Absorption Spectra of Co-ordination Compounds. IV. Ethylenediamine Cobaltic Complexes.

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Introduction. I. On Absorption Bands: In the previous papers,(1)(2)(3) one of the authors discussed on the origins of the selective absorption bands, which complex salts show in the near infra-red, the visible and the near ultra-violet regions of the spectrum, concluding as follows:

(a) The first absorption band: This may be attributed to electron transitions in an unsaturated transition shell of the central ion. Accordingly, if the central ion belongs to a group of typical elements, this band does not appear, because such an ion has no unsaturated transition shell. Again we should not expect this band, when the central ion, even if this belongs to a group of transition elements, has an electronic configuration of the pseudo-inert-gas or inert-gas type. An example for the former case is potassium mercuric iodide, $K_2[HgI_4]$(4), and one for the latter potassium chromate, $K_2[CrO_4]$(3).

The first absorption bands are found almost always in the visible region. Luther and others(5) discussed on the relation between the stability and the colour of complex salts. We can not determine, however, the stability of complex salt by its colour or by the position of its first absorption band, the band owing its origin to electrons of the central ion alone and not to co-ordination electrons combining the central atom to the ligands.

(b) The second absorption band: This may be explained as due to a kind of incomplete dissociation of the complex radical by irradiation. Showing the excited states of the co-ordination electrons, therefore, this band may be considered as giving the measure of stability of complex salts or co-ordination compounds in a wider sense.

(c) The third absorption band: This appears, when (i) a pair or pairs of negative ligands are situated in trans-positions to each other in octahedral or square complex radicals, e.g., $[Co(NH_3)_4Cl_{2\left\{\substack{(1)\\(6)}\right\}}]^{+}$(6) and $[Co(NH_3)_4(NO_2)_{2\left\{\substack{(1)\\(6)}\right\}}]^{+}$(7) or $[Ni(CN)_4]^{--}$(8), and (ii) two or more negative ligands are co-ordinated around the central ion in tetrahedral complex radicals such as chromate ion, CrO_4^{--}(3).

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

(2) R. Tsuchida, *ibid.*, **13** (1938), 436.

(3) R. Tsuchida, *ibid.*, **13** (1938), 471.

(4) R. Tsuchida, *J. Chem. Soc. Japan*, **59** (1938), 733; S. Kashimoto, R. Tsuchida, *ibid.*, **60** (1939), 347.

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

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

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

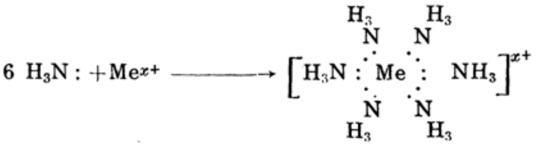
(8) H. Kuroya, R. Tsuchida, *ibid.*, **61** (1940), 597.

(d) The special absorption band: This band found in special cases is due to absorption band proper to the ligand itself⁽³⁾, or to a new strongly absorbing centre⁽²⁾ which has been formed by co-ordination of the particular ligand.

These conclusions have been reached by one of the authors after a series of experimental works and the results have been carefully developed to explain absorption spectra of various compounds, inorganic and organic.

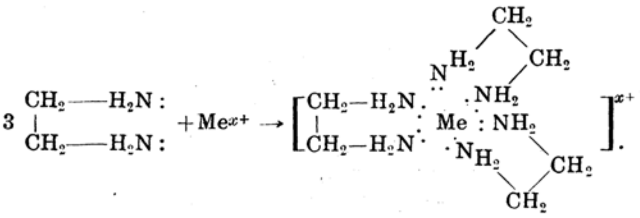
II. On Ethylenediamine Complex Salts: It is a well-known fact that the complex salt of ethylenediamine, which can be regarded as a substitution product of the corresponding ammine complex, is much more stable than the ammine salt, although their colours are similar to each other. For example, praseo-cobalti-salt $[Co(NH_3)_4Cl_2\left\{\begin{smallmatrix}1\\6\end{smallmatrix}\right\}]X$ is decomposed faster in aqueous solutions than the corresponding ethylenediamine salt $[Co\,en_2Cl_2\left\{\begin{smallmatrix}1\\6\end{smallmatrix}\right\}]X$. Of the two possible isomers of $[Co(NH_3)_4(H_2O)_2]X_3$ only cis-diaquo-salt is known, whereas in the more stable diaquo-ethylenediamine-compounds both the cis- and the trans-forms have been obtained.

Ammonia forms ammine complexes, being co-ordinated around the central atoms by its lone pair of electrons, and such an interpretation can be adopted also for the formation of ethylenediamine complexes: thus



$$6\,H_3N: + Me^{x+} \longrightarrow \left[H_3N : \underset{\underset{H_3\ \ H_3}{N\ \ N}}{\overset{\overset{H_3\ \ H_3}{N\ \ N}}{Me}} : NH_3\right]^{x+}$$

and



The similarity between properties of ammine salts and those of the corresponding ethylenediamine complexes may thus be understood.

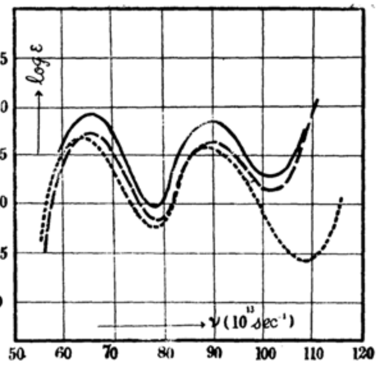
According to the postulates proposed by the authors, however, we can expect a shift of the second absorption band of ethylenediamine complex towards the more spectrally stable direction, or in other words, the shorter wave-lengths, compared with the less stable ammine salt.

