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Mesotomisation of Diammine=dinitro=oxalo=cobalt Complex and Determination of the Configurations of this Complex and of Diammine=tetranitro=cobalt Complex.

by

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In a recent communication [Yuji Shibata, *Recherches sur les spectres d'absorption des ammines-complexes métalliques I. Spectres d'absorption des solutions aqueuses des ammines-complexes cobaltiques;* Journ. Coll. Scien. Imp. Univ. Tokio, vol. XXXVII, Art. 2, 1915.] one of the authors discussed the relation between the constructions of various cobalt ammine complexes and the absorption spectra of their aqueous solutions.

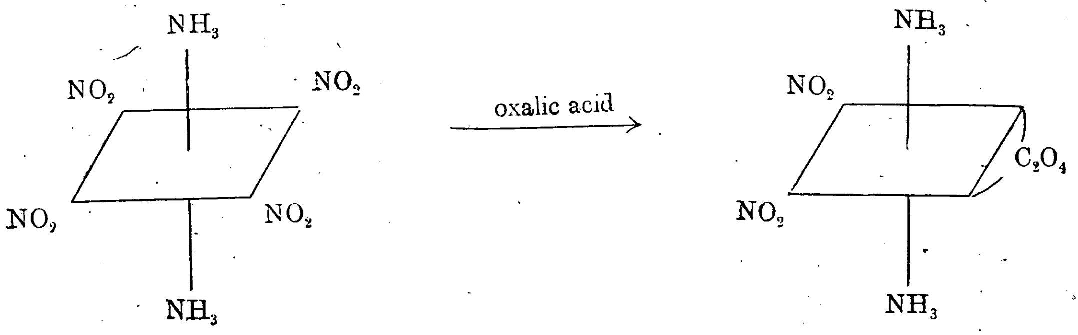
Among those studied, some nitrammine cobalt complexes were also included, and it was found that their absorption spectra are strongly influenced by the difference of the space positions of nitro-groups in the complex ions. Thus, if at least two nitro-groups occupy the furthest corners of a regular octahedron, which is considered to represent the space model of such metal-ammine complexes, three distinct bands appears in their absorption spectra, the absorption maxima existing respectively at about 2000, 3000 and 4000 of frequencies. Another group of nitrammine cobalt complexes, which have their nitro-groups only in the adjacent positions, shows merely two absorption bands and lacks the one in the most refrangible region of the spectrum.

From these diversities in the optical behavier of these complexes, the author was able to determine the spacial arrangements of the nitro-groups in several nitrammine cobalt complexes. Thus, the result of the investigation of the absorption spectrum of diammine-dinitro-oxalo-cobalt complex $[Co(NH_3)_2(NO_2)_2C_2O_4]'\,Me^{\bullet}$ easily led him to ascertain that its two nitro-groups are in the adjacent positions (cis-position), this complex showing only two bands at about 2000 and 3000 of frequencies.

Now, if we could determine the space positions of the two ammonia molecules in this complex, the configuration of the salt would become quite clear, the oxalic acid-residue necessarily occupying the cis-position [A. Werner, *Ann.*, **386**, 10, 1912]. Further, the configuration of diammine-dinitro-oxalo-cobalt complex having once been determined, that of its mother substance, diammine-tetranitro-cobalt complex $[Co(NH_3)_2(NO_2)_4]'\,Me^{\bullet}$, will be easily ascertained, the one being readily obtainable from the other by the action of oxalic acid [Jörgensen, *Zeitsch. anorg. Chem.*, **11**, 440, 1896]. Thus:—

