

On the Stereochemical Configurations of Cobalt Complexes with Anomalous Coordination Numbers.

By

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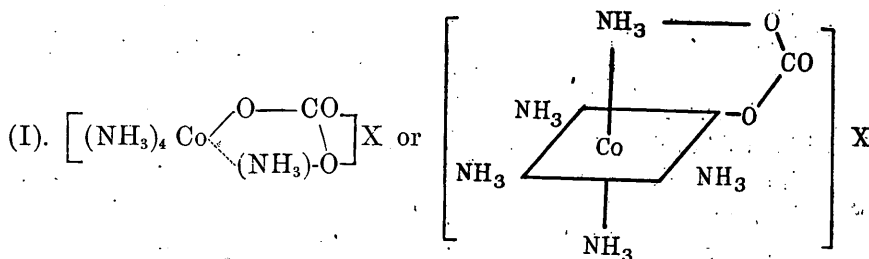
With 6 Figures.

Introduction.

The configurations of cobalt complex salts having the coordination numbers greater than six are the chief subjects discussed in this paper. They are as follows :

- I. $[\text{Co}(\text{NH}_3)_6\text{C}_2\text{O}_4]\text{X}$. II. $[\text{Co}(\text{NH}_3)_6\text{CO}_3]\text{X}$
III. $[\text{Co}(\text{NH}_3)_6\text{SO}_4]\text{X}$ IV. $[\text{Co}(\text{NH}_3)_6\text{SO}_3]\text{X}$.

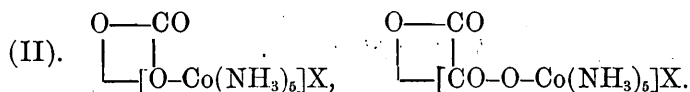
These salts have five molecules of ammonia and a dibasic acid radicle in their complex nuclei. As to the constitutions of these salts, Werner (Ber., 36, 2380, 1903; Neuere Anschauungen auf dem Gebiete der anorganischen Chemie, 4. Aufl., S. 57) gave the following formula for carbonato-pentammine cobaltic salt :



If such a configuration were given to this salt, since the carbonic acid radicle is supposed to combine with the central cobalt atom directly with one limb and indirectly with the other, either the central cobalt atom would be divalent and the nitrogen of ammonia which attaches to the carbonic acid radicle tetravalent, or such a radicle as $\begin{array}{l} \text{---NH}_3\text{---O} \\ \text{---O} \end{array} \text{CO}$, i. e., a radicle with two hydrogen atoms less than acid ammonium carbonate,

would take two coordination positions. However, the fact that this salt has, in its formation and properties, a close relation with the purpureo and roseo salts, confirms the theory that the central cobalt atom is trivalent. Also the five ammonia molecules of these salts behave themselves quite similarly. Consequently it is clear that this configuration (I) is not probable.

The most reasonable formula ever given for these salts is as follows :



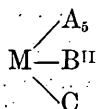
In this configuration (II), only one limb of the dibasic acid radicle is coordinated to the central cobalt atom, whereas the other seems to be attached to the complex radicle in the form of a "bound" ion (Urbain: *Introduction a la chimie des complexes*, p. 283; Duff: *Jour. Chem. Soc.*, 123, 560, 1923). This idea may be dismissed from our consideration in view of the spatial arrangement of the compounds of higher order and the extension of Werner's theory of coordination numbers.

According to Werner's theory, the maximum coordination number of complexes, in the vast majority of elements, is six, while only a few, viz., those of the second group in the periodic system, have the lower value of four. This number is, within extended limits, independent of the atomic volume. Further, the maximum number of coordination positions must be considered as having reference to the space around the surface of the atom, or in other words, the number of atoms or atom groups arranging in the first sphere of attraction of the central atom. The mode of spatial arrangement leads to many inferences, which can be confirmed by experimental facts. As is well known, the maximum number of coordination positions of carbon and nitrogen is four; and four atoms or atom groups which are connected with these elements can arrange themselves symmetrically around the central atoms. The isomeric phenomena of these compounds have been satisfactorily explained, by considering that these groups would occupy the four summits of a tetrahedron having these elements at its centre. The six corners of a regular octahedron represent the symmetrical spatial positions, which could be occupied by six atoms or atom groups coordinated around the central atom whose maximum coordination number is six, and many brilliant experiments which have been carried out by Werner and his co-workers have successfully proved this important hypothesis in the case of the following elements, viz., cobalt, chromium, nickel and members of the platinum group.

Let us carry this idea a little further. Suppose eight atoms or atom groups happen to combine directly with the central atom, then they would take up the positions of the eight corners of a cube, for they could arrange themselves symmetrically as in the case of the tetrahedral and octahedral positions which should be occupied by the atoms or atom groups when the maximum numbers of coordination of the central atom are respectively four and six. In reference to this point, since the number of auxiliary valencies of an atom is variable, as in the case of copper, silver, zinc and cobalt amines, and the saturation of the coordination number is dependent on the atoms or atom groups around the central atom, it can be expected that the maximum of the coordination numbers of metallic elements may be greater than six. Considering that the spatial arrangement of atoms or atom groups in a complex radicle which is coordinatively saturated should be symmetrical, the following five cases of the saturated coordination number may be figured out, namely, four, six, eight, twelve and twenty, each of these numbers corresponding respectively to the corners of the following regular polyhedrons: tetrahedron, octahedron, cube, pentagonal dodecahedron and icosahedron.*

