On the Absorption Spectra of Polynuclear Complex Salts.

By Yoshihiko OHYAGI.

(Received April 8, 1940).

The commercial 90% phosphoric acid dissolves many oxides or salts insoluble in water, and gives stable solutions. In the last year, H. Shiba and T. Inoue(1) found that the solution of cobaltic complex salt is also stable, and its absorption spectrum gives the same results with the aqueous solution: namely, the absorption maxima lie on the same wave-length of the spectrum.

In the present work the author attempted to examine the absorption spectra of the polynuclear complex salt of cobalt that is very unstable in the aqueous solution.

On this subject, there exist a few treatises previously, and among them the research of Y. Shibata(2) on the acidic aqueous solution is the most attractive, but in the present work it is shown that the absorption spectra of the phosphoric acid solution do not always coincide with the result of Y. Shibata.

Apparatus. In the present work the author used a new micro type of Baly-tube as shown in Fig. 1. The sliding full rod and the window are made of quartz for the purpose of ultra-violet spectroscopy; and, drawing out the rod, the solution is let into the tube from the upper ditch that plays the part of reservoir. Now, with this tube, as the thickness (d) of solution varies from 4 cm to 0.4 mm, so a solution of 2.5-times of concentration should be prepared to get the corresponding result of ordinary Baly-tube; but when this solution is prepared, the next experiment with 1/10 concentration can be carried out with changing the thickness (d) of solution from 4 mm. to 0.04 mm. For this purpose the tube is clamped on a wooden stand with a vernier-scale as shown in Fig. 2, and is let to slide to any position desired. If this apparatus is used, the experiment is perfectly carried out with a little quantity of material as it requires about 0.5 to 1 c.c. of solution only.

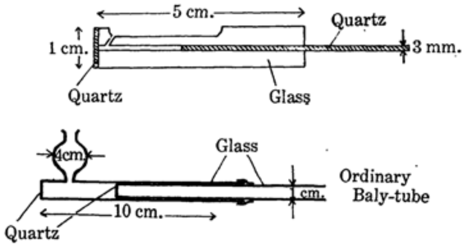


Fig. 1.

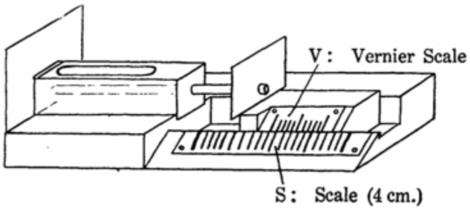


Fig. 2.

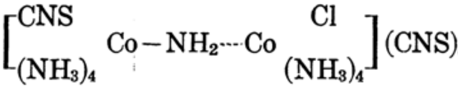
---

(1) H. Shiba and T. Inoue, Unpublished result.

(2) Y. Shibata, *J. Faculty Sci., Imp. Univ. Tokyo*, Art II, **37** (1915), 6. *J. Chem. Soc. Japan*, **38** (1916), 99.

As the light source, a hydrogen Geissler-tube is used with 3000 volts and 150-milliamperes; it gives a fine continuous spectrum from 6500Å to about 2200Å.

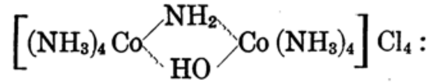
Experimental and Discussion. The polynuclear cobalt complex salts are prepared in the method described by A. Werner.⁽³⁾ They are derived from the so-called "Melanochloride" and "Vortmann's Fusco-sulphate" with some exception. In this experiment the author studied on 23 salts as shown in Table 1.

Among them, however,  $\left[\begin{matrix}\mathrm{CNS}\\(\mathrm{NH_3})_4\end{matrix}\mathrm{Co-NH_2\cdots Co}\begin{matrix}\mathrm{Cl}\\(\mathrm{NH_3})_4\end{matrix}\right](\mathrm{CNS})_3$ is unstable in phosphoric acid. It decomposes at once with the evolution of gas, so the absorption spectrum cannot be observed. But this is not the characteristic property of this salt; other complex salts containing CNS-group are unstable or insoluble in the phosphoric acid also.

For the experiment, a solution of 0.025 mol. (for one atom of Co) is prepared to get the corresponding results of the ordinary condition of 0.01 mol., and the "Oriental" panchromatic plate is used; the duration of exposure is 30 seconds.

The commercial 90% phosphoric acid is a colourless viscous fluid. Its absorption curves has no selective absorption at all and the end absorption also lies in the range shorter than 2800Å. as shown in Fig. 3, so it may be used as a solvent without any refinement. This end absorption seems to be the effect of $Fe^{\cdot\cdot\cdot}$-ion, and with repeated recrystallization the absorption end are shifted slightly towards the shorter wave-length.