For the purpose of confirming this point of view, the authors have prepared fourteen ethylenediamine complex salts and investigated their absorption spectra, comparing them with those of the corresponding ammine salts, which had been measured in this laboratory. In this paper the results of these experiments are dealt with, and the bearings of the observations on the problem of configuration or chemical combination will be discussed.

Experimental Results and Discussions. The experimental results are summarized in Table 1, while the absorption curves thus obtained are shown in Fig. 1–12 together with those of the corresponding ammine complexes for the purpose of comparison.

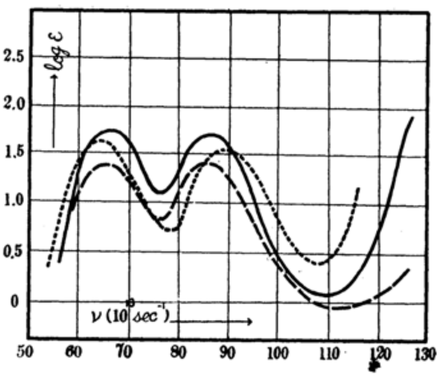
Table 1.

Complex salt	First band		Second band		Third band		Special band	
	$\nu_1(10^{13})$	log ε	$\nu_2(10^{13})$	log ε	$\nu_3(10^{13})$	log ε	$\nu_s(10^{13})$	log ε
$[\mathrm{Co(NH_3)_6}]\ \mathrm{Cl_3}$	63.2	1.66	88.8	1.58				
$[\mathrm{Co\ en_2\ (NH_3)_2}{}_{\left\{ {(1) \atop (6)} \right\}}]\ \mathrm{Br_3}$	64.8	1.72	89.2	1.62				
$[\mathrm{Co\ en_3}]\ \mathrm{Br_3}$	64.6	1.88	89.2	1.81				
$[\mathrm{Cr(NH_3)_6}]\ \mathrm{Cl_3}$	65.0	1.44	85.4	1.45				
$[\mathrm{Cr\ en_3}]\ \mathrm{Cl_3}$	66.0	1.78	85.6	1.75				
$[\mathrm{Co(NH_3)_5\ Cl}]\ \mathrm{Cl_2}$	58.0	1.65	83.1	1.66				
$[\mathrm{Co\ en_2\ NH_3\ Cl}{}_{\left\{ {(1) \atop (2)} \right\}}]\ \mathrm{Cl_2}$	58.0	1.76	83.0	1.76				
$[\mathrm{Co\ py_4\ NH_3\ Cl}]\ \mathrm{Cl_2}$	56.8	1.95	82.6	1.93				
$[\mathrm{Co(NH_3)_4\ (NO_2)_2}{}_{\left\{ {(1) \atop (6)} \right\}}]\ \mathrm{Cl}$	67.9	2.32	87.0	3.54	119.6	4.08	?	?
$[\mathrm{Co\ en_2\ (NO_2)_2}{}_{\left\{ {(1) \atop (6)} \right\}}]\ \mathrm{NO_3}$	69.9	2.20	88.6	3.44	120.4	4.37	?	?
$[\mathrm{Co(NH_3)_4(NO_2)_2}{}_{\left\{ {(1) \atop (2)} \right\}}]\ \mathrm{Cl}$	65.5	1.99	91.2	3.10			?	?
$[\mathrm{Co\ en_2\ (NO_2)_2}{}_{\left\{ {(1) \atop (2)} \right\}}]\ \mathrm{NO_3}$	69.0	2.10	92.8	3.68			?	?
$[\mathrm{Co(NH_3)_4Cl.NO_2}{}_{\left\{ {(1) \atop (6)} \right\}}]\ \mathrm{Cl}$	63.2	1.87	88.8	3.13	123.0	4.07	(80.4)	(2.42)
$[\mathrm{Co\ en_2\ Cl.NO_2}{}_{\left\{ {(1) \atop (6)} \right\}}]\ \mathrm{Cl}$	68.8	2.00	89.6	3.37	124.2	4.35	(79.6)	(2.22)
$[\mathrm{Co\ en_2\ Cl.NCS}{}_{\left\{ {(1) \atop (2)} \right\}}]\ \mathrm{Cl}$	59.6	2.18	(88.4)	(2.75)			?	?
$[\mathrm{Co\ en_2\ Cl.NCS}{}_{\left\{ {(1) \atop (6)} \right\}}]\ \mathrm{Br}$	54.0	2.10	(86.8)	(2.93)	110.4	3.43	92.5	3.36
$[\mathrm{Co\ en_2\ NO_2.NCS}{}_{\left\{ {(1) \atop (2)} \right\}}]\ \mathrm{Cl}$	64.8	2.34	?	?			?	?
$[\mathrm{Co\ en_2\ NO_2.NCS}{}_{\left\{ {(1) \atop (6)} \right\}}]\ \mathrm{NCS}$	65.3	2.30	?	?	?	?	?	?
$[\mathrm{Co\ (NH_3)_4CO_3}]\ \mathrm{Cl}$	57.4	2.03	82.8	2.02				
$[\mathrm{CO\ en_2\ CO_3}]\ \mathrm{Cl}$	58.6	2.08	83.6	2.04				
$[\mathrm{Co\ (NH_3)C_2O_4}]\ \mathrm{Cl}$	59.0	1.78	83.4	1.73				
$[\mathrm{Co\ en_2C_2O_4}]\ \mathrm{Br}$	60.0	1.96	84.2	2.10				
$\left[\mathrm{Co}\left\{ {\mathrm{OH} \atop \mathrm{OH}} \!>\! \mathrm{Co\ (NH_3)_4} \right\}_3\right] \mathrm{Cl_6}$	60.8	2.28	?	?			99.2	3.84
$\left[\mathrm{Co}\left({\mathrm{OH} \atop \mathrm{OH}} \!>\! \mathrm{Co\ en_2} \right)_3\right] \mathrm{(NO_3)_6}$	61.2	2.44	?	?			99.0	3.82
$\left[\mathrm{(NH_3)_4\ Co} \!<\! {\mathrm{OH} \atop \mathrm{OH}} \!>\! \mathrm{Co\ (NH_3)_4}\right] \mathrm{Cl_4}$	57.0	2.28	79.2	2.40			107.4	3.34
α-$[\mathrm{Co(glycine)_3}]$	56.8	1.98	81.0	2.16				