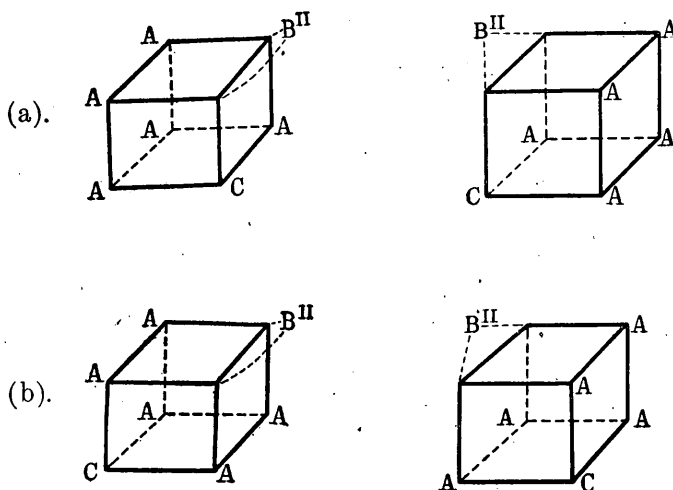
Although symmetrical spatial arrangement may not be the only cause of the formation of coordinatively saturated complexes, this idea leads to an important deduction which is experimentally of interest.

As in the case of tetrahedral and octahedral configurations, the cubic structure of a complex radicle, the eight corners of which are occupied by eight atoms or atom groups, admits of two pairs of isomers each in optical antipodes, when the coordinated groups are in the relation where M



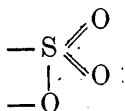
represents the central atom, A and C each take one position while B^I takes two positions of coordination, thus :

* In such complexes as: $[\text{Mg}(\text{H}_2\text{O})_{12}]\text{PtCl}_6$, $[\text{Mg}(\text{H}_2\text{O})_{12}]\text{PtBr}_6$, $[\text{Zn}(\text{H}_2\text{O})_{12}]\text{PtBr}_6$, $[\text{Zn}(\text{H}_2\text{O})_{12}](\text{AuCl}_4)_2$, $[\text{Mn}(\text{H}_2\text{O})_{12}]\text{PtBr}_6$, $[\text{Mn}(\text{H}_2\text{O})_{12}](\text{AuCl}_4)_2$, $[\text{Ca}(\text{H}_2\text{O})_{12}]\text{PtBr}_6$, $[\text{Ca}(\text{H}_2\text{O})_{12}]\text{PtI}_6$, $[\text{Mg}(\text{H}_2\text{O})_{12}](\text{AuCl}_4)_2$, $[\text{Co}(\text{H}_2\text{O})_{12}](\text{AuCl}_4)_2$, (Werner: *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*, 2. Aufl., S. 134.), their central atoms may be regarded as having twelve as the maximum number of coordination. Werner, however, gave them the octahedral configuration, supposing that two molecules of water occupy one summit of the octahedron.



Complexes of the type $[\text{Co}(\text{NH}_3)_5\text{X}^{\text{II}}\text{X}^{\text{I}}]$, where X^{II} represents a dibasic acid radicle and X^{I} denotes a monovalent radicle, should therefore exist in two isomeric forms both of which have optical isomers. This structure could be applied to the complexes $[\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4]\text{X}$, $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{X}$, $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{X}$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_3]\text{X}$, if we regard the monovalent ions outside the complex radicle coordinate with the central atom. Following this idea, the resolutions of $[\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{SO}_4\text{H}]$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4\text{SO}_4\text{H}]\cdot 2\text{H}_2\text{O}$ have been tried with the result that two optical isomers of both complexes have been obtained.

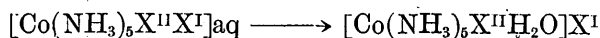
As to pentammine-carbonato- and pentammine-sulphito-cobaltic salts, $[\text{Co}(\text{NH}_3)_5\text{CO}_3\text{X}]$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_3\text{X}]$, similar constitutions could be considered. The resolutions of these salts have not been tried. By means of spectral studies, however, it has been shown that pentammine-oxalato- and pentammine-carbonato-cobaltic salts have the same configuration. The absorption curve of pentammine-sulphato-cobaltic salt was found to be different from that of pentammine-sulphito-cobaltic salt, which necessarily demands different constitutions in the two salts. But it is very probable that this disagreement of their absorption curves is due to the coordinated acid group SO_3 , which combines asymmetrically, i. e., as



with the cobalt, and accordingly is not due to an entirely different spatial arrangement. (Werner u. Gröger : Z. anorg. Chem., 16, 399, 1898).

The electrolytic conductivities of these salts in their aqueous solutions have also been measured in order to determine whether negative radicles, such as Cl, NO₃, I, SO₄, etc., which are generally considered to combine with complex positive ions, coordinate with the central atom in the complex radicle.

In considering the results obtained, it has been established that the following substitutional reaction takes place when the salt dissolves in water, thus:



Jörgensen (Journ. prakt. Chemie, 31, 262, 1885) pointed out that water could not be driven off from $[\text{Co}(\text{NH}_3)_5\text{SO}_4]_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$, when it was heated to about 100° C. This is evidently one of the verifications of the existence of eight as maximum number of coordination, for if we give the formula $[\text{Co}(\text{NH}_3)_5\text{SO}_4\text{H}_2\text{O}]_2\text{PtCl}_6$ to the complex salt, this fact can easily be explained.

Experimental.

(a) Materials.

The following salts were prepared by the methods given by Werner, Jörgensen, and Grüger. The materials were carefully purified and their compositions ascertained by analysis.