$$[Co(NH_3)_2(NO_2)_4]Me + C_2O_4H_2 = [Co(NH_3)_2(NO_2)_2C_2O_4]Me + 2NO_2H$$

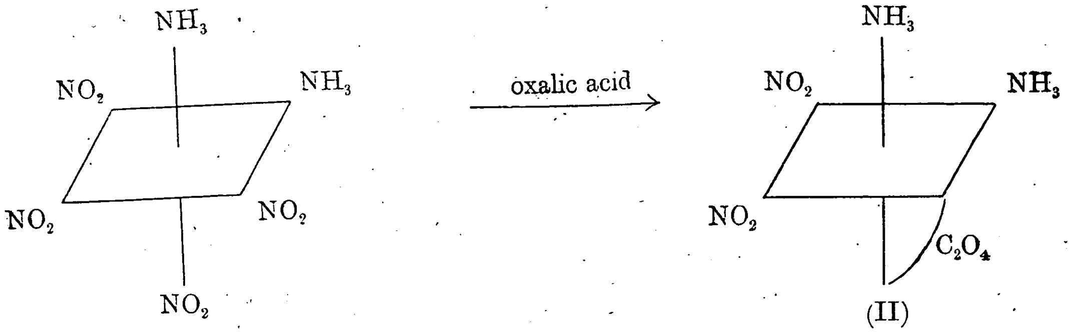
Now, owing to the fact that there are two possibilities in the spacial arrangements of the ammonia molecules in the complex ion, we may express the above chemical reaction in either of the following ways:—



(Ammonia molecules in the trans-position.)

(I)

or



(Ammonia molecules in the cis-position.)

(II)

The choice between these two formulae for diammine-dinitro-oxalo-cobalt complex offers little difficulty, when we take their constructions into account. As may be seen, formula (I) is constructed quite symmetrically, which allows no possibility of the existence of enanthiomorphs, while with formula (II), the construction of which is obviously asymmetric, the resolution of the complex into optically active isomers has to be expected.

Accordingly, mesotomisation of diammine-dinitro-oxalo-cobalt complex has been tried, with the result that both of the optical isomers have actually been obtained. Details of our proceedure will be described in the experimental part, but its essential points may here be outlined. The cobalt complex, which was initially prepared as an ammonium salt, was first transformed into the corresponding barium salt. To a concentrated solution of this salt, sulphate of an alkaloid, such as brucine, strychinine or cinchonine, was added, the precipitated barium sulphate was filtered off, and the alkaloid salt of the complex, which readily crystallised out from the filtrate, was then fractionated in the usual manner.

The most easily and difficultly soluble portions of the alkaloid complexes, which were thus obtained by repeated fractionations, were then converted into the potassium salts by the action of potassium iodide. The two potassium diammine-dinitro-oxalo-cobaltiates $[Co(NH_3)_2(NO_2)_2C_2O_4]K$ thus obtained from the two extreme fractions were both proved to be optically active, as had been anticipated, and the one was found to be the optical antipode of the other, having the following specific rotatory power:

$$[\alpha]_D = \pm 115^\circ.$$

The possibility of the mesotomisation of this complex shows that it is asymmetrically constructed and that, therefore, its two ammonia molecules must be in the adjacent positions, corresponding to the space formula (I) (see page 2). Consequently the position of the two ammonia molecules in diammine-tetranitro-cobalt complex, the mother substance, must also be adjacent.

The mesotomisation of diammine-dinitro-oxalo-cobalt complex not only affords us a means of determining its configuration in the manner above described, but it also offers us some interesting facts concerning the stereochemistry of metal complexes. In so far as this asymmetrically constructed complex ion is found to be an anion, this is virtually the first example of a mesotomised complex anion containing a cobalt atom(1), the large number of optically active cobalt complexes hitherto obtained by A. Werner and his pupils being all of them cations. Moreover the type of the optically active anion $[Co(NH_3)_2(NO_2)_2C_2O_4]'$ is entirely new in respect to the molecular asymmetry of such metal complexes.

When A. Werner found optical activity in some cobalt-ammine complexes, he drew attention to the fact that the activity is due sometimes to the asymmetric cobalt atom, sometimes to an asymmetric structure of the complex ion as a whole. Those in which optical activity is due to the asymmetric structure of the complex ion as a whole were further classified by him into the two types $[MeA_2B^I{}_2]$ (or $[MeA_2C^{II}]$) and $[MeA_3]$(2), calling them respectively the type of molecular asymmetry I and the type of molecular asymmetry II. For example, *cis*-dinitro-diethylene-diamine-cobalt complex $[Co\underline{en}_2(NO_2)_2{}^{(1)}_{(2)}]^{\bullet}$, and carbonato-diethylene-

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(1) A. Werner mesotomised formerly a chromium complex containing a complex anion $[Cr(C^2O_4)^3]'''$. [*Ber.*, **45**, 3061, 1912].