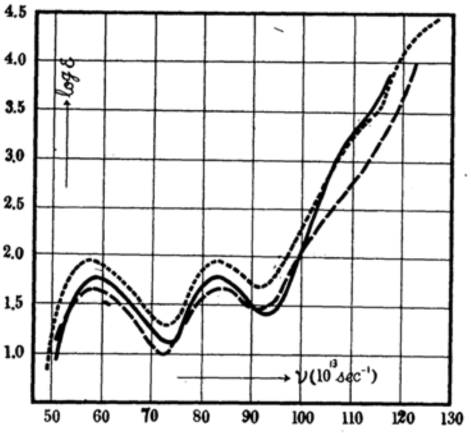
(1) ——— $[\mathrm{Co\,en_3}]\mathrm{Br_3}$
(2) – – – $[\mathrm{Co\,en_2(NH_3)_2}\{^{(1)}_{(6)}\}]\mathrm{Br_3}$
(3) -------- $[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3}$

Fig. 1.



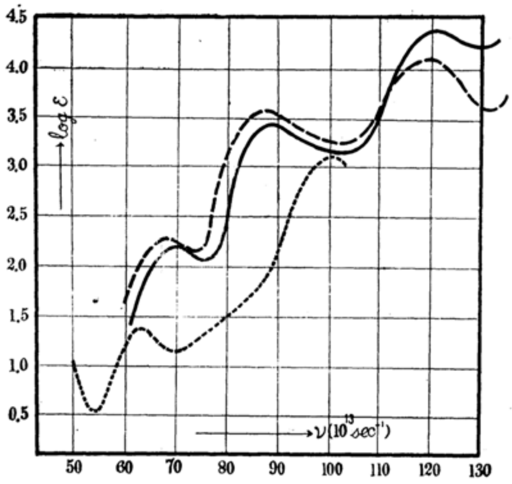
(1) ——— $[\mathrm{Cr\,en_3}]\mathrm{Cl_3}$
(2) – – – $[\mathrm{Cr(NH_3)_6}]\mathrm{Cl_3}$
(3) -------- $[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3}$

Fig. 2.



(1) ——— $[\mathrm{Co\,en_2NH_3Cl}\{^{(1)}_{(2)}\}]\mathrm{Cl_2}$
(2) – – – $[\mathrm{Co(NH_3)_5Cl}]\mathrm{Cl_2}$
(3) -------- $[\mathrm{Co\,py_4NH_3Cl}]\mathrm{Cl_2}$

Fig. 3.



(1) ——— $[\mathrm{Co\,en_2(NO_2)_2}\{^{(1)}_{(6)}\}]\mathrm{NO_3}$
(2) – – – $[\mathrm{Co(NH_3)_4(NO_2)_2}\{^{(1)}_{(6)}\}]\mathrm{Cl}$
(3) -------- $[\mathrm{Co\,en_2Cl_2}\{^{(1)}_{(6)}\}]\mathrm{Cl}$

Fig. 4.

There can be found distinct shifts of both the first, the second, and even the third absorption band in most cases towards the shorter wavelengths in ethylenediammine compounds compared with the corresponding ammine salts. In a few cases, these bands have frequencies equal to those of the corresponding ammine salts. It is also noteworthy that in nearly all the ethylenediamine salts, their extinction coefficients are larger than those of the ammine salts.

Now, when we compare the absorption spectra of $[\mathrm{Co\,en_3}]\mathrm{Br_3}$ and less stable $[\mathrm{Cr\,en_3}]\mathrm{Cl_3}$, it can be found that the first absorption band

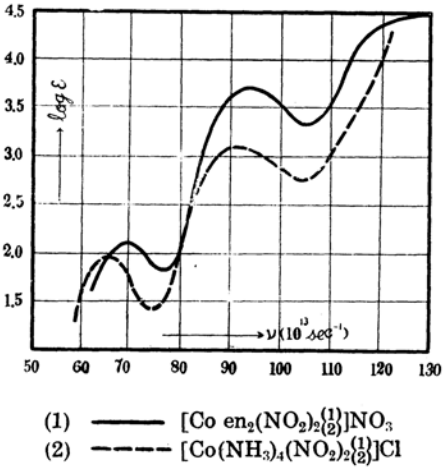


Fig. 5.

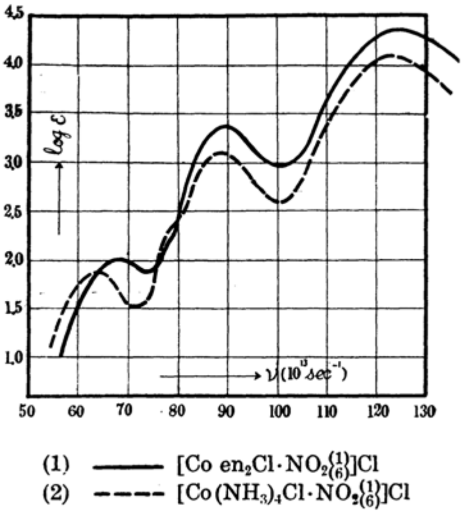


Fig. 6.