- I. $[\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4]\text{Cl} \cdot \text{HCl}$, $[\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4]\text{SO}_4 \cdot \text{H}_2\text{O}$,
 $[\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4]_2\text{C}_2\text{O}_4 \cdot 4\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, $[\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4]_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$. (S. M. Jörgensen: Z. anorg. Chem., 11, 417, 1896).
- II. $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{NO}_3 \cdot \text{H}_2\text{O}$, $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{Br} \cdot \text{H}_2\text{O}$,
 $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{I} \cdot \text{H}_2\text{O}$ (A. Werner: Ber., 36, 2380, 1903).
- III. $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{SO}_4 \cdot \text{H}_2\text{O}$, $[\text{Co}(\text{NH}_3)_5\text{SO}_4]_2\text{SO}_4 \cdot \text{H}_2\text{O}$,
 $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$ (S. M. Jörgensen: J. prakt. Chem., 31, 262, 1885).
- IV. $[\text{Co}(\text{NH}_3)_5\text{SO}_3]\text{NO}_3$, $[\text{Co}(\text{NH}_3)_5\text{SO}_3]\text{Cl}$, $[\text{Co}(\text{NH}_3)_5\text{SO}_3]_2\text{SO}_3 \cdot 2\text{H}_2\text{O}$
(Werner u. H. Grüger: Z. anorg. Chemie, 16, 398, 1898).

(b) Molecular Conductivities.

As it is well known that the number of ions of cobaltamines is proportional to the conductivity of the salts (Werner: Neuere Anschau. auf d. Gebiete d. anorg. Chem., 4. Aufl., S. 235; the Author: This Journal, Vol. XLI, Art. 10), the determination of the molecular conductivities of these salts was carried out in order to verify the formulae suggested for them. All measurements were made at 25°C. The apparatus used was that

devised by Ostwald. The results will be seen in the following tables, where μ represents the molecular conductivity and ϕ the dilution.

TABLE I.

ϕ	[Co(NH ₃) ₅ C ₂ O ₄ -SO ₄ -C ₂ O ₄ (NH ₃) ₅ Co]3aq.		[Co(NH ₃) ₄ CO ₃] ₂ SO ₄
	t (min.)	μ	μ
100	0	76.67	78.83
"	5	77.29	
"	10	77.59	
"	20	78.20	
"	30	78.20	
"	40	78.36	
"	50	78.52	
"	60	78.83	
200		86.78	87.18
400		91.22	92.94
800		107.9	99.13
1600		111.5	106.2

TABLE II. a.

ϕ	[Co(NH ₃) ₅ CO ₃ NO ₃]		[Co(NH ₃) ₅ CO ₃ I]aq.		[Co(NH ₃) ₅ CO ₃ Br]aq.	
	t (min.)	μ	t (min.)	μ	t (min.)	μ
100	0	113.6	0	126.1	0	121.0
"	10	137.9	2	134.1	5	139.1
"	20	146.6	7	146.0	10	146.6
"	30	150.8	10	150.2	20	154.4
"	40	155.1	15	155.1	30	158.9
"	50	156.3	20	159.2	40	160.8
"	60	156.3	30	163.7	50	161.7
"	90	158.2	40	166.3	60	163.4
"	160	166.0	50	169.0	70	164.7
"			60	170.7	80	165.7

TABLE II. b.

ϕ	[Co(NH ₃) ₅ CO ₃ NO ₃]	[Co(NH ₃) ₅ CO ₃ I]	[Co(NH ₃) ₅ CO ₃ Br]	[Co(NH ₃) ₄ C ₂ O ₄]Cl
	μ	μ	μ	μ
100	113.6	126.1	121.0	105.4
200	161.4	169.5	167.8	111.9
400	175.0	179.9	179.4	118.4
800	192.8	194.2	200.6	126.3
1600	221.3	226.8	225.9	136.5

TABLE III.

ϕ	[Co(NH ₃) ₆ SO ₄ NO ₃]		[Co(NH ₃) ₅ SO ₄ -SO ₄ -SO ₄ (NH ₃) ₅ Co]	[Co(NH ₃) ₄ CO ₃] ₂ SO ₄
	t (min.)	μ	μ	μ
100	0	118.4	77.91	78.83
"	5	124.3	80.42	
"	10	125.8	82.04	
"	20	127.7	84.35	
"	30	128.8	86.76	
"	40	129.9	88.92	
"	50	130.9	90.69	
"	60	132.4	91.96	
"	70	134.6		
"	80	137.9		
200		140.1	94.28	87.13
400		148.3	102.8	92.94
800		156.1	111.5	99.13
1600		156.2	125.3	106.2

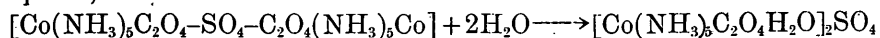
TABLE IV.

ϕ	[Co(NH ₃) ₅ SO ₃ Cl]		[Co(NH ₃) ₅ SO ₃ NO ₃]	[Co en ₂ SO ₃]Cl
	μ (1)	μ (2)	μ	μ
100	90.59	89.52	92.06	96.23
200	96.98	97.38	105.9	102.9
400	109.3	112.0	121.3	108.4
800	102.1	110.6	133.8	112.0
1600	132.7	139.4	150.2	122.4

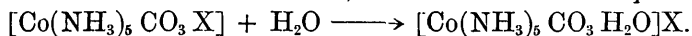
TABLE V.