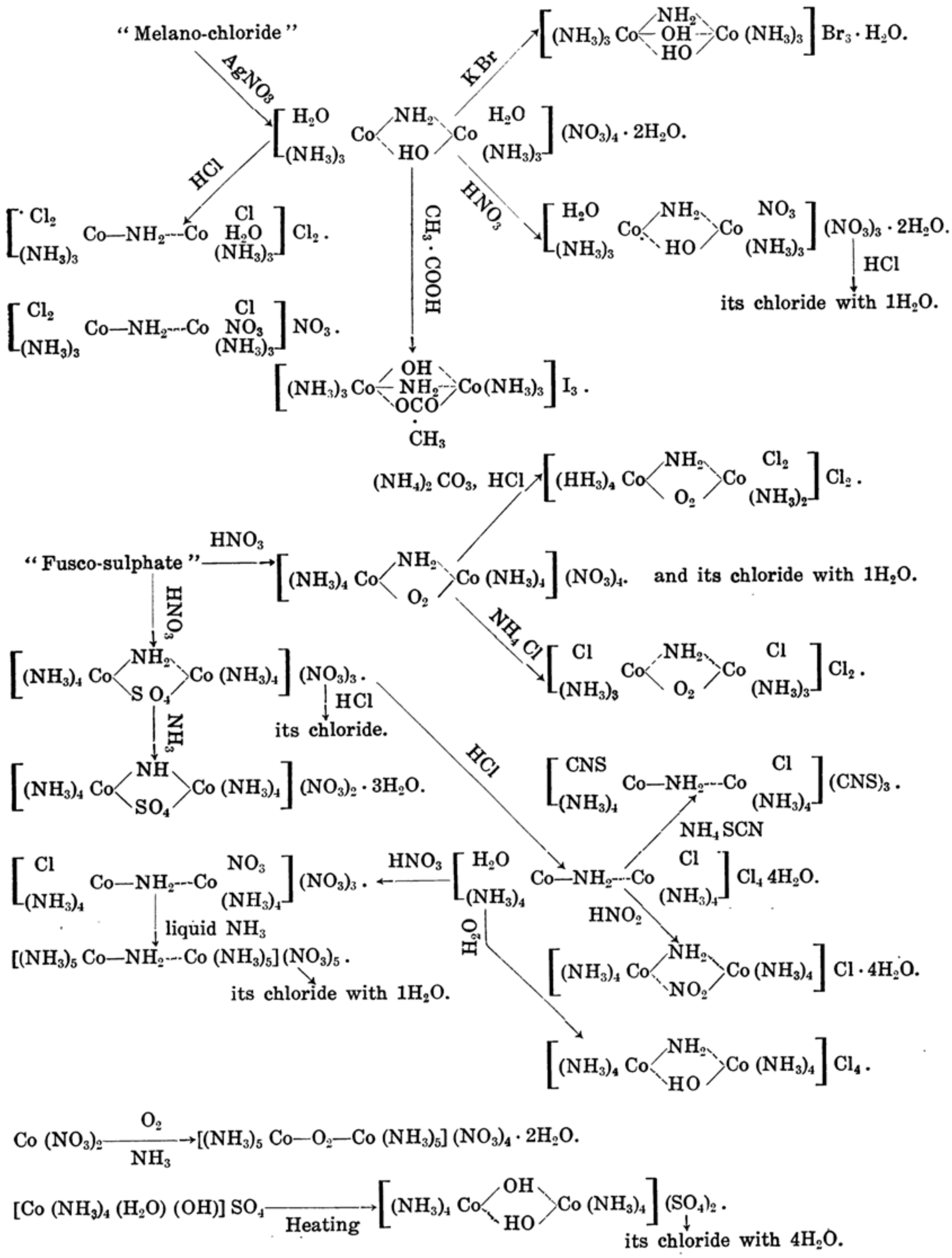
(1) $[(NH_3)_5Co-NH_2\cdots Co(NH_3)_5](NO_3)_5$ and its chloride with $1H_2O$: The nitrate is a red needle with a bluish tint, and the chloride is a pink powder. The former gives a red phosphoric acid solution, and the absorption spectrum has three bands: viz., at 1900 mm^{-1}, 2780 mm^{-1}, and 3850 mm^{-1} as shown in Fig. 4. This third band was doubted to be the absorption of the nitrate ion at first; but, as the chloride has been proved to have the same absorption (Fig. 4) and $NaNO_3$ is found to have only a very small absorption at 3730 mm^{-1} with a 0.02 mol. solution (Fig. 10), this 3840 mm^{-1} absorption may be considered as the characteristic one for this quinqui-valent cation.

(2)  $\left[(\mathrm{NH_3})_4\mathrm{Co}\begin{matrix}\mathrm{NH_2}\\\mathrm{HO}\end{matrix}\mathrm{Co}(\mathrm{NH_3})_4\right]\mathrm{Cl_4}$: This salt may be considered as the OH-derivative of the salt (1). Two molecules of ammonia of the latter are substituted with a OH-group. It is a brownish red crystal and gives a deep red phosphoric acid solution, the absorption curve of which is shown in Fig. 4 also. Its absorption maxima exist at 1825 mm^{-1}, 2710 mm^{-1} and 3410 mm^{-1}; and from its shape the effect of one OH-group may be regarded as a bathochromic one especially for the third band and probably hypochromic for all these three bands, but this "hypochromic" effect is inconsistent a little with the result of the next salt.

---

(3) A. Werner and his co-workers, *Z. anorg. Chem.*, **16** (1898), 109: **21** (1899), 96; *Ber.*, **40** (1907), 2103, 4426, 4434, 4605, 4834; **41** (1908), 3879, 3912; *Ann.*, **375** (1910), 1.

Table 1.