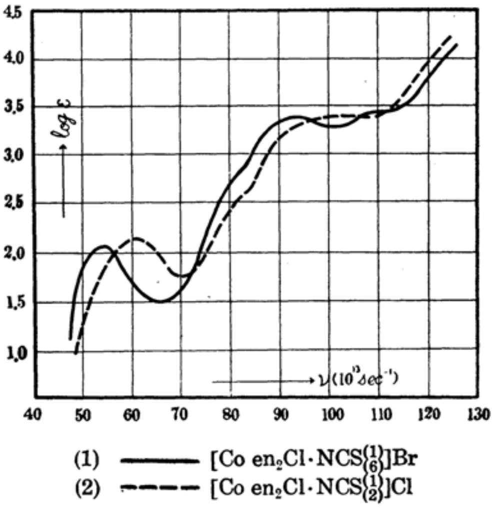


Fig. 7.

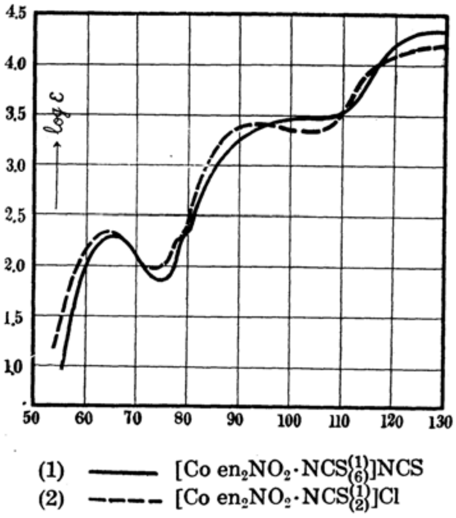
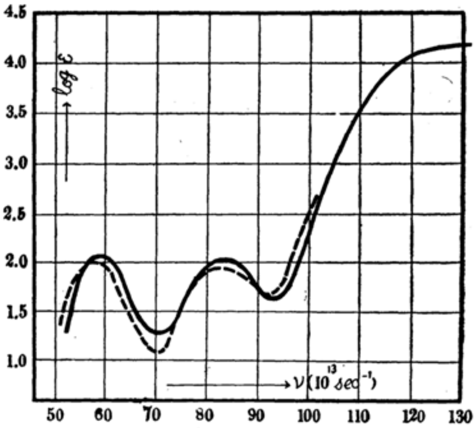


Fig. 8.

of the $\mathrm{Cr^{III}}$-salt has shorter wave-lengths, while the second band of the $\mathrm{Co^{III}}$-salt is, on the contrary to the first band, more hypsochromic than the $\mathrm{Cr^{III}}$-salt. Similar relation can be seen for $[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3}$ and $[\mathrm{Cr(NH_3)_6}]\mathrm{Cl_3}$. Such positions of the bands may be regarded as a proof of the validity of the author's hypothesis stated above, that the second absorption band is a scale for the stability of co-ordination compound, while the first absorption band is unqualified to be so. It is an important fact that the luteo-$\mathrm{Co^{III}}$-salts are, despite of their more intense colours, not inferior in the stability to the luteo-$\mathrm{Cr^{III}}$-salts, in agreement with the order of their second absorption bands.

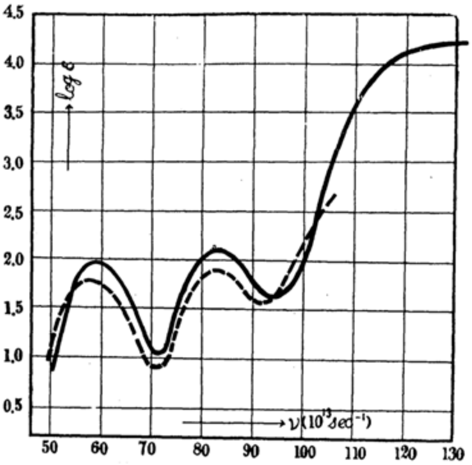
In the following, the individual cases will be described.



(1) ——— $[\mathrm{Co\ en_2CO_3}]\mathrm{Cl}$

(2) – – – $[\mathrm{Co(NH_3)_4CO_3}]\mathrm{Cl}$

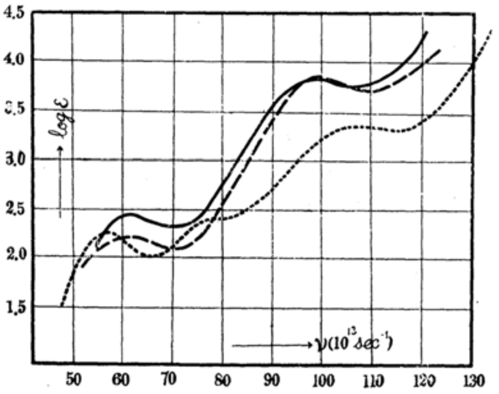
Fig. 9.



(1) ——— $[\mathrm{Co\ en_2C_2O_4}]\mathrm{Br}$

(2) – – – $[\mathrm{Co(NH_3)_4C_2O_4}]\mathrm{Cl}$

Fig. 10.

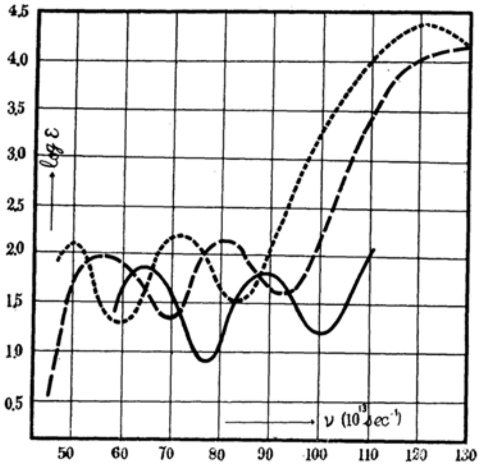


(1) ——— $\left[\mathrm{Co}\left(\begin{matrix}\mathrm{OH}\\\mathrm{OH}\end{matrix}>\mathrm{Co\ en_2}\right)_3\right](\mathrm{NO_3})_6$

(2) – – – $\left[\mathrm{Co}\left\{\begin{matrix}\mathrm{OH}\\\mathrm{OH}\end{matrix}>\mathrm{Co(NH_3)_4}\right\}_3\right]\mathrm{Cl_6}$

(3) --------- $[(\mathrm{NH_3})_4\mathrm{Co}<\begin{matrix}\mathrm{OH}\\\mathrm{OH}\end{matrix}>\mathrm{Co(NH_3)_4}]\mathrm{Cl_4}$

Fig. 11.