(2) In these general formulae, A means a molecule of organic amine bases which corresponds to two molecules of ammonia, or a bivalent acid radical, while B and C represent respectively mono-and bivalent acid radicals.

diamine-cobalt complex $[\mathrm{Co}\underline{\mathrm{en}}_2\mathrm{CO}_3]^{\cdot}$ belong to the type of molecular asymmetry I, while triethylene-diamine-cobalt complex $[\mathrm{Co}\underline{\mathrm{en}}_3]^{\cdot\cdot\cdot}$ and trioxalo-chromium complex $[\mathrm{Cr(C_2O_4)_3}]'''$ belong to that of molecular asymmetry II.

Now, it will be noticed that the optical activity of diammine-dinitro-oxalo-cobalt complex is due not to the asymmetry of the cobalt atom but to a molecular asymmetry, the central cobalt atom in this complex ion which may be expressed by the general formula $[\mathrm{CoE_2F_2D^{II}}]'$ being by no means asymmetric, as is the case with $[\mathrm{Co}\underline{\mathrm{en}}_2\cdot\mathrm{NO_2}\cdot\mathrm{Cl}]^{\cdot}$, $[\mathrm{Co}\underline{\mathrm{en}}_2\cdot\mathrm{NH_3}\cdot\mathrm{Br}]^{\cdot\cdot}$ etc [compare A. Werner, *Ber.*, **44**, 1887 and 2445, 1911]. This new type of molecular asymmetry to which attention has just been called is, therefore, to be introduced into the stereochemistry of inorganic complex compounds and, in extension of Werner's classification, it may be called the type of molecular asymmetry III.

Experimental.

1) Preparation of Barium Diammine-dinitro-oxalo-cobaltiate.

To start with, ammonium diammine-tetranitro-cabaltiate $[\mathrm{Co(NH_3)_2(NO_2)_4]NH_4}$ was first of all prepared according to the method described by Jörgensen [*Zeitsch. anorg. Chem.*, **17**, 476, 1898], this substance having the advantage of being easily converted into the barium salt and the barium salt being required in later operations.

The large yellowish-brown coloured crystals of the ammonium salt thus obtained were carefully purified by repeated recrystallisation, and subsequently converted into ammonium diammine-dinitro-oxalo-cobaltiate $[\mathrm{Co(NH_3)_2(NO_2)_2C_2O_4}]\cdot\mathrm{NH_4}$ by the action of oxalic acid upon a concentrated aqueous solution of the original salt [Jörgensen, *Zeitsch. anorg. Chem.*, **11**, 440, 1896].

The oxalo-complex thus obtained was then dissolved in water, and finely pulverised barium chloride was added in portions. When one molecular proportion of barium chloride was added to two molecular proportions of the complex, barium diammine-dinitro-oxalo-cobaltiate began to crystallise out from the solution in the form of fine brownish red needles containing 3 molecules of water [Jörgensen, *ibid.*, 445]. This important salt was also repeatedly recrystallised, until the estimation of cobalt in the complex gave a quite satisfactory value.

2) Mesotomisation of Diammine-dinitro-oxalo-cobalt Complex as Brucine Salt.

To a saturated aqueous solution of barium diammine-dinitro-oxalo-cobaltiate, which was kept at about 40°C, finely pulverised brucine sulphate $(C_{23}H_{26}N_2O_4)_2SO_4H_2, 7H_2O$ was added in small portions under constant agitation. The barium sulphate formed was filtered off after the whole of the calculated amount of brucine sulphate was added.