" Melano-chloride "
$AgNO_3$
$[(H_2O)(NH_3)_3Co(NH_2)(HO)Co(H_2O)(NH_3)_3](NO_3)_4 \cdot 2H_2O$.
KBr
$[(NH_3)_3Co(NH_2)(OH)(HO)Co(NH_3)_3]Br_3 \cdot H_2O$.
HCl
$[Cl_2(NH_3)_3Co—NH_2—Co\,Cl\,H_2O(NH_3)_3]Cl_2$.
$[Cl_2(NH_3)_3Co—NH_2—Co\,Cl\,NO_3(NH_3)_3]NO_3$.
$CH_3 \cdot COOH$
$[(NH_3)_3Co(OH)(NH_2)(OCO \cdot CH_3)Co(NH_3)_3]I_3$.
HNO_3
$[(H_2O)(NH_3)_3Co(NH_2)(HO)Co(NO_3)(NH_3)_3](NO_3)_3 \cdot 2H_2O$.
HCl
its chloride with $1H_2O$.
$(NH_4)_2CO_3$, HCl
$[(HH_3)_4Co(NH_2)(O_2)Co\,Cl_2(NH_3)_2]Cl_2$.
" Fusco-sulphate "
HNO_3
$[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4](NO_3)_4$. and its chloride with $1H_2O$.
NH_4Cl
$[Cl(NH_3)_3Co(NH_2)(O_2)Co\,Cl(NH_3)_3]Cl_2$.
HNO_3
$[(NH_3)_4Co(NH_2)(SO_4)Co(NH_3)_4](NO_3)_3$.
HCl
its chloride.
NH_3
$[(NH_3)_4Co(NH)(SO_4)Co(NH_3)_4](NO_3)_2 \cdot 3H_2O$.
HCl
$[CNS(NH_3)_4Co—NH_2—Co\,Cl(NH_3)_4](CNS)_3$.
NH_4SCN
$[H_2O(NH_3)_4Co—NH_2—Co\,Cl(NH_3)_4]Cl_4\,4H_2O$.
HNO_3
$[Cl(NH_3)_4Co—NH_2—Co\,NO_3(NH_3)_4](NO_3)_3$.
liquid NH_3
$[(NH_3)_5Co—NH_2—Co(NH_3)_5](NO_3)_5$.
its chloride with $1H_2O$.
HNO_2
$[(NH_3)_4Co(NH_2)(NO_2)Co(NH_3)_4]Cl \cdot 4H_2O$.
H_2O
$[(NH_3)_4Co(NH_2)(HO)Co(NH_3)_4]Cl_4$.
$Co(NO_3)_2 \xrightarrow[NH_3]{O_2} [(NH_3)_5Co—O_2—Co(NH_3)_5](NO_3)_4 \cdot 2H_2O$.
$[Co(NH_3)_4(H_2O)(OH)]SO_4 \xrightarrow[Heating]{} [(NH_3)_4Co(OH)(HO)Co(NH_3)_4](SO_4)_2$.
its chloride with $4H_2O$.

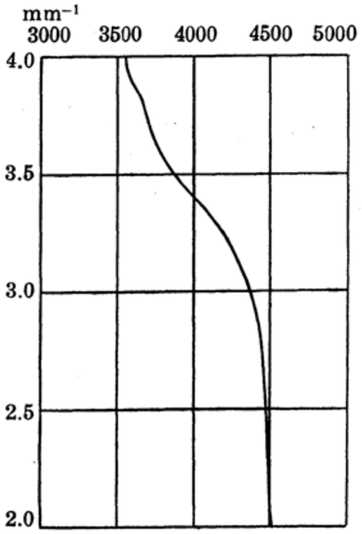


Fig. 3. Phosphoric acid. (90%)

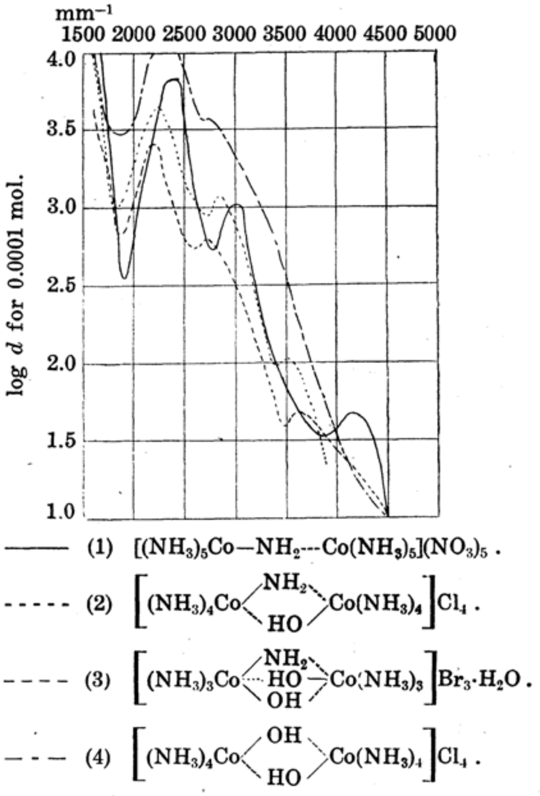
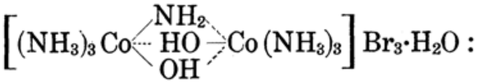
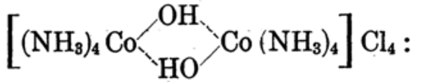
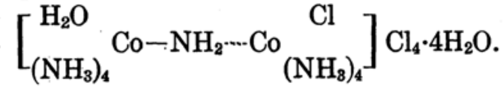


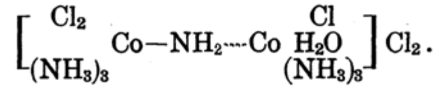
Fig. 4.

