then becomes

$$h\nu=\psi+E-I \qquad (2)$$

Then, we have only to calculate the crystal potential constants. The crystal structures of hexamminecobalt(III) iodide and perchlorate were determined by Meisel and Tiedje[38], et al. being an anti- $(NH_4)_3FeF_6$ type (see Fig. 7). On the other hand, the iodide selenate, iodide sulfate and bromide sulfate have an anti- K_2PtCl_6 type structure according to Hassel and Bödtker Naess[8], et al. (Fig. 8).

Now, we assume that the +3 charges on the hexamminecobalt(III) ion are concentrated on the cobalt. The assumption is justified in so far as potential constants are concerned, since the calculation based on the assumption that the charge is zero on the cobalt, therefore +1/2 on each nitrogen atom, according to Pauling's neutrality principle[39], gives the potential constant of 6.88 which is very close to that of 6.93 calculated on the former assumption, even for the nearest halogens. Thus, we are justified for treating our crystals as having a BiF_3 or a CaF_2 type structure. Their crystal potential constants can easily be obtained using the potential data calculated for the cubic lattice by the method of Ewald. The potential, $a\psi(xyz)$, at the lattice point (000) due to the simple cubic lattice situated on lattice points $a\,(xyz)$ are given as follows[40]:

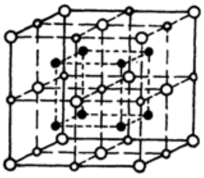

Fig. 7.

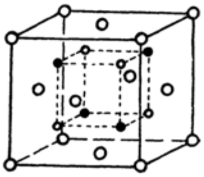

Fig. 8.

Fig. 7. Crystal structure of hexamminecobalt(III) iodide and perchlorate; the large circles are the hexamminecobalt (III) ions, and the small ones, open and solid, are the iodide or perchlorate ions.

Fig. 8. Crystal structure of hexamminecobalt(III) iodide sulfate, iodide selenate and bromide sulfate; the large circles are the hexamminecobalt(III) ions, the small open circles are the halogen ions and the small solid ones the sulfate or selenate ions.

$$\begin{aligned}
a\psi(000)&=\varphi_0=-2.83729\\
a\psi(00\tfrac12)-\varphi_0&=\varphi_1=2.7414\\
a\psi(0\tfrac12\tfrac12)-\varphi_0&=\varphi_2=2.2548\\
a\psi(\tfrac12\tfrac12\tfrac12)-\varphi_0&=\varphi_3=2.0354\\
a\psi(\tfrac14\tfrac14\tfrac14)-\varphi_0&=\varphi_4=2.6368.
\end{aligned}$$

From Figs. 7 and 8 and taking into consideration the +3 charges on the hexamminecobalt(III) ions and the −2 charges on the sulfate and selenate ions, our expressions for the crystal potential constants are given as follows:

for the iodide and the perchlorate,

$$\begin{aligned}
A'&=-3\varphi_1-3\varphi_2-\varphi_3+8\varphi_4\\
A'''&=9\varphi_1-27\varphi_2+3\varphi_3+24\varphi_4\,;
\end{aligned}$$

for the iodide selenate, the iodide sulfate and the bromide sulfate,

$$\begin{aligned}
A'&=-6\varphi_1-3\varphi_2-2\varphi_3+12\varphi_4\\
A'''&=-27\varphi_2+36\varphi_4.
\end{aligned}$$

B is easily calculated to be 6.9282. The values of A' and A''' are listed in Table II, together with r_α, ψ and E. The differences of the $h\nu$'s calculated between four salts are also given as well as the observed values.

Table II indicates that there is fairly good agreement between the $\Delta h\nu$'s calculated and

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[*5] In the crystal of hexamminecobalt (III) iodide, there are two kinds of iodide ions, whose distances from the complex ion are not the same (see Fig. 7). We assume that the edge absorption in this crystal is due to the transition of the electron of the iodide ion nearer to the complex ion.

37) Y. Uehara, *J. Chem. Soc. Japan(Pure Chem. Sec.)*, **63**, 1041 (1942); S. Kikuchi and S. Umano, ibid., **70**, 94 (1949).

[*6] According to Klemm, Ω_X is represented by $\Omega_X=e^2\alpha_X/2r_0^4$, where α_X is the polarizability of a halogen atom which is assumed to be 70% of that of the corresponding ion, and r_0 is the shortest cation-anion distance.

38) K. Meisel and W. Tiedje, *Z. anorg. Chem.*, **164**, 223 (1927).