ϕ	[Co(NH ₃) ₅ SO ₃ -SO ₃ -SO ₃ (NH ₃) ₅ Co]	[Co(NH ₃) ₄ CO ₃] ₂ SO ₄	[CoH ₂ O(NH ₃) ₅] ₂ (SO ₄) ₃
	μ	μ	μ
100	100.6	78.83	117.3
200	116.7	87.13	151.8
400	124.8	92.94	182.2
800	140.6	99.13	217.9
1600	160.0	106.2	265.1

The molecular conductivity of pentammine-oxalato-cobaltic sulphate (Table I) is practically equal to that of tetrammine-carbonato-cobaltic sulphate, which is evidence of the substitutional reaction :

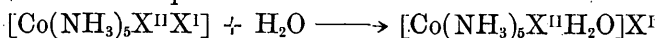


It is also noticeable that pentammine-oxalato-cobaltic sulphate is rather stable and has less variation of conductivity with both time and dilution than pentammine-carbonato-cobaltic salts. The conductivities of the latter are compared with that of tetrammine-oxalato-cobaltic chloride (Table II). The molecular conductivities of pentammine-carbonato-cobaltic nitrate, iodide and bromide at a dilution of 1600 are respectively 221.3, 226.8 and 225.9, which are all greater than 136.5, the molecular conductivity of tetrammine-oxalato-cobaltic chloride. The above numbers do not correspond to the molecular conductivity of three ions but rather indicate that of two ions. Therefore, the substitution takes place thus:



The conductivities of pentammine-sulphato- and sulphito-cobaltic salts are shown in Tables III, IV and V. Pentammine-sulphato-cobaltic nitrate shows the existence of two ions and pentammine-sulphato-cobaltic sulphate indicates three ions, when they are dissolved in water. The conductivities of pentammine-sulphito-cobaltic chloride and nitrate are in the same order as that of $[\text{Co en}_2 \text{SO}_3]\text{Cl}$. The conductivity of pentammine-sulphito-cobaltic sulphite lies between those of tetrammine-carbonato-cobaltic sulphate and roseo-cobaltic sulphate.

Consequently, it has been confirmed that cobalt complexes, which can be written according to the type $[\text{Co}(\text{NH}_3)_5 \text{X}^{\text{II}} \text{X}^{\text{I}}]$ undergo the following substitution in their aqueous solutions.



This view is also supported by the results of the measurement of the absorption-spectra of these salts.

(c) Resolution of $[\text{Co}(\text{NH}_3)_5 \text{C}_2\text{O}_4 \text{SO}_4\text{H}]\text{H}_2\text{O}$.

As already mentioned in the introduction, the resolution of this salt into optically active isomers had been expected from the consideration of the spatial arrangement of this kind of complex salts. The result is of vital importance as supporting the hypothesis. Accordingly, the resolution of this salt has been carried out, with the result that both the optical isomers have been obtained.

To a saturated cold solution of $[\text{Co}(\text{NH}_3)_5 \text{C}_2\text{O}_4 \text{SO}_4\text{H}]$, an excess of barium tartrate was added in portions under constant agitation until the solution became neutral, which was tested with a piece of congo-red test-paper. Barium sulphate and the excess of barium tartrate were then filtered off and the filtrate was put in a vacuum over sulphuric acid. Crystals with the light red colour began to separate out first, and on

further evaporation another portion of crystals with the same colour and of a greater solubility than the former were obtained from the mother liquor. The first and the last fractions were analysed.

From 0.1644 gr. of the first salt, 0.0704 gr. of cobalt sulphate was obtained.

Co=16.29% found,

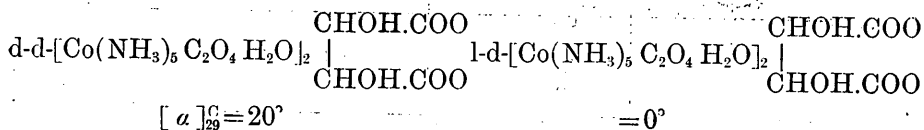
Co=16.63% required as $[\text{Co}(\text{NH}_3)_5 \text{C}_2\text{O}_4 \text{H}_2\text{O}]_2 \text{C}_4\text{H}_4\text{O}_6$.

0.1500 gr. of the second salt was analysed and 0.0650 gr. of CoSO_4 was obtained.

Co=16.48% found,

Co=16.63% required.

No loss of weight was observed, when these salts were heated at 100-110°C. for 2 hours. The specific rotations were measured.

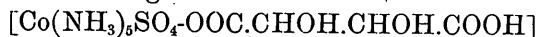


It was thus found that the fractions were the d-tartaric salt of d- and l-pentammine-oxalato-cobaltic complexes. The tartaric acid radicle of the above salts was eliminated by adding barium chloride in excess to the aqueous solutions of these salts. After filtration of the produced barium tartrate, alcohol was added to the filtrate to precipitate the rest of the barium tartrate and it was again filtered; d- and l-pentammine-oxalato-cobaltic chloride were then produced and purified by recrystallisation from the corresponding tartaric salts. Their analytical and optical data were as follows:

	d- $[\text{Co}(\text{NH}_3)_5 \text{C}_2\text{O}_4 \text{Cl}]$		l- $[\text{Co}(\text{NH}_3)_5 \text{C}_2\text{O}_4 \text{Cl}]$	
	Observed	Theoretical	Observed	
Co	22.01%	22.04%	21.91%	
Cl	13.02%	13.25%	—	
$[\alpha]_{25}^{\text{c}}$	+16°		-16°	

(d) Resolution of $[\text{Co}(\text{NH}_3)_5 \text{SO}_4 \text{SO}_4 \text{H}]2\text{H}_2\text{O}$.