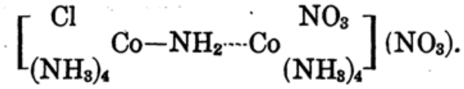
(3) 
$\left[(NH_3)_3Co\begin{matrix}NH_2\\HO\\OH\end{matrix}Co(NH_3)_3\right]Br_3\cdot H_2O$: This reddish brown crystal dissolves in phosphoric acid with great difficulties and gives a dark red solution. And according to its small solubility, its 0.025 mol. solution cannot be prepared; so a 0.0125 mol. solution is used for the experiment and the results are rearranged for 0.025 mol. The absorption maxima exist on 1880 mm^{-1}, 2660 mm^{-1} and 3495 mm^{-1}; these position are almost coincide with those of the salt (2) except the 2nd band, though they are much more hyperchromic than the latter. Now, this salt may be regarded as an OH-derivative of the salt (2), and from the above mentioned result, its absorption is expected to be a more hypochromic one than that of the salt (2) with the substitution of one more OH-group. Perhaps, however, this inconsistency has its base in the peculiar condition of the three bridging groups. On the other hand, this salt is regarded as a NH$_2$-derivative of the next salt (4) also. Then, with the substitution of NH$_2$-group the absorption of the latter brows to a very hyperchromic one, and moreover, a third band appears; namely, the NH$_2$-group has a hyperchromic effect on the 1st and 2nd band, and causes a 3rd band to appear. So, the 3840 mm^{-1}-absorption of the salt (1) may also be regarded as the effect of the NH$_2$-group probably.

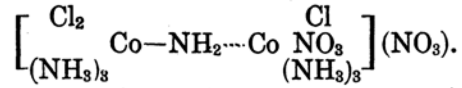
(4) 
$\left[(NH_3)_4Co\begin{matrix}OH\\ HO\end{matrix}Co(NH_3)_4\right]Cl_4$: A bluish red crystalline powder. It gives a red phosphoric acid solution. The absorption curve has two bands: viz., at 1875 mm^{-1}, and 2670 mm^{-1} and they are much more hypochromic than the other salts as shown in Fig. 4.

And as it may be said that the OH-group in the complex ion causes an almost same result of hydrolysis to that ion, this diol-complex salt has a comparatively weak combination between two cobalt atoms and two OH-groups as compared with the other polynuclear complex salts. In the salt (3) this weak combination is strengthened probably with a NH_2-group.

(5) 
$\left[\begin{matrix}H_2O\\ (NH_3)_4\end{matrix}Co-NH_2-Co\begin{matrix}Cl\\ (NH_3)_4\end{matrix}\right]Cl_4\cdot 4H_2O$.

(6) 
$\left[\begin{matrix}Cl_2\\ (NH_3)_3\end{matrix}Co-NH_2-Co\begin{matrix}Cl\\ H_2O\\ (NH_3)_3\end{matrix}\right]Cl_2$.

(7) 
$\left[\begin{matrix}Cl\\ (NH_3)_4\end{matrix}Co-NH_2-Co\begin{matrix}NO_3\\ (NH_3)_4\end{matrix}\right](NO_3)$.

(8) 
$\left[\begin{matrix}Cl_2\\ (NH_3)_3\end{matrix}Co-NH_2-Co\begin{matrix}Cl\\ NO_3\\ (NH_3)_3\end{matrix}\right](NO_3)$. These salts are also considered as the derivatives of the salt (1), but the effect of the co-ordinated Cl-atom seems to be a profound one.

The salt (5) is a brownish violet crystal and the phosphoric acid solution is also brownish violet. The absorption maxima lie on 1820 mm^{-1}, 2750 mm^{-1} and 3400 mm^{-1} as shown in Fig. 5.

The salt (6) is a violet-black crystal and the phosphoric acid solution is deep violet. The absorption maxima lie on 1850 mm^{-1}, 2460 mm^{-1} and 3200 mm^{-1}.

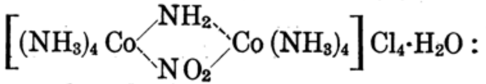
The salt (7) is a brownish violet crystal lighter than the first, and the phosphoric acid solution is violet. The absorption maxima lie on 1830 mm^{-1}, 2650 mm^{-1} and 3400 mm^{-1}.

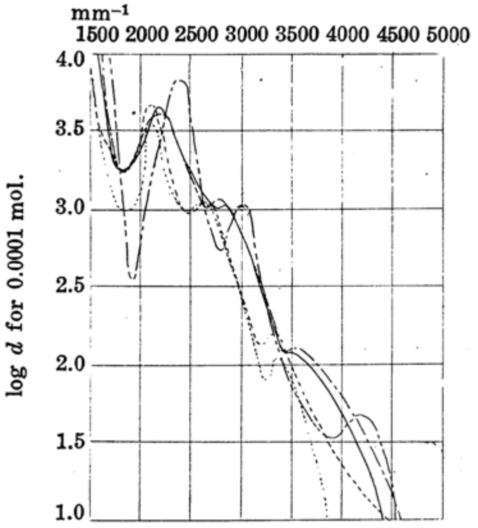
The salt (8) is a violet-black crystal and the phosphoric acid solution is dark violet. The absorption maxima lie on 1800 mm^{-1}, 2500 mm^{-1} and 3200 mm^{-1}.