(1) ——— $[\mathrm{Co\ en_3}]\mathrm{Br_3}$

(2) – – – $[\mathrm{Co(glycine)_3}]$

(3) --------- $\mathrm{K_3[Co(C_2O_4)_3]}$

Fig. 12.

(i) Luteo-salts: Showing the absorption bands of the almost identical frequency, the stabilities of $[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3}$, $[\mathrm{Co\ en_2(NH_3)_2}\{\begin{smallmatrix}1\\6\end{smallmatrix}\}]\mathrm{Br_3}$ and $[\mathrm{Co\ en_3}]\mathrm{Br_3}$ are equal to each other. The case is also similar in the luteo-$\mathrm{Cr^{III}}$-salts.

(ii) Purpureo-salts: Three salts, $[\mathrm{Co(NH_3)_5Cl}]\mathrm{Cl_2}$, $[\mathrm{Co\ en_2NH_3Cl}\{\begin{smallmatrix}1\\2\end{smallmatrix}\}]\mathrm{Cl_2}$ and $[\mathrm{Co\ py_4NH_3Cl}]\mathrm{Cl_2}$, are of the almost identical colour, and in fact, the first and the second bands of them lie in practically the same positions respectively. With regard to the configuration of the tetrapyridine salt, there are two possible cases, namely cases of cis- and transconfigurations, concerning the positions of NH_3-molecule and Cl-ion. It is difficult, however, to decide whether this salt has cis- or trans-configuration, only from the absorption spectrum. In the present state, the cis-form is more probable, because this salt can be prepared by interaction of aqueous ammonia with $[\mathrm{Co\,py_4Cl_2}]\mathrm{Cl}$, which, according to A. Werner⁽⁹⁾, has its Cl-ions in trans-positions, and, therefore, by entirely the same procedure as in the preparation of $[\mathrm{Co\,en_2NH_3Cl}\genfrac{\{}{}{0pt}{}{(1)}{(2)}]\mathrm{Cl_2}$ from the praseo-salt $[\mathrm{Co\,en_2Cl_2}\genfrac{\{}{}{0pt}{}{(1)}{(6)}]\mathrm{Cl}$.

(iii) Croceo-salts: It will be found that the third absorption band of the ethylenediamine salt can be observed distinctly in the region of $\nu=120-130$, overlapping with the special band due to the co-ordinated ethylenediamine molecules, while the ammine croceo-salt is well known to be an example for the salt having the third absorption band. By comparing the absorption curves of both the salts, we can see that every member of the three bands is much more stabilized by the remarkable shift towards the shorter wave-lengths in the ethylenediamine compound, compared with the ammine salt.

It will be added, moreover, that the special absorption band due to the co-ordinated nitro-radicals⁽¹⁰⁾ could not be distinguished from the second band.

(iv) Flavo-salts: Comparing the absorption of $[\mathrm{Co(NH_3)_4(NO_2)_2}\genfrac{\{}{}{0pt}{}{(1)}{(2)}]\mathrm{Cl}$ and $[\mathrm{Co\,en_2(NO_2)_2}\genfrac{\{}{}{0pt}{}{(1)}{(2)}]\mathrm{NO_3}$, we can observe shifts of both the first and the second band to the side of shorter wave-lengths in the latter.

A hump of the absorption curve of the ethylenediamine salt in the region of $\nu=120-130$ is attributed to the selective absorption proper to the co-ordinated ethylenediamine molecules, and the third absorption band due to trans-negative radicals is naturally out of question here.

(v) 1,6-Chloro-nitro-salts: $[\mathrm{Co\,en_2Cl.NO_2}\genfrac{\{}{}{0pt}{}{(1)}{(6)}]\mathrm{Cl}$ has been proved to have the third band in the present work, while the third band of the corresponding ammine salt had been reported previously⁽¹¹⁾. The special absorption bands proper to the nitro-radicals are illustrated here; they can be seen approximately at $\nu=80$. Regarding the relative positions, the bands of the ethylenediamine salt seem more hypsochromic.

(vi) Chloro-rhodanato-salts: Of the two possible isomers, cis- and trans-form, the latter ought to have a third band, because of co-ordination of the negative ligands in trans-positions. A small band at $\nu=110.4$ may be assigned to it. On the other hand, one special band due to the co-ordinated rhodanato-radical is to be expected for each of them, and then inflection of their absorption curves in the middle between $\nu=80$ and 90 can be explained as the results of overlapping of the special bands upon the second bands.

It is regretable that there do not exist the ammine salts corresponding to either of the two isomers of $[\mathrm{Co\,en_2Cl.NCS}]\mathrm{X}$.

For the interesting problem, which of the two isomers is more stable, no answer can be given from the spectra alone, as their second bands are unable to be determined.

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(9) A. Werner, R. Feenstra, *Ber.*, **39** (1906), 1538.

(10) H. Kuroya, R. Tsuchida, *J. Chem. Soc. Japan*, **59** (1938), 1142.