39) L. Pauling, *J. Chem. Soc.*, **1948**, 1461.

40) T. Nagamiya and T. Matsubara, "The Theory of Solids", Vol. I, Kyoritsu Shuppan Co., Tokyo (1951), p. 234.

TABLE II

Crystal	A'	A'''	r_α(A)	ϕ(e.V.)	E(e.V.)	$\Delta h\nu_{calc.}$	$\Delta h\nu_{obs.}$
$[Co(NH_3)_6](ClO_4)_3$	4.0704	33.1824	11.38	16.20			
$[Co(NH_3)_6]I_3$	4.0704	33.1824	10.91	16.90	3.12	>0.96	0.96
$[Co(NH_3)_6]I(SeO_4)$	4.3580	34.0452	10.79	17.86	3.12	>0.13	0.09
$[Co(NH_3)_6]I(SO_4)$	4.3580	34.0452	10.71	17.99	3.12	>0.74	0.82
$[Co(NH_3)_6]Br(SO_4)$	4.3580	34.0452	10.51	18.33	3.52		

observed. Thus, the red shift of the edge absorption in the order listed in the table could be interpreted using the theory of the exciton. Unfortunately, the lattice structures of the chloride, the bromide and the chloride sulfate are unknown[*7]. The complete explanation of the observed order in $h\nu$ is, therefore, impossible, but it will be suggested that the increase in E and the probable decrease in r_α will be the major factors determining the increasing tendency of $h\nu$, though potential constants are necessarily different from that of a cubic lattice in the monoclinic lattice of the chloride and the rhombic one of the bromide.

As was stated previously, in the crystals containing oxy-acidic anions, the possibility of interpreting the edge absorption by the red shift of the anion's absorption was not excluded. However, it must be pointed out here that the fact that the edge absorptions exist at shorter wave lengths in those salts shown in Fig. 3 than those of the halogenides will be interpreted by the electron transfer theory, since the large ionization potential of oxygen (10 e.V. in perchlorate ion[30]) may be the principal factor determining the increase in $h\nu$.

Effect of a Crystaline Field on the Second Absorption Band.—In the preceding paragraphs, we neglected to discuss the behavior of the second band in crystals. Now, we shall briefly consider below the effect of a crystalline field on this band. The crystalline field theory mentioned above tells us that the stronger the crystalline field becomes, the larger the splitting of a d level, say in our case, the difference between the excited level, $(d\varepsilon^5 d\gamma)^1F_2$, which is responsible for the second band and the ground one, $(d\varepsilon^6)^1A_1$, becomes. The expectation is attained in our crystals, as the second band exists at shorter wave lengths in crystals (330–336 mμ) than in aqueous solutions (339 mμ). This is also true for the larger shifts of the second band in the chloride and the chloride perchlorate than that of the others, since the crystalline field in these complexes is expected to be stronger than in the others.

It is of interest to note here that if the edge absorption were of similar origin with the second band, it must shift to shorter wave lengths as compared with the one in aqueous solutions, contrary to our results. This is another reason why the two-electron jump hypothesis must be discarded.

Summary

(1) The ultraviolet absorption spectra of the crystals of fourteen hexamminecobalt(III) salts were qualitatively measured using a reflecting microscope (magnification 100×), a quartz spectrograph and a recording microphotometer.

(2) All the crystals investigated showed, besides the weak absorption bands due to the complex ion, the strong absorption edges which were situated at longer wave lengths than those in aqueous solutions, and the positions of which were largely affected by anions. The most remarkable example was the iodide, the absorption edge of which extended to the visible region.

(3) It is concluded that, at least in the case of the halogenides, all the possible transitions within the complex ion and an anion are inadequate explanations and the electron transfer from an anion to the complex ion is most statisfactory for the origin of these strong absorption bands.

(4) The differences between the wave lengths of the absorption edges of hexamminecobalt(III) iodide, iodide selenate, iodide sulfate and the bromide sulfate were calculated by the energy cycle method and the results agreed fairly well with the experimental values, thus showing that these bands corresponded to the excition bands in ionic crystals.

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[*7] In the famous W. Hückel's "Anorganische Strukturchemie", Ferdinand Enke Verlag, Stuttgart (1948), p. 548, Fig. 68b, hexamminecobalt(III) chloride is illustrated as having a cubic lattice. This is incorrect, since its crystal form is monoclinic. It seems to the present author that its lattice structure has not so far been analysed as well as that of the bromide.