Structures of the Erdmann's Salt, $NH_4[Co(NH_3)_2(NO_2)_4]$ and Some Other Related Nitro-ammine-cobalt (III) Complexes

By Yoshimichi KOMIYAMA

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Introduction

Since the pioneer work of Shibata and Maruki[1], many attempts have been made to determine the configuration of tetranitro-diammine-cobaltiate ion, $[Co(NH_3)_2(NO_2)_4]^-$. As disubstituted octahedral complex has two stereoisomers, the *cis*- and the *trans*-form, there exist two possibilities in the configuration of the complex ion $[Co(NH_3)_2(NO_2)_4]^-$; i.e. the forms (A) and (A′) shown in Fig. 1.

Shibata and Maruki[1] converted ammonium tetranitro-diammine-cobaltiate, $NH_4[Co(NH_3)_2(NO_2)_4]$, (Erdmann's salt) into an oxalato compound, $NH_4[Co(NH_3)_2(NO_2)_2(C_2O_4)]$. If this is derived directly from the *trans*-tetranitro-diammine (A), it can not show optical isomerism; if from the *cis*-compound (A′), two oxalato compounds should be formed, one of which, (C), has a plane of symmetry while the other (D) has no plane of symmetry so that it should be resolvable. They reported that the oxalato compound from Erdmann's salt was resolved into optical isomers ($[\alpha]_D = \pm 115°$) in the form of a potassium salt, by using brucine, strychnine and cinchonine as resolving agents and concluded that the Erdmann's salt has the *cis*-structure.

Riesenfeld and Klement[2] reported that the same attempt to resolve the oxalato compound into optical isomers was unsuccessful. Taking its chemical properties into account, they came to the conclusion that the Erdmann's salt has the *trans*-structure.

On the other hand, Thomas[3] repeated fractional crystallization of the barium

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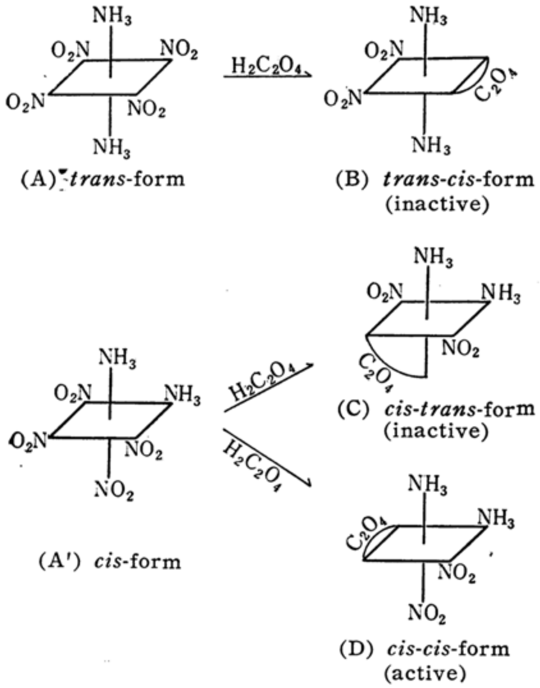
[1] Y. Shibata and T. Maruki, *J. Chem. Soc. Japan*, **37**, 1142 (1916).

[2] F. H. Riesenfeld and R. Klement, *Z. anorg. Chem.*, **124**, 1 (1922).

[3] W. Thomas, *J. Chem. Soc.*, **123**, 617 (1923).



(A) *trans*-form

(B) *trans-cis*-form (inactive)

(C) *cis-trans*-form (inactive)

(A′) *cis*-form

(D) *cis-cis*-form (active)

Fig. 1.

salt of the oxalato compound and obtained two different fractions; one was rhombohedral and the other was monoclinic. The rhombohedral fraction was found to be resolvable by means of strychnine and α-phenylethylamine. The specific rotations of the optically active potassium salts measured by Na–D line were ±154° respectively. Therefore, Thomas concluded that the two fractions had the structure (C) and (D) respectively, and assigned the *cis*-structure (A′) to the Erdmann's salt.