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

(vii) Nitro-rhodanato-salts: In these, there will be expected several absorption bands, namely, the first, the second, and the special bands due to the co-ordinated nitro- und rhodanato-radicals in the case of cis-form, and moreover, in addition to them, the third absorption band in the case of trans-form. In reality, however, only the first bands can be distinguished in the both isomers, surely because of complex superposition of these bands.

(viii) Tetrammine-carbonato- and -oxalato-salts: It can be seen obviously from Figs. 8 and 9 that the ethylenediamine compound is more stable in every set of carbonato- and oxalato-salts, for the bands, especially the second, are more hypsochromic in the ethylenediamine compounds.

(ix) Hexol-salts: With regard to the first bands only, which are distinct in both the ammine and the ethylenediamine salt, the latter is more hypsochromic than the former. The second bands, however, could not be discriminated due to their complex configurations.

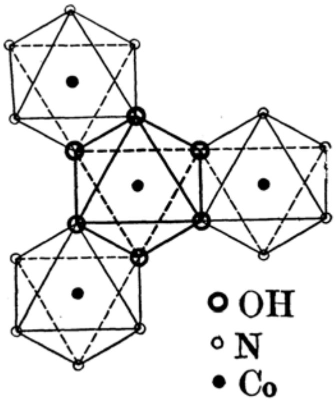

Fig. 13. Configuration of hexol-salt.

At the beginning of the present work, we expected the existence of a third absorption band in hexol-salts, because OH-radicals as many as six are co-ordinated around the innermost Co-atom, forming thus three pairs of trans-anions. The bands having their absorptive maxima nearly at ν=99, however, should not be considered as the expected third bands, for there is a similar band in the absorption curve of the diol-salt, which is not at all qualified to possess its third band. Such being the case, the absence of the third absorption band of hexol-salts seemed to be difficult to explain at first sight. The lack of the third band in hexol-salts, however, may be understood by comparing them with aquo-complex salts; the OH-radical in hexol salts are quite similar to the OH_2-molecule in aquo-salts, with regard to the co-ordinative behaviour of the O-atom which has three ligands, two hydrogen atoms and one metallic ion in the aquo-salts and one hydrogen atom and two metallic ions in hexol-salts.

In addition, a few words may be said of the questionable bands at $\nu\approx99$; the present authors would like to explain these as being due to co-ordination of the ligands around the central O-atoms, because Prof. Tsumaki(12) had shown previously the appearances of similar bands in some of organic complex salts.

(x) α-[Co(glycine)$_3$] (violet form): Two forms are theoretically possible for cobaltic triglycine: cis-cis- and cis-trans-form (Fig. 14). In fact, Ley and Winkler(13) had prepared these two isomers. A question, however, is left unsolved, which of the two isomers, violet α- or red β-form, is to be a cis-cis-, and the other a cis-trans-form. Attempting to solve this problem, the present authors have measured the absorption of the

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(12) R. Tsuchida, T. Tsumaki, this Bulletin, **13** (1938), 527.
(13) H. Ley, H. Winkler, *Ber.*, **42** (1909), 3900.

violet form only, the red form being unavailable for measurements because of its insolubility in water. Now, were the violet form a cis-trans-form, its absorption curve would show a third band on account of the carboxyl radicals distributed in trans-positions.

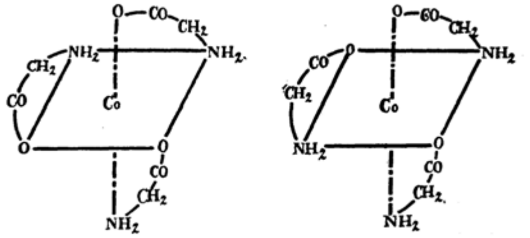
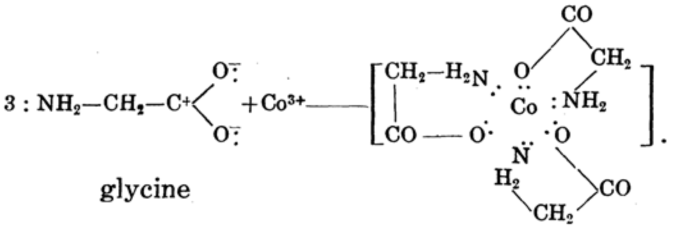


Fig. 14.

In the present work, however, no band was detected, which might be described as the third band. This may be considered as a favorable proof for the cis-cis-configuration.

It is well known that a molecule of α-amino acid can co-ordinate itself to an ion of heavy metals, e.g., Cu^{++}, Co^{3+}, etc., in order to form the so-called "inner complex", which is usually insoluble in water. Co-ordination must take place through the agency of its lone pairs of electrons, which belong to the NH_2-radical and the oxygen atoms of carboxyl radical; thus:



Accordingly, apart from the configuration referred to above, it may be reasonable to consider, that cobaltic triglycine is intermediate between $[Co\,en_3]^{3+}$ and $[Co(C_2O_4)_3]^{3-}$, concerning the modes of co-ordinative combinations.

Hereupon, it is desirable to compare the absorption spectra of those salts. In Table 2, the frequencies, at which they show the maximum ε-values respectively, are tabulated, and their absorption curves are arranged side by side in Fig. 12.

Table 2.

Complex Salt	First band ν_1 (10^{13})	Second band ν_2 (10^{13})	Third band ν_3 (10^{13})
$[Co\,en_3]Br_3$	64.6	88.2	—
$[Co(glycine)_3]$	56.8	81.0	—
$K_3[Co(C_2O_4)_3]$(14)	49.6	71.0	122.4

As can be seen from the table as well as the figure, the triglycine compound in question lies intermediate between the other two, offering

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

an obvious proof for the supposition that the chemical combination through a N-Co-bond might be stronger than that through a O-Co-bond.