As the filtrate became cooler, brown needles aggregating in a radial form gradually began to appear here and there on the walls of the vessel. After allowing the solution to stand over night at the ordinary temperature, these crystals were gathered on a filter as the first fraction. The mother liquor was then kept in a vacuum over sulphuric acid, and the crystals, which separated out from it, were gathered from time to time. In this way four fractions in all were obtained.

An estimation of cobalt and water with one of these fractions gave the following results:

obs	calc. for $[Co(NH_3)_2(NO_2)_2C_2O_4]\cdot H(C_{23}H_{26}N_2O_4), H_2O$
$Co=8{\cdot}52\%$	$Co=8{\cdot}59\%$
$H_2O=2{\cdot}72$ "	$H_2O=2{\cdot}63$ "

The four fractions gave the following values for their specific rotations in an aqueous solution (0.3%, 10 cm):

I	$[\alpha]_D^{23°} = -21{\cdot}3°$
II	$[\alpha]_D^{28.5°} = +21{\cdot}3°$
III	$[\alpha]_D^{28°} = +27°$
IV	$[\alpha]_D^{27°} = +29.3°$

The first fraction which consisted of the least soluble crystals was found to be fairly unstable when dissolved in water, for on standing the insoluble free alkaloid gradually separated out from the solution. However, by working rapidly but cautiously we were able to effect its further fractional crystallisation and purification, and ultimately a crop of crystals which had as high a specific rotation as

$$[\alpha]_{D}^{27.5^\circ} = -70{\cdot}7^\circ$$

was obtained, a value which has not been increased by further recrystallisation. These crystals we have designated as fraction Ia.

Fractions II, III and IV, having been ascertained to show comparatively small differences in their rotatory power, were now together dissolved in the mother liquor from fraction Ia, and this solution was again kept in a vacuum in order to repeat the fractionation. Two more fractions were thus obtained, fractions V and VI, which had the following specific rotations:

$$\text{V} \qquad [\alpha]_{D}^{27^\circ} = 0^\circ$$
$$\text{VI} \qquad [\alpha]_{D}^{27^\circ} = +45^\circ$$

Fraction VI was once more dissolved in a small quantity of water and refractionated by partial crystallisation in a vacuum (fractions VII and VIII), Fraction VIII, which was most easily soluble in water, had a specific rotation of $[\alpha]_{D}^{28^\circ} = +68{\cdot}3$. As this value remained unchanged even after further recrystallisations, it was concluded that the fractions Ia and VIII were essentially the *l*-brucine salt of *l*-and *d*-diammine-dinitro-oxalo-cobalt complex respectively.

Elimination of the brucine molecule from these fractions was then proceeded with. For this purpose, the example set by A. Werner, who mesotomised trioxalo-chromium complex $[\mathrm{Cr(C_2O_4)_3)}]'''\cdot\mathrm{Me}'_3$ (*loc. cit.*) as strychinine salt and subsequently decomposed it by means of potassium iodide in order to eliminate strychinine as its insoluble iodide, was followed.

The operation was carried out in the following manner: the brucine complex was first dissolved in a small quantity of water, and to this solution a calculated amount of solid potassium iodide was then added. On vigorous agitation the hardly soluble brucine hydroiodide completely separated out from the solution, and the precipitates thus formed were immediately filtered off. In order to avoid autoracemisation, which might occur in the dissolved active complex, absolute alcohol was added to the filtrate in small portions, until a slight but permanent turbidity was established. The walls of the vessel were then strongly rubbed with platinum spatula to accelarate crystallisation, when fine brownish red needles were readily formed. These crystals were collected and well sucked on a filter, washed first with a small quantity of water and then with absolute alcohol, until they had no more a bitter, but slightly sweet taste.