The method of procedure was quite the same as in the previous case. As the pure tartaric salts of d- and l-complexes had shown acidic reactions, the following formula was given to them:



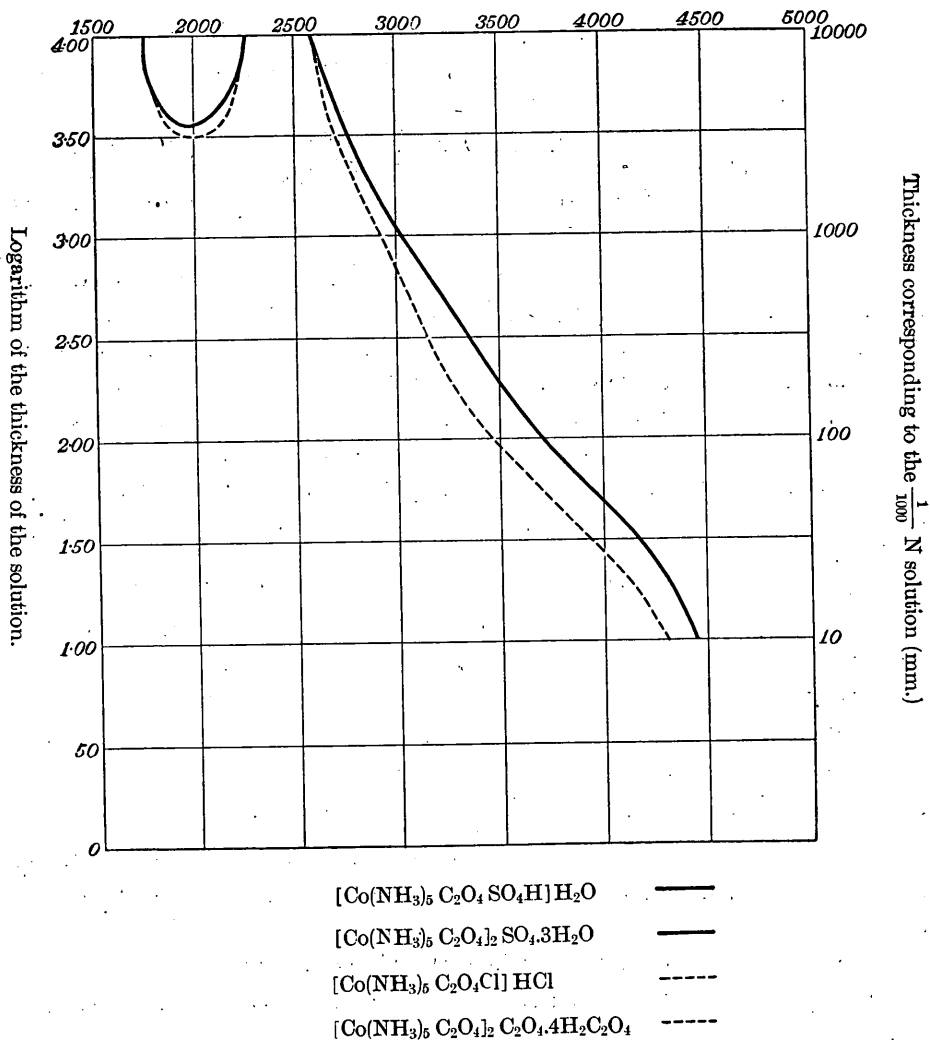
The percentage of cobalt and the specific rotations were estimated to be:—

	Theoretical	d-d- Observed	d-l- Observed
Co	15.12%	15.22%	—
$[\alpha]_D^{25}$		15°	0°

The d- and l- $[\text{Co}(\text{NH}_3)_5\text{SO}_4\text{Cl}]$ were obtained. The results of analysis and their specific rotations were :

Fig. I.

Frequency.

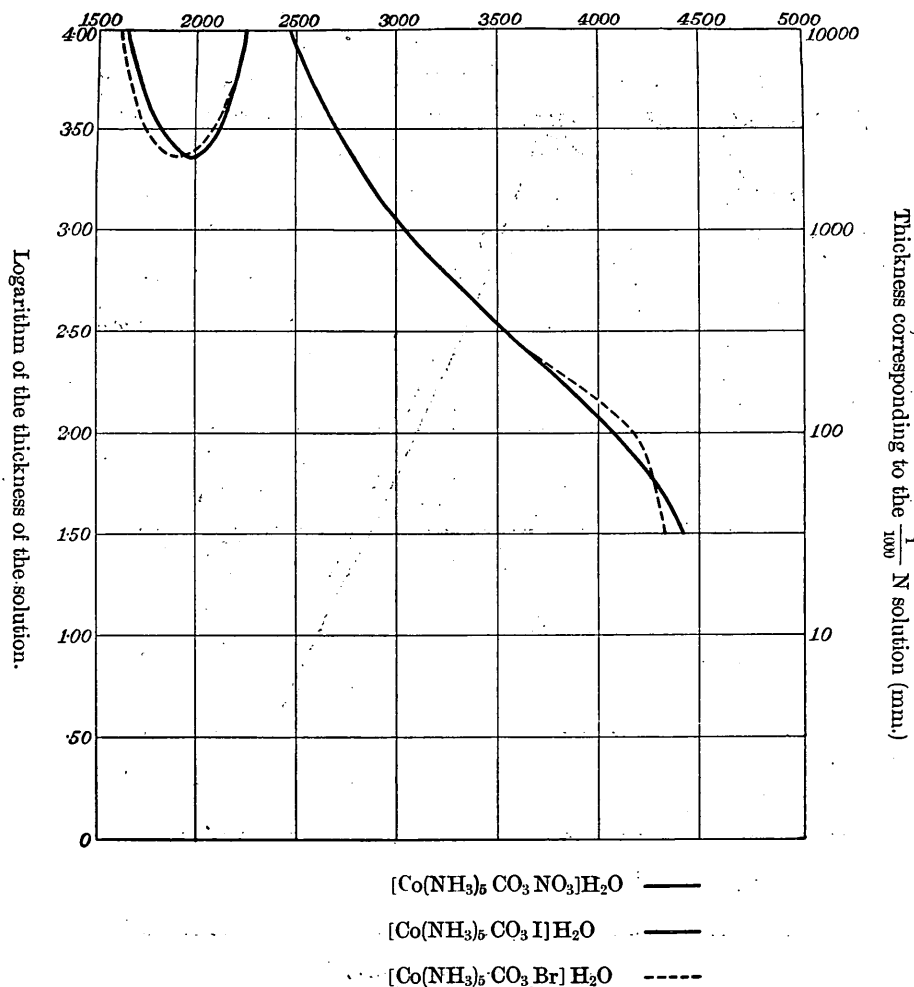


	d-[Co(NH ₃) ₅ SO ₄ Cl]	l-[Co(NH ₃) ₅ SO ₄ Cl]
Co	Theoretical 21.39%	Observed 21.40%
[α] _D ²⁵	+25°	-7.5°

On account of the scantiness of the material, the rotatory power of l-pentammine-sulphato-cobaltic chloride could not be obtained in sufficient strength.