However, the result obtained by Ray[4] was quite contradictory. He reported that it was impossible to resolve the oxalato compound by means of salts of strychnine and l-[Co en$_3$]$^{3+}$. This result combined with the absorption spectrum and chemical behaviour of the compound led him to conclude that Erdmann's salt had the *trans* structure and the two fractions obtained by Thomas had been nothing but two different modifications of one compound (C).

In 1949, Kuroya and Yamasaki[5] repeated fractional crystallizations of ammonium and barium salts of the oxalato compound very carefully and concluded that the *cis*- and the *trans*-isomers of $[Co(NH_3)_2(NO_2)_4]^-$ should coexist in solution at room temperature as an equilibrium mixture.

In determining the configuration of a complex ion by various indirect means, as mentioned above, it has to be assumed that the mechanism of substitution reaction is such that they do not bring about any change of the configuration at any stage. This assumption, however, does not always seem to be valid in the case of Erdmann's salt.

Wells[6] was the first who determined the configuration of the complex anion by direct means; the crystal structure of a silver salt, $Ag[Co(NH_3)_2(NO_2)_4]$, was determined by the use of X-rays and it was shown that the complex ion possessed the *trans*-configuration. Recently, the same result was reported by E. A. Gilinskaya[7], too.

In view of the confusing results obtained by many authors, it would be of interest to determine the configuration of the complex anion in crystals of Erdmann's salt itself. As a first step, the author determined the crystal structure of a potassium salt, $K[Co(NH_3)_2(NO_2)_4]$, which was isotype to the Erdmann's salt, and the details of the work were published already in the previous report[8]. In this paper, the crystal structure of Erdmann's salt will be described, and some discussions will be given concerning the structures of various nitro-ammine-cobalt (III) complex salts, whose crystal structures[8–11] have been analyzed mainly by the author for these several years. Furthermore, the results of absorption measurements on their aqueous solutions will be reported. Since many investigators[12–14] have found interesting and important relations between the absorption spectra and the stereochemical configurations of cobalt (III) co-ordination compounds, it may be worth while to re-examine their absorption spectra.

Experimental

Erdmann's salt, $NH_4[Co(NH_3)_2(NO_2)_4]$, has been prepared according to the method described by Jörgensen[15]. The crystals belong to the orthorhombic bipyramidal class with the axial ratio;

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[4] B. C. Ray, *J. Indian Chem. Soc.*, 440 (1937).

[5] Read at the meeting of Chem. Soc. Japan, (1949).

[6] A. F Wells, *Z. Krist.*, (A)., **95**, 74 (1936).

[7] E. A. Gilinskaya, *Ser. Fiz-Mat. i Estestven. Nauk*, **3**, 133 (1953).

[8] Y. Komiyama, This Bulletin, **29**, 300 (1956).

[9] Y. Tanito, Y. Saito and H. Kuroya, This Bulletin, **25**, 188 (1952).

[10] Y. Tanito, Y. Saito and H. Kuroya, ibid., **25**, 328 (1952).

[11] Y. Tanito, Y. Saito and H. Kuroya, ibid., **26**, 420 (1953).

[12] H. Sueda, *J. Chem. Soc. Japan*, **57**, 406 (1936).

[13] H. Kuroya, *J. Inst. Polytech*, Osaka City Univ., Vol. 1, Ser. C, 1 (1950).

[14] M. Linhard and M. Weigel, *Z. anorg. Allgem. Chem.*, **267**, 113 (1951).

[15] S. M. Jörgensen, *Z. anorg. Chem.*, **17**, 477 (1898).

TABLE I

ABSORPTION MAXIMA OF NITRO-AMMINE-COBALT(III) COMPLEXES

	λ_1(mμ)	log ε_1	λ_2(mμ)	log ε_2	λ_3(mμ)	log ε_3
Cis$[Co(NH_3)_4(NO_2)_2]NO_3$	442.0	2.21	325.0	3.62	233.5	4.27
Trans$[Co(NH_3)_4(NO_2)_2]Cl$	429.0	2.49	341.5	3.83	251.5	4.37
$[Co(NH_3)_3(NO_2)_3]$	432.0	2.46	340.0	3.81	251.0	4.35
$[Co(NH_3)_3(NO_2)_2Cl]$	452.0	2.18	334.0	3.62	236.0	4.15
$K[Co(NH_3)_2(NO_2)_4]$	421.0	2.71	348.0	4.05	253.5	4.43

$a:b:c=0.8837:1:0.5226$ and are dark reddish brown in colour. They are well-formed and elongated along the c-crystal axis. In these respects they resemble the corresponding potassium salt.