The effect of Cl' is bathochromic for any band; especially for the 3rd band. But it seems that this bathochromic effect cannot be found on the 2nd band with single Cl' as compared the curve of (5) with that of (1).

On this case, the 2nd band is found more hypochromic but not bathochromic at all. In the next place, however, this band is shifted towards the longer wave-length region with a NO_3-ion substituted in the place of H_2O (the case (7)), or with two more atoms of Cl co-ordinated one to every one cobalt atom (the case (6)). The bathochromic effect of Cl' is already known with the mononuclear complex-salt, but, from this result it may be doubted that in the case of the polynuclear complex salt this effect appears for the first time with another anion (in this case the NO_3-ion) co-ordinated with the other cobalt atom.

However, this NO_3-ion cannot change the third band of the salt (5): this band is shifted towards the longer wave-length for the first time with that two shared Cl-atoms (the case (6) and (8)).

(9) 
$\left[(NH_3)_4Co\begin{matrix}NH_2\\ NO_2\end{matrix}Co(NH_3)_4\right]Cl_4\cdot H_2O$: This salt is a brownish orange crystal and gives an orange red phosphoric acid solution. Its absorption curve has three distinct bands as shown in Fig. 6: viz., at 2030 mm^{-1}, 2820 mm^{-1} and 3400 mm^{-1}.



—— (5) $\left[\begin{matrix}H_2O\\ (NH_3)_4\end{matrix}Co—NH_2\cdots Co\begin{matrix}Cl\\ (NH_3)_4\end{matrix}\right]Cl_4\cdot 4H_2O$.

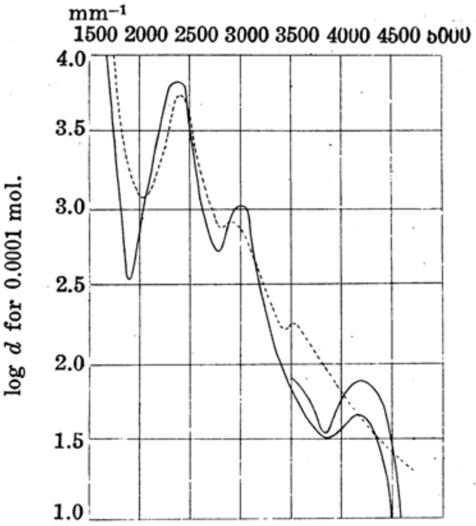
- - - - - (6) $\left[\begin{matrix}H_2O\\ Cl\\ (NH_3)_3\end{matrix}Co—NH_2\cdots Co\begin{matrix}Cl_2\\ \\ (NH_3)_3\end{matrix}\right]Cl_2$.

— — — (7) $\left[\begin{matrix}Cl\\ (NH_3)_4\end{matrix}Co—NH_2\cdots Co\begin{matrix}NO_3\\ (NH_3)_4\end{matrix}\right](NO_3)_3$.

- - - - (8) $\left[\begin{matrix}Cl_2\\ \\ (NH_3)_3\end{matrix}Co—NH_2\cdots Co\begin{matrix}Cl\\ NO_3\\ (NH_3)_3\end{matrix}\right](NO_3)_3$.

- - - — (1) $[(NH_3)_5Co—NH_2\cdots Co(NH_3)_5](NO_3)_5$.

Fig. 5.

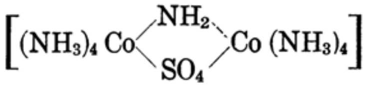


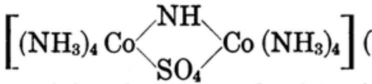
—— (1) $[(NH_3)_5Co—NH_2\cdots Co(NH_3)_5](NO_3)_5$, Cl_5.

- - - - - (9) $\left[(NH_3)_4Co\begin{matrix}NH_2\\ NO_2\end{matrix}Co(NH_3)_4\right]Cl_4\cdot H_2O$.

Fig. 6.

The effect of NO_2-group is hypsochromic with the 1st band as it is in the mononuclear complex salt; but, on the contrary, with the 2nd band it is also hypsochromic. Perhaps this change is caused by the NH_2-group co-ordinated in the cis-position to it. With the third band, the effect is found to be bathochromic.

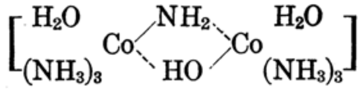
(10) 
$\left[(NH_3)_4Co\begin{matrix}NH_2\\ SO_4\end{matrix}Co(NH_3)_4\right](NO_3)_3$ and its chloride.

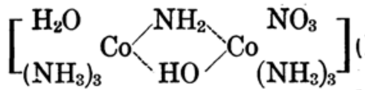
(11) 
$\left[(NH_3)_4Co\begin{matrix}NH\\ SO_4\end{matrix}Co(NH_3)_4\right](NO_3)_2\cdot 3H_2O$: These three salts are all reddish violet fine crystals (the imino-salt is a little lighter coloured

than the other), and give violet phosphoric acid solutions. Their absorption curves are given in Fig. 7.