Conclusion. By summarizing the results obtained above, it is confirmed decisively a hypothesis of the authors, that the second absorption band may be attributed to co-ordination electrons combining the central atom to the ligands, and, therefore, the stability of the co-ordination compound may be measured by its second absorption band, because the second band of ammine complex is, in general, more bathochromic than that of the corresponding ethylenediamine salt which is practically much more stable.

Then, it must come into question, why the ethylenediamine complexes are more stable in these ways. If a linkage of N-C-C-N of an ethylenediamine molecule is supposed to be on a plane, a simple calculation indicates the N-N-distance as equal to 2.5Å., assuming the atomic radius $R_N=0.7$ and $R_C=0.77$Å.$^{(15)}$, while, on an assumption of $R_{Co}=1.22$Å.$^{(15)}$ and the angle N-Co-N=90°, N-N must have the value 2.7Å. An ethylenediamine molecule, therefore, can be easily co-ordinated to a central cobalt atom, if a little distortion would be permitted around its bonds. According to P. Trunel's measurement$^{(16)}$ of dipole moment, there are completely free rotations around the C-C- and C-N-bond in an ethylenediamine molecule. Under this circumstance, the co-ordinating procedure will be very smooth and steady$^{(17)}$.

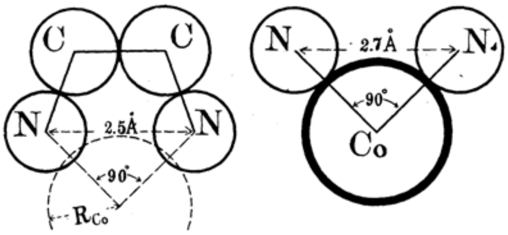

Fig. 15.

In addition to this condition, the both ends of ethylenediamine molecule are bonded to the central atom, making thus the combination in the co-ordination sphere much more poor in chances of its being broken out than in ammine complex, in which every member of the co-ordinated NH_3-molecules is singly bonded to the central atom.

Experimental. (1) Diethylenediamine cobaltic complexes: Prepared by the methods of A. Werner$^{(18)}$ by the processes shown in Table 3.

(2) $[\mathrm{Co\,en_3}]\mathrm{Br_3.3H_2O}$ (Luteo-cobaltic-salt): This salt can be synthesized by use of $[\mathrm{Co(NH_3)_5Cl}]\mathrm{Cl_2}$ and ethylenediamine with facility, but also will be obtained in a comparatively good yield as a by-product, when the praseo-salt $[\mathrm{Co\,en_2Cl_2}\left\{\begin{smallmatrix}1\\6\end{smallmatrix}\right\}]\mathrm{Cl}$, which is a starting substance of the diethylenediamine series, is prepared. The authors' method of separation from a mixture of the luteo- and the praseo-salt is given in Table 4.

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(15) L. Pauling, "The Nature of the Chemical Bond", 2nd Ed., 164 and 182, New York (1940).

(16) P. Trunel, *Compt. rend.*, **203** (1936), 563.

(17) Cf. J. P. Mathieu, *Bull. soc. chim.*, **5** (1938), 749.

(18) A. Werner, *Ann.*, **386** (1912), 1.

Table 3.

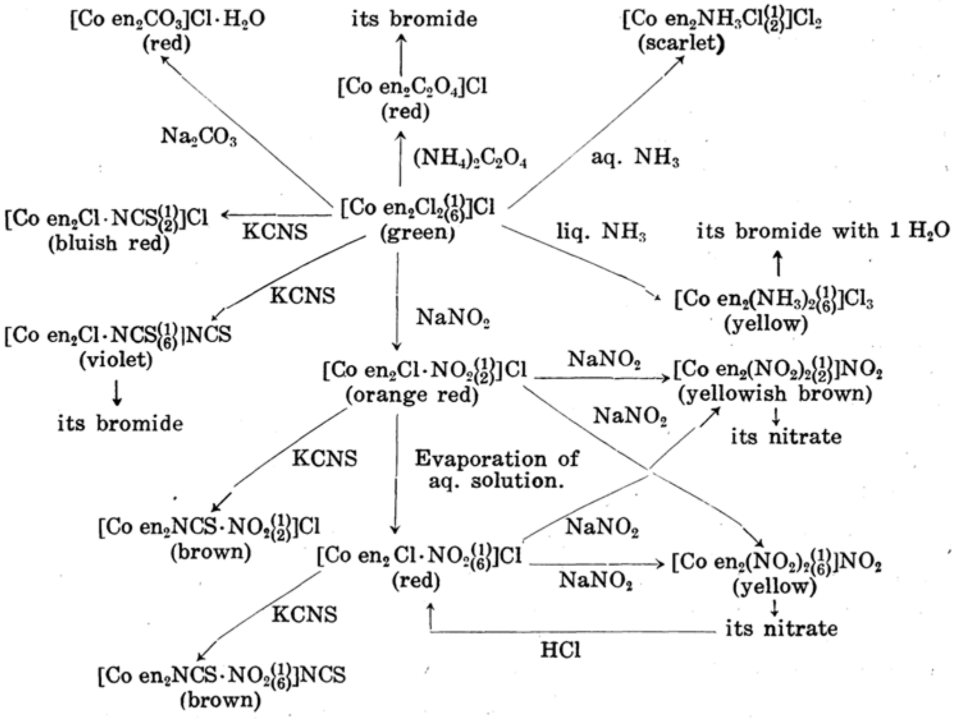
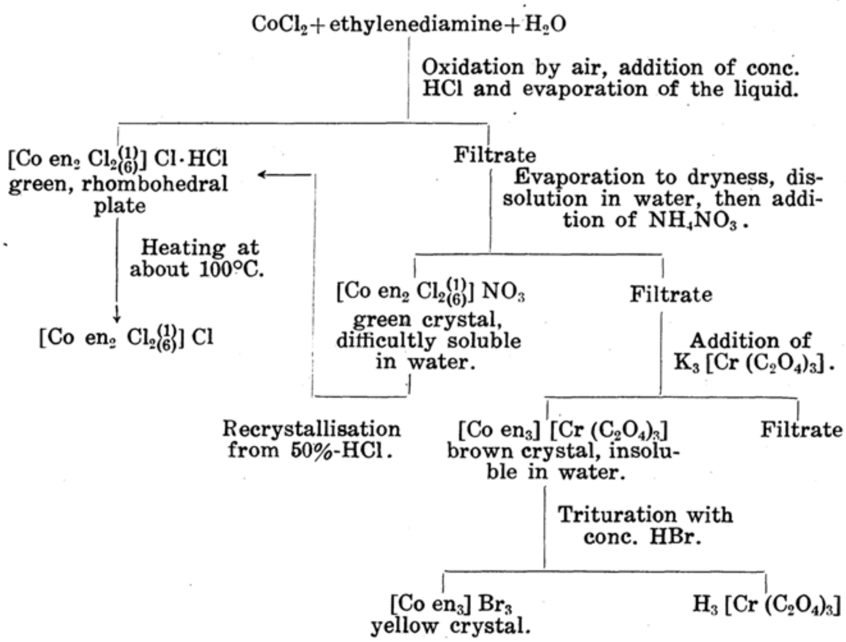
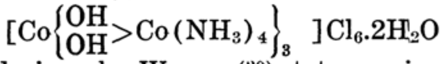