The resolutions of sulphito- and carbonato-pentammine cobaltic salts have not been tried, as they are far less stable in aqueous solutions than oxalato- and sulphato-complex salts.

Fig. II.
Frequency.



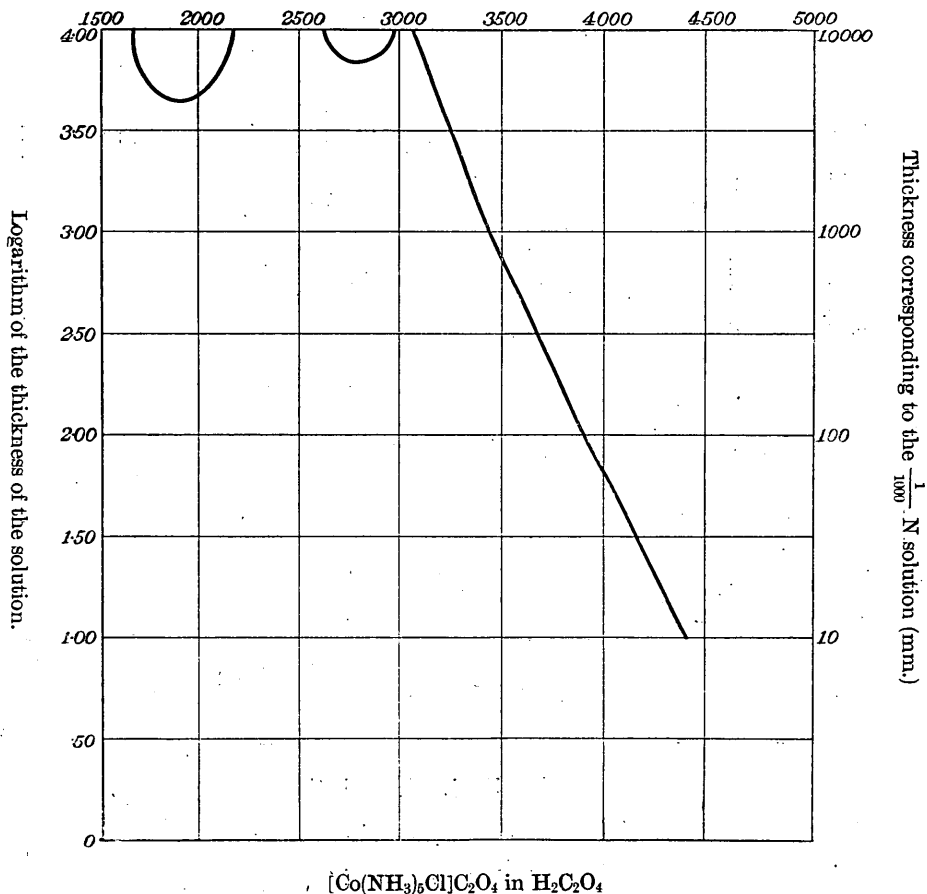
(e) Spectrographical Studies.

The absorption spectra of these salts were also studied in order to discuss the configurations from the stand-point of the absorption curves. As to the results, it has been found that the curves obtained from $[\text{Co}(\text{NH}_3)_6\text{C}_2\text{O}_4\text{X}]$ (Fig. I) and $[\text{Co}(\text{NH}_3)_5\text{CO}_3\text{X}]$ (Fig. II) are remarkably similar, showing that their constitutions are also similar. This is analogous to the phenomena in the case of $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]\text{X}$ and $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{X}$ (Y. Shibata: This Journal, Vol. XXXVII, Art. 8, 1916). If formulae (I) and (II) were true, the curves of these salts should be identical with that of roseo cobaltic salt, which was not the case.

The two isomers $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{C}_2\text{O}_4$ and $[\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4]\text{Cl}$ were ex-