There are two distinct absorption bands at 1850 mm^{-1} and 2700 mm^{-1}, but the absorption of the imino-salt is a little more hypochromic than the other, and all of them have not the 3rd band: namely, the most conspicuous effect of the SO_4-group is that it wipes out the 3rd band of the salt (1).

The effect on the 1st band is a little hypsochromic and on the 2nd band bathochromic. On the spectrum the difference between NH_2- and NH- is not serious.

(12) 
$$\left[\begin{array}{ccccc} H_2O & & NH_2 & & H_2O \\ & Co & & Co & \\ (NH_3)_3 & & HO & & (NH_3)_3 \end{array}\right](NO_3)_4\cdot 2H_2O :$$

(13) 
$$\left[\begin{array}{ccccc} H_2O & & NH_2 & & NO_3 \\ & Co & & Co & \\ (NH_3)_3 & & HO & & (NH_3)_3 \end{array}\right](NO_3)_3\cdot 2H_2O$$ and its chloride with $1H_2O$.

The former is a light reddish brown crystal and the latter two are reddish orange crystals. All these three give reddish orange phosphoric acid solution. Their absorption curves are shown in Fig. 8. The 1st salt at 1910 mm^{-1}, 2550 mm^{-1} and 3200 mm^{-1}; the 2nd salt at 1910 mm^{-1}, 2560 mm^{-1} and 3390 mm^{-1}; the 3rd chloride at 1910 mm^{-1}, 2530 mm^{-1} and 3350 mm^{-1}.

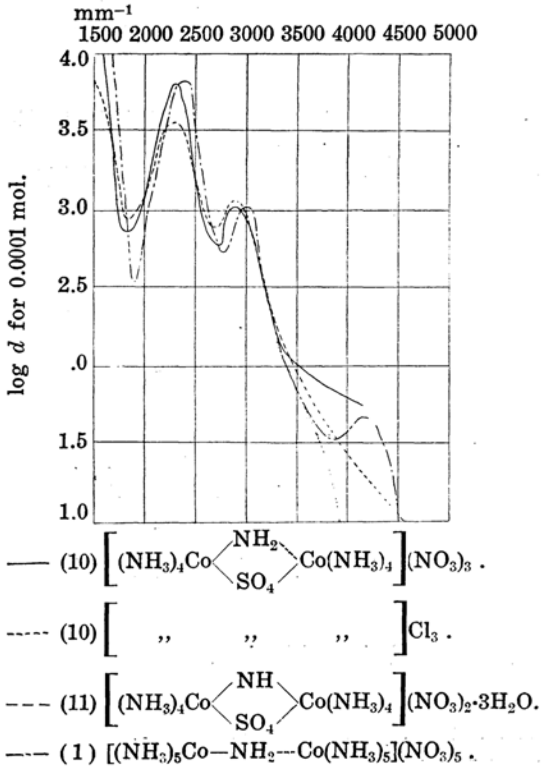


Fig. 7.

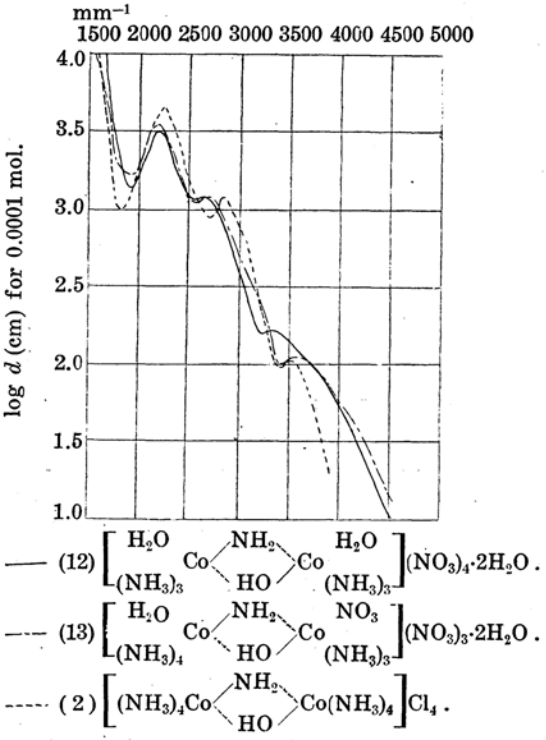
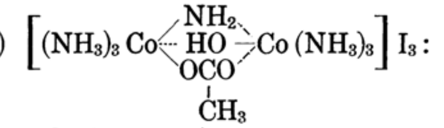


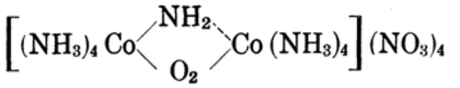
Fig. 8.

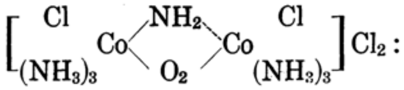
These three salts are regarded as derivatives of the salt (2), and from the result it is shown that in this case the effect of NO_3-group appears only on the 3rd band: viz., it is hypo- and hypsochromic. The effect of H_2O-molecule is serious in this case as it is hypsochromic on the 1st band and bathochromic on the 2nd and 3rd band, moreover, it is hypochromic for all of these three bands. So, the fact, that by the above mentioned salt (5) three bands are all found hypochromic, is probably the effect of H_2O.