An estimation of cobalt, potassium and water in the product thus obtained from fraction Ia gave the following numbers, proving that the desired potassium salt of the complex was obtained:

obs.	calc. for $[Co(NH_3)_2(NO_2)_2C_2O_4]K \cdot 1\frac{1}{2}H_2O$
Co=17·88%	Co=17·38%
K=10·96 "	K=11·53 "
H_2O= 6·45 "	H_2O= 7·96 "

Its specific rotation was found to be:

$$[\alpha]_D^{27°} = -115° \quad (0{\cdot}1\%, 10\,\mathrm{cm})$$

The salt prepared from fraction VIII in the same manner gave the following analytical and optical data:

obs.	theor.
Co=17·95%	Co=17·38%
K=11·59 "	K=11·53 "
H_2O= 7·17 "	H_2O= 7.96 "

Sp. rot.: $[\alpha]_D^{23°} = +115°$ (0.1%, 10 cm)

It is evident, therefore, that as already pointed out, the least soluble fraction consisted of *l*-brucine-*l*-diammine-dinitro-oxalo-cobalt complex, while the most easily soluble fraction consisted of *l*-brucine-*d*-diammine-dinitro-oxalo-cobalt complex.

3) Mesotomisation of Diammine-dinitro-oxalo-cobalt Complex as Strychinine Salt.

Mesotomisation of diammine-dinitro-oxalo-cobalt complex with strychinine sulphate $(C_{21}H_{22}N_2O_2)SO_4H_2$, $6H_2O$ was next tried.

The mode of proceedure was quite the same as before; but in view of the fact that the solubility of strychinine sulphate is considerably less than that of brucine sulphate a slight modification was introduced in taking a less concentrated solution of the barium salt of the complex and in keeping its temperature at about 50°C, instead of at 40°. The filtrate from the precipitated barium sulphate soon yielded a quantity of pale brown needles, showing that the strychinine salt of the complex is likewise much less soluble than the corresponding brucine salt.

An analysis of these crystals gave the following numbers:

obs.	calc. for $[Co(NH_3)_2(NO_2)_2C_2O_4]\cdot H\cdot(C_{21}H_{22}N_2O_2)\cdot H_2O$
Co=9·60%	Co=9·41%
H_2O=3·62 "	H_2O=2·88 "

In the course of the fractionations of the strychinine salt of the complex, it was observed that the least soluble fraction, which contained *l*-strychinine-*l*-diammine-dinitro-oxalo-cobalt complex, was, in the state of a solution, even more unstable than the corresponding brucine salt; consequently, an accurate measurement of its rotatory power in a dilute solution could not be made. The strychinine salt after two recrystallisations was, therefore, converted into the potassium salt in the manner already described, and the specific rotation of the potassium diammine-dinitro-oxalo-cobaltiate thus obtained was determined with the following result:

$$[\alpha]_D^{27°} = -104° \quad (0{\cdot}1\%,\ 10\ \text{cm})$$

Due perhaps to the small solubility of the strychinine salt the *d*-variety of the complex could not be separated even by repeated fractionations.

4) Mesotomisation of Diammine-dinitro-oxalo-cobalt Complex as Cinchonine Salt.

As the alkaloids used in the two preceeding cases were themselves laevorotatory, the optically active cobalt complex obtained as the first fraction by using a salt of these alkaloids was also, in each case, found to be laevorotatory. With the view, therefore, of obtaining a *d*-variety of the optically active complex as the first fraction, mesotomisation of diammine-dinitro-oxalo-cobalt complex was next tried with cinchonine sulphate $(C_{19}H_{22}N_2O)_2SO_4H_2$, which is itself dextrorotatory.

The method of proceedure was quite the same as in the previous cases. The cinchonine salt of the complex forms fine pale brown needles which are anhydrous. The results of the analysis were

obs.	calc. for $[Co(NH_3)_2 \cdot (NO_2)_2 \cdot C_2O_4] \cdot H \cdot (C_{19}H_{22}N_2O)$
Co = 10·64%	Co = 10·40%
H_2O = 0 „	H_2O = 0 „

At first, the cinchonine salt was separated in three fractions; the first fraction consisted of the crystals obtained directly from the solution, while the second and third fractions consisted of those obtained by partial crystallisation in a vacuum.