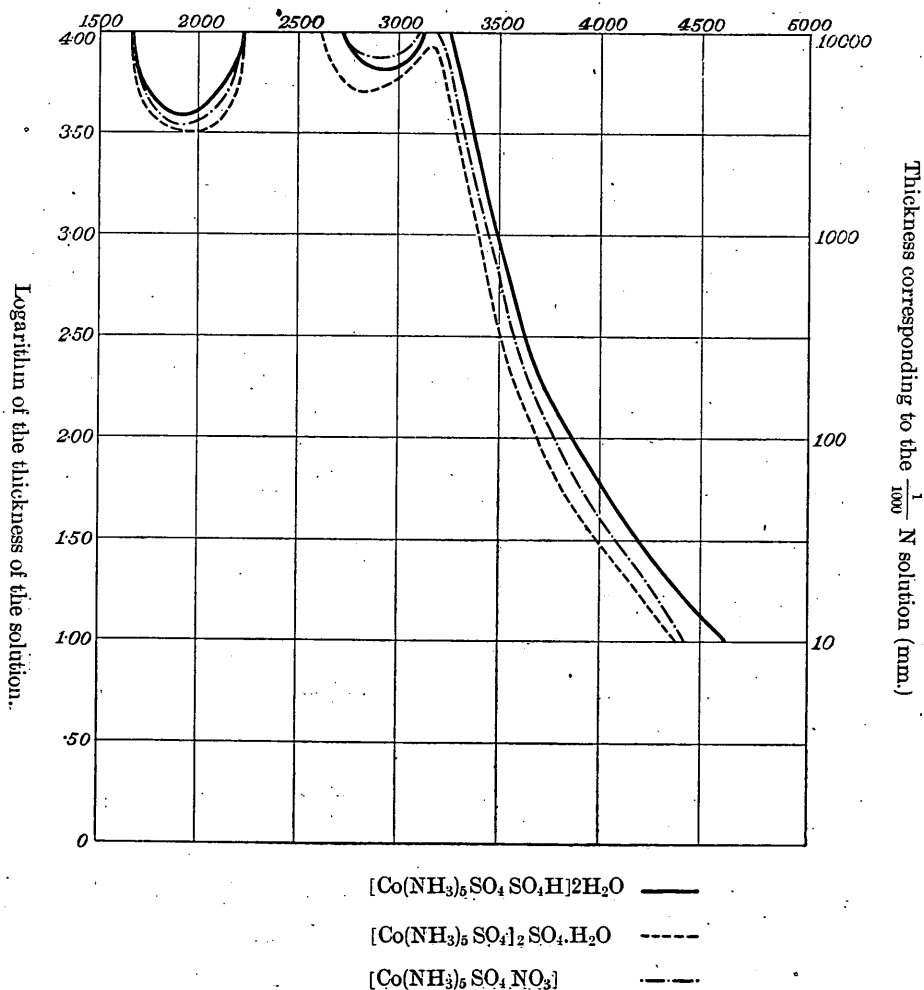
Fig. III.

Frequency.

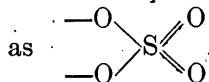


aminated. The former being insoluble in water, oxalic acid solution was used as its solvent. Their curves, Fig. III and Fig. I, were found to be of entirely different types, from which it is evident that the oxalato group of $[\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4]\text{Cl}$ is attached to the central cobalt and the acid radicle outside the first sphere of complex has no effect on the light absorption. The fact that $[\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{X}]$ and $[\text{Co}(\text{NH}_3)_5\text{CO}_3\text{X}]$ gave quite different absorption curves from those of $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]\text{Cl}$ and $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Cl}$, is added evidence that the former must have different structural constitutions from the latter. As seen in the curve of $[\text{Co}(\text{NH}_3)_5\text{SO}_4\text{X}]$ (Fig. IV),

Fig. IV.
Frequency.

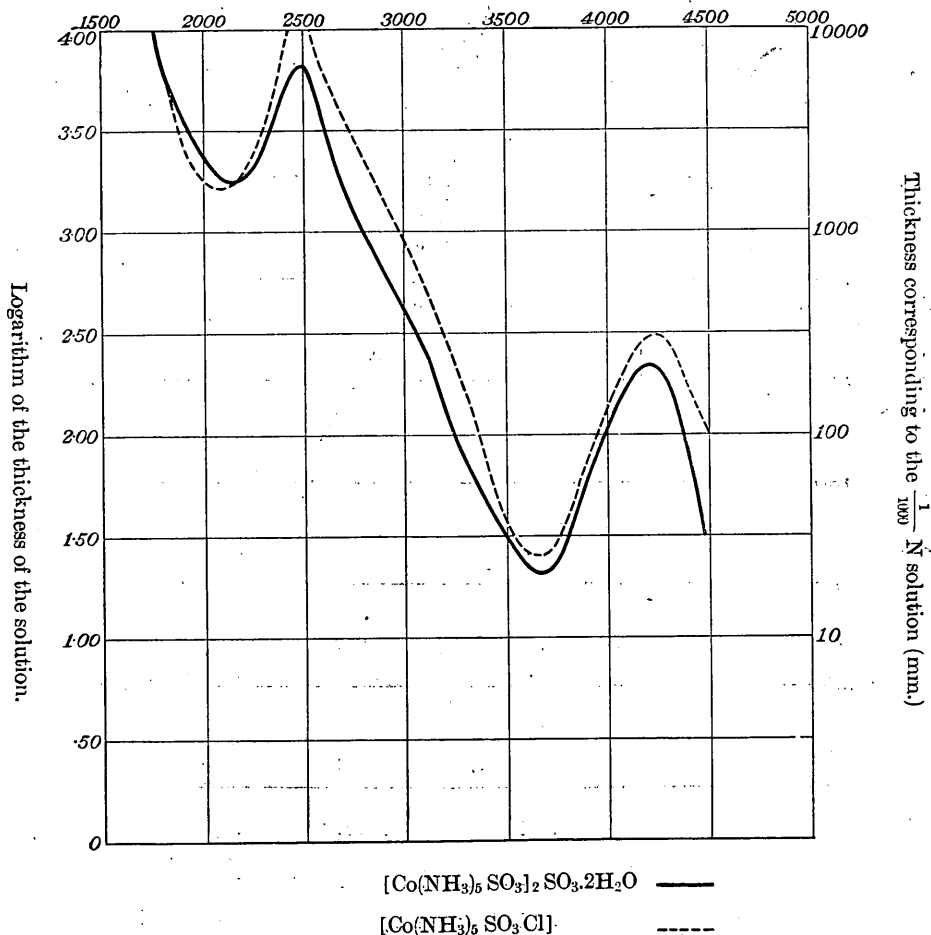


it has been found that the behaviors of the second and the end absorptions are somewhat similar to those of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{X}$ and $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]\text{X}$, while the position of the first absorption band is identical with that of $[\text{Co}(\text{NH}_3)_6\text{C}_2\text{O}_4]\text{X}$ and $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{X}$. It is, therefore, most probable that the sulphuric acid radicle coordinates in a symmetrical manner, i. e.,