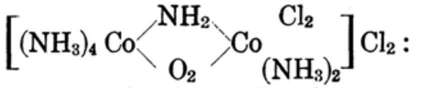
(14)  $\left[(NH_3)_3Co\begin{array}{c}NH_2\\ HO\\ OCO\\ |\\ CH_3\end{array}Co(NH_3)_3\right]I_3$: This is a yellowish red fine powder and gives an orange phosphoric acid solution. But as its solubility is very small, its 0.025 mol. solution cannot be prepared. So, a solution of 0.00625 mol. was used, and afterwards the result has been rearranged for the position of 0.025 mol. The absorption curve is shown in Fig. 9. It has three bands at 1890 mm^{-1}, 3310 mm^{-1} and 2650 mm^{-1}. This 3310 mm^{-1}-absorption is very distinct and seems to be the characteristic one for this "acetato" complex salt; and when this salt is considered to be the derivative of the salt (2), the acetato-group effects on the 3rd band of the latter as bathochromic.

The absorption at 2650 mm^{-1} is a very small one, and possibly seems to be an inflection point: but it is certainly the transformed 2nd band originally found in the salt (2). With all these results it may be said that the acetato-group effects much hyperchromic and bathochromic.

(15) $[(NH_3)_5Co-O_2-Co(NH_3)_5](NO_3)_4\cdot 2H_2O$:

(16)  $\left[(NH_3)_4Co\begin{array}{c}NH_2\\ O_2\end{array}Co(NH_3)_4\right](NO_3)_4$ and its chloride with $1H_2O$.

(17)  $\left[\begin{array}{c}Cl\\ (NH_3)_3\end{array}Co\begin{array}{c}NH_2\\ O_2\end{array}Co\begin{array}{c}Cl\\ (NH_3)_3\end{array}\right]Cl_2$:

(18)  $\left[(NH_3)_4Co\begin{array}{c}NH_2\\ O_2\end{array}Co\begin{array}{c}Cl_2\\ (NH_3)_2\end{array}\right]Cl_2$: The salt (15) is an oxidation product of ammoniacal cobalt nitrate solution, and presents itself as a large dark greenish brown crystal.

It gives a greenish brown solution in the phosphoric acid, and its absorption curve has two great bands at 2000 mm^{-1} and 3360 mm^{-1} with a very fine one at 2900 mm^{-1} as shown in Fig. 10. The absorption at 3360 mm^{-1} is exceptionally hyperchromic, and, at first, it was doubted to be the absorption caused by the nitrate ion, but $NaNO_3$ has been proved to have a small one at 3730 mm^{-1}, this 3360 mm^{-1}-absorption may be regarded as the effect of the complex cation. Still more it seems to have another absorption in the infra-red region, but it cannot be observed for the sake of the small sensitivty of plate. That fine absorption at 2900 mm^{-1} is found in this salt only.

In the case of this salt, the absorption in the infra-red region is probably the first absorption band, and the apparently first 2000 mm^{-1}-absorption is really the second.

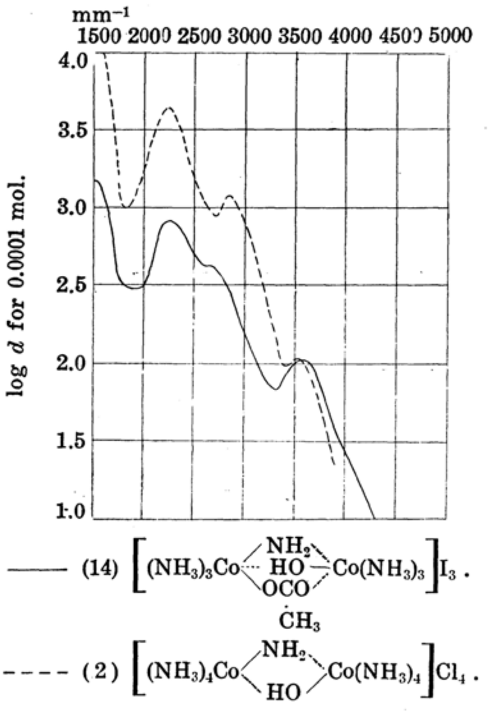


Fig. 9.

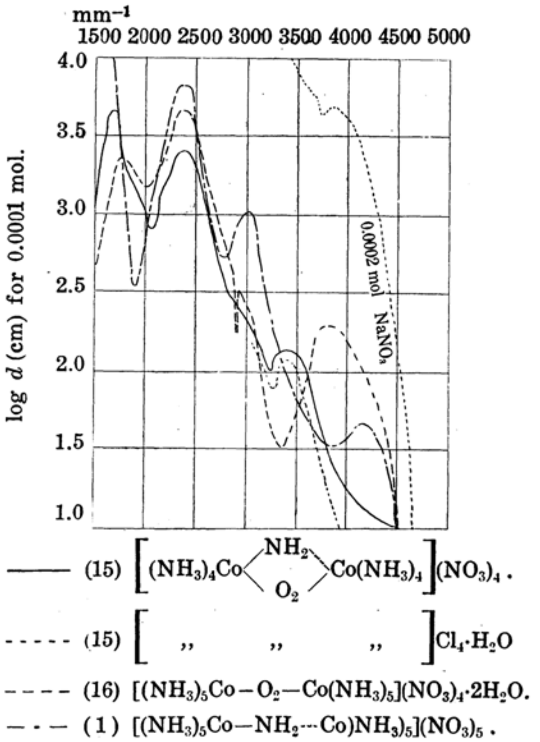


Fig. 10.