The three fractions had the following specific rotations:

I	$[\alpha]_D^{27^\circ} = +88 \cdot 5^\circ$	(0.2 %, 10 cm)
II	$[\alpha]_D^{9^\circ} = +88^\circ$	(0·25%, „)
III	$[\alpha]_D^{21^\circ} = -28 \cdot 8^\circ$	(„ , „)

The first two of these were then mixed together and recrystallised from water. The least soluble portion of the crystals thus obtained gave the value

$$[\alpha]_D^{27^\circ} = +149^\circ$$

for its specific rotation, which remained unaltered even after further recrystallisations. This fraction was then transformed into the potassium salt. It had the following specific rotation:

$$[\alpha]_D^{27^\circ} = +111^\circ \quad (0 \cdot 1\%, 10\,\mathrm{cm})$$

On account of the scantiness of the material, we were unable to obtain, from the more soluble portions, the corresponding *l*-variety of a sufficiently strong rotatory power.

5) Optically Active Ammonium Diammine-dinitro-oxalo-cobaltiate.

Optically active ammonium salts of this cobalt complex

$[Co(NH_3)_2(NO_2)_2C_2O_4]NH_4$ were prepared from *l*-brucine-*l*-diammine-dinitro-oxalo-cobalt complex and *d*-cinchonine-*d*-diammine-dinitro-oxalo-cobalt complex, in quite the same manner as in the case of the potassium salts, only using ammonium iodide instead of potassium iodide.

The *l*-and *d*-ammonium salts of the complex thus obtained had the following specific rotations:

$$[\alpha]_D^{27°} = -107° \quad (0{\cdot}1\%, 10\,\text{cm})$$
$$,, \quad = +116° \quad (,, \;,\; ,,)$$

These values are practically the same as those of the potassium salts. This is probably due to the fact that the difference between the molecular weights of the potassium- (=302) and ammonium- (=291) salts is not large enough to exert any distinct influence upon their rotatory powers, which were always measured in so diluted a solution as 0·1%, because of a fairly intense colour of the solution.

Sammary.

1. Diammine-dinitro-oxalo-cobalt complex $[Co(NH_3)_2(NO_2)_2C_2O_4]'Me^{\cdot}$ has been resolved into the optically active isomers by fractionation of the salts of brucine, strychinine and cinchonine.

2. In the fractionation of the alkaloid salts of the complex, either the *l*-alkaloid-*l*-cobalt complex or *d*-alkaloid-*d*-cobalt complex was always found to separate out as the least soluble fraction, while either the *l*-alkaloid-*d*-cobalt complex or *d*-alkaloid-*l*-cobalt complex always constituted the most easily soluble fraction.

3. The specific rotations of potassium and ammonium diammine-dinitro-oxalo-cobaltiates, which have been obtained by replacing the alkaloid molecules with potassium-and ammonium ions respectively, were measured, and found to have the values of *ca* ±115°, using sodium light.

4. As a results of the mesotomisation of diammine-dinitro-oxalo-cobalt complex, the configurations of this complex and also of its mother substance, diammine-tetranitro-cobalt complex, have been made clear, the possibility of mesotomisation indicating that

the complex ion $[Co(NH_3)_2(NO_2)_2C_2O_4]'$ is constructed asymmetrically, which means that the two ammonia molecules in this complex ion occupy the adjacent spacial position. As to the two nitro-groups, their position was previously determined, by one of the authors (Shibata), by a spectroscopic study.

5. The molecular asymmetry of the above mentioned complex ion, which is the first example of a mesotomised complex anion containing a cobalt atom, belongs to a new type and has been introduced into the stereochemistry of the metal complexes, calling it the type of molecular asymmetry III, in extension of Werner's classification.

The senior author, Yuji Shibata, has profound sorrow in recording here the death of his collaborator Mr. Toshio Maruki, *Rigakushi*, which occurred during the progress of the investigation recorded in this paper. At the same time, he has much pleasure in expressing his hearty thanks to Messrs. K. Matsuno, *Rigakushi*, and S. Mitsukuri for the great assistance they have given him in completing this work.

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