If the sulphurous acid radicle of $[\text{Co}(\text{NH}_3)_5\text{SO}_3]\text{X}$ be symmetrically coordinated, i. e., as $\text{O}=\text{S} \begin{array}{l} \diagup \text{O—} \\ \diagdown \text{O—} \end{array}$, its absorption curve should be identical with

Fig. V.
Frequency.



that of $[\text{Co}(\text{NH}_3)_6\text{SO}_4\text{X}]$. The experiments have shown disagreement with this supposition. Fig. V represents the curve of $[\text{Co}(\text{NH}_3)_5\text{SO}_3\text{X}]$, which is absolutely different from Fig. IV. $[\text{Co en}_2\text{SO}_3]\text{X}$ gave a curve (Fig. VI) similar to that of $[\text{Co}(\text{NH}_3)_5\text{SO}_3\text{X}]$, only with the difference that the second absorption band of the latter is far deeper than that of the former. It is, therefore, evident that the sulphurous acid radicle plays an important

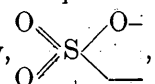
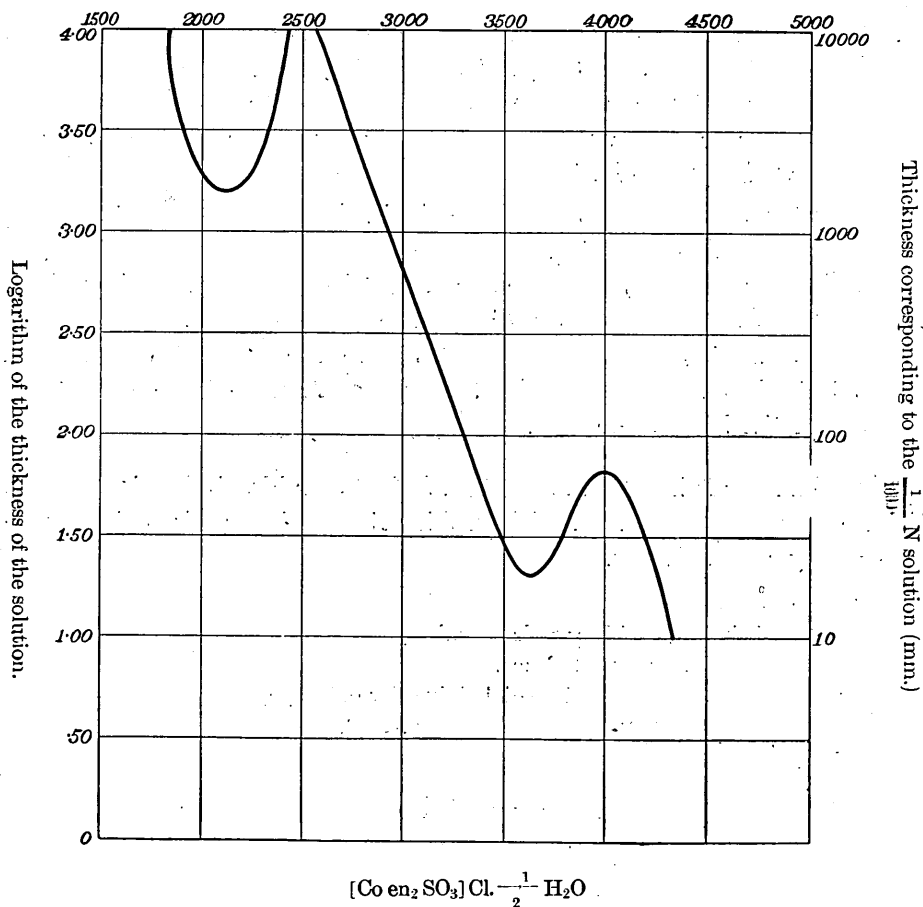
part in the absorption, and that it coordinates asymmetrically, , with cobalt, while the sulphuric acid radicle becomes symmetrical in the first sphere of attraction of the central atom.

Fig. VI.
Frequency.



To summarise these spectrographical studies, it has, by means of this analysis, been established, first that pentammine-oxalato- and carbonato-cobaltic salts should have a similar configuration, which is not of the type given in (I) and (II), and which is also different from those of tetrammine-oxalato- and carbonato-cobaltic salts; secondly that pentammine-sulphato-cobaltic salts should have a constitution which resembles that of tetrammine-carbonato- and oxalato-cobaltic salts in one way and that of pentammine-oxalato- and carbonato-cobaltic salts in another way; and thirdly that the sulphuric acid radicle coordinates symmetrically with cobalt, while the sulphurous acid radicle does so asymmetrically.

Consequently, these facts should be a strong verification of the theory that the new cubic configuration is suitable in the case of these salts.

Summary.

1. The configurations of complexes $[\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{X}]$, $[\text{Co}(\text{NH}_3)_5\text{CO}_3\text{X}]$, $[\text{Co}(\text{NH}_3)_5\text{SO}_4\text{X}]$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_3\text{X}]$ have been determined.
2. The theory of the maximum coordination number has been discussed and the cubic configuration has been introduced for complexes of the type $[\text{Co}(\text{NH}_3)_5\text{X}^{\text{II}}\text{X}^{\text{I}}]$.
3. Optically active isomers have been obtained from $[\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{SO}_4\text{H}]$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4\text{SO}_4\text{H}]$.
4. The absorption spectra of the above mentioned substances have been measured and the results obtained have been discussed.
5. The view that strong acid radicles have the weakest coordination affinity has been verified by the measurements of the electrolytic conductivities of these salts.

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