The salt (16) is regarded to be the intermediate compound of (1) and (16). It has a dark green colour and the phosphoric acid solution is greenish brown. Its absorption curve has also two distinct bands at 2080 mm^{-1} and 3270 mm^{-1}, and probably one more in the infra-red region as shown in Fig. 10., and there is almost no difference between nitrate and chloride. Its absorption at 3270 mm^{-1} is considerably more hypochromic than that of the salt (15).

Now, when to this salt (16) two Cl-atoms are entered, there appears two salts (17) and (18) according to the position of Cl-atoms: viz., if these two are co-ordinated together to one atom there yields the salt (18), and if co-ordinated apart to the different cobalt atoms, there yields the salt (17).

The former is a brownish violet crystalline powder and gives a dark greenish brown phosphoric acid solution. Its absorption maxima lie on 1920 mm^{-1}, 2640 mm^{-1} and 3140 mm^{-1} as shown in Fig. 11.

The latter is a green powder and gives a dark green solution with great difficulties. Its absorption maxima lie on 1950 mm^{-1}, 2885 mm^{-1}, 3150 mm^{-1} and 3560 mm^{-1}. But this 2885 mm^{-1}-absorption seems to be a little uncertain one. In either case, these two salts differ not only in their crystalline colour but also in their absorption. The 3150 mm^{-1}-absorption is common for these two salts and probably it is the third bands; it is a little more hypo- and bathochromic than that of (15). But for the other part of the absorption curve and for the existence of a quadrivalent cobalt atom, regularities have not yet been found.

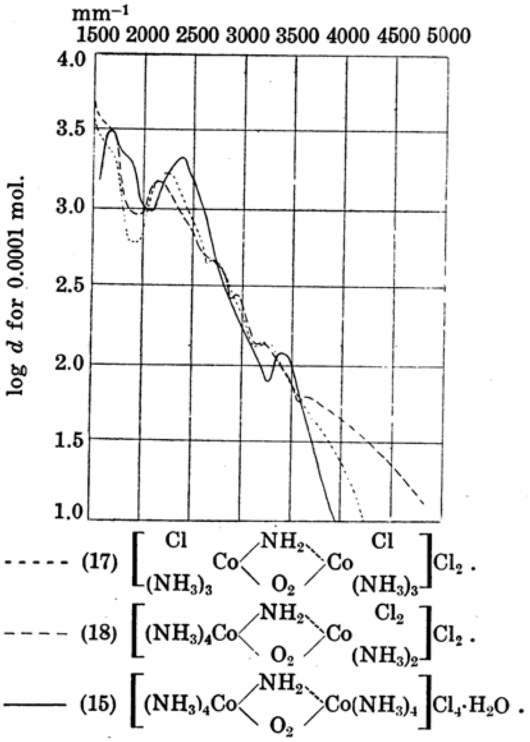
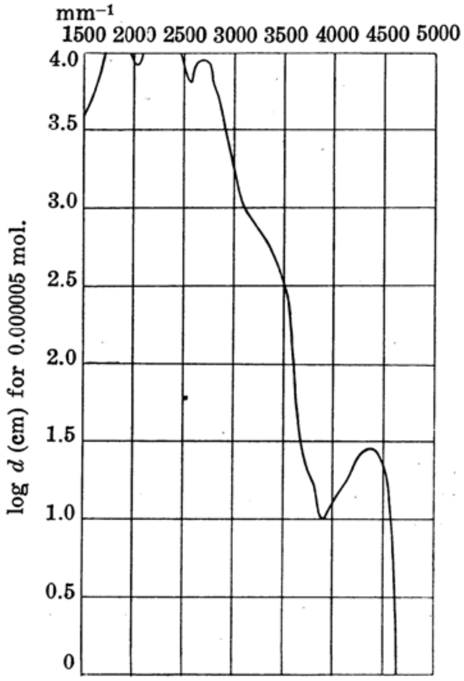


Fig. 11.



trans-[Co(NH$_3$)$_4$Cl$_2$]Cl·H$_2$O (Praseo)

Fig. 12.

According to the opinion⁽⁴⁾ that the third band is caused with two anionic ligands co-ordinated in the trans-position, the author observed the absorption spectrum of the trans-$[Co(NH_3)_4Cl_2]Cl \cdot H_2O$ (Praseochloride) also in the phosphoric acid solution as shown in Fig. 12.; the results, however, are proved to be of no use. But this great band at 3900 mm^{-1} is a very peculiar one.

Summary.

The absorption spectra of the polynuclear cobalt complex salts are observed in the phosphoric acid solution. They are stable in it, and give distinct absorption spectra.

In conclusion the author expresses his hearty thanks to Dr. H. Shiba and Dr. T. Inoue of The Institute of Physical and Chemical Research, and further to Prof. Y. Shibata of The Imperial University of Tokyo. This paper is dedicated to the soul of my late wife, Yoshiko, who had aided me very much and died on March 30th, 1940.

The Institute of Physical and
Chemical Research, Tokyo.

---

(4) R. Tsuchida, this Bulletin, **13** (1938), 388, 436. etc.