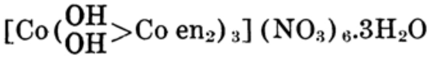
Table 4.

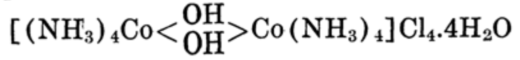


(3) $[\mathrm{Cr\ en_3}]\mathrm{Cl_3.3.5H_2O}$ (Luteo-chromic-salt): Pfeiffer⁽¹⁹⁾ had prepared this salt, using ethylenediamine hydrate and partially dehydrated, grey-coloured chrome alum. The authors followed his method. Both the luteo-Cr-salt and the luteo-Co-salt are yellow, the former being lighter in hue.

(4) $[\mathrm{Co\ py_4NH_3Cl}]\mathrm{Cl_2}$: This can be obtained, being derived from $[\mathrm{Co\ py_4Cl_2}]\mathrm{Cl}$, which was originally synthesized by A. Werner⁽⁹⁾ by oxidising a cold solution of cobaltous chloride in pyridine with chlorine; the tetrapyridine salt, the colour of which is bluish green, is tritulated with small quantity of aqueous ammonia, then the chloro-ammine salt may be formed immediately, causing a colour change from green to violet-red.

(5)  $[\mathrm{Co}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}>\mathrm{Co(NH_3)_4}\right\}_3]\mathrm{Cl_6.2H_2O}$ (Hexol-salt): According to the method given by Werner⁽²⁰⁾, tetrammine chloro-aquo-cobaltic sulphate, $[\mathrm{Co(NH_3)_4Cl.H_2O}]\mathrm{SO_4}$, was dissolved in a closed vessel containing 10% aqueous ammonia solution, and, after several hours, there was found the aimed, difficulty soluble hexol-sulphate, forming flat, scale-like and almost black crystals. This sulphate was then converted into its chloride by use of barium chloride.

(6)  $[\mathrm{Co}(\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}>\mathrm{Co\ en_2})_3](\mathrm{NO_3})_6.3\mathrm{H_2O}$ (Ethylenediamine hexol-salt): Prepared by the method of Werner⁽²¹⁾, who obtained this hexol-salt by oxidation of a solution containing cobaltous nitrate and ethylenediamine in an airy place. This salt is considerably richer in brownish colour than the corresponding ammine-hexol.

(7)  $[\mathrm{(NH_3)_4Co}<\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}>\mathrm{Co(NH_3)_4}]\mathrm{Cl_4.4H_2O}$ (Diol-salt: The sulphate was prepared by the method of Werner⁽²²⁾, a dehydration of tetrammine hydroxo-aquo-cobaltic sulphate, $[\mathrm{Co(NH_3)_4H_2O.OH}]\mathrm{SO_4}$, at temperatures between 100 and 110°, and this diol-sulphate was converted into its chloride by use of barium chloride.

(8) α-$[\mathrm{Co(glycine)_3}].2\mathrm{H_2O}$ (violet form): Cobaltic hydroxide, $\mathrm{Co(OH)_3}$, and pure glycine were together boiled in aqueous solution for several hours, according to the method of Ley and Winkler⁽¹³⁾. One modification thus formed, the red β-form, being insoluble in water, the liquid was filtered off and from this could be crystallised the violet α-salt.

Summary.

1. Absorption spectra of a number of ethylenediamine cobaltic complex salts have been observed. Generally speaking, their absorption bands, especially the second, are more hypsochromic than those of the corresponding ammine salts.

2. The results have proved that the author's hypothesis on the absorption spectra holds good for the ethylenediamine complex salts.

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(19) P. Pfeiffer, *Ber.*, **37** (1904), 4277.

(20) A. Werner *Ber.*, **47** (1914), 3087; S. M. Jörgensen, *Z. anorg. Chem.*, **16** (1898), 186.

(21) A. Werner, *Ber.*, **40** (1907), 2119.

(22) A. Werner, *ibid.*, **40** (1907), 4437.

3. Examples of the third absorption bands have been found in the diethylenediamine cobaltic complexes of known configurations.

4. A new method of separating $[\mathrm{Co\,en_3}]^{3+}$ and $[\mathrm{Co\,en_2Cl_2}{}_{\substack{(1)\\(6)}}]^{+}$ has been devised.

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