The ammonium salt has $a=11.39\pm0.02$ Å, $b=12.97\pm0.02$ Å, and $c=6.74\pm0.01$ Å, $Z=4$. These values give the axial ratio $a:b:c=0.878:1:0.520$, which are in good agreement with those obtained by crystal measurement.

From the systematic absences; $(h00)$, $(0k0)$ and $(00l)$ for h, k and l odd, the space group was found to be $P2_12_12_1$. The calculated density 1.966 g./cc. is in agreement with that observed, 1.954 g./cc. at 25.5°C.

All the equatorial reflections around the three principal axes were recorded by using Fe K_α radiation on a pack of three films and the intensity of the reflections were visually estimated. The usual correction factors were applied by means of Cochran's chart[16]. Observed structure amplitudes were then placed on the absolute scale by Wilson's method[17].

The measurements of absorption spectra of these nitro-ammine-complexes and two others for reference, were made over the range from 220 to 500 mμ with Beckman Model DU spectrophotometer. Concentrations of aqueous solution used for measuring absorption was ranging from 10^{-3} to 10^{-5} mol./l.. The absorption maxima are tabulated in Table I.

Determination of the Structure

By comparing the general features of structure amplitudes and Patterson projections along the three principal axes of Erdmann's salt with those of the potassium salt, it was seen that they are isotype. As the first step, therefore, F values were calculated by using the parameter values of the potassium salt. The agreement between the observed and calculated F values was good enough to enable the usual Fourier refinement to be started. Then all the parameter values were refined successfully and the final parameters listed in Table II were obtained. A final electron density projection on a plane perpendicular to the c-axis is shown in Fig. 2.

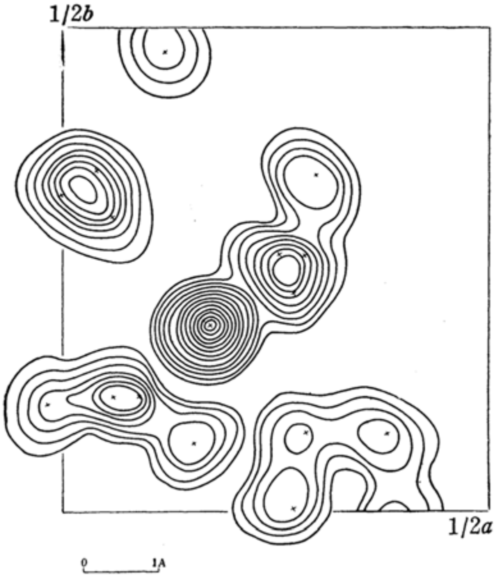

Fig. 2. Electron densities along c-axis of $NH_4[Co(NH_3)_2(NO_2)_4]$. Contours are at intervals of 2 e.Å^{-2}.

The atomic scattering factors used for the calculation of the structure factors were those listed in the International Tables. A temperature factor of the form $\exp-B(\sin\theta/\lambda)^2$ was used, where B was given the value 2.5 Å^2. The value of B and the scale factor were estimated by plotting the values of $\log F_c/F_o$ versus $(\sin\theta)^2$ at the final stage. The reliability factors $R=\sum||F_o|-|F_c||/\sum|F_o|$ are 0.160, 0.243 and 0.208 for $(hk0)$, $(0kl)$ and $(h0l)$ respectively. The weighted mean value of R is 0.188, for which only the observed reflections up to $\sin\theta/\lambda=0.501$ have been used.

Description of the Structure

The structure projected upon a plane normal to the c-crystal axis is shown in Fig. 3. The structure is built of ammonium ions and complex anions $[Co(NH_3)_2(NO_2)_4]^-$, thus being essentially ionic.

Interatomic distances and bond angles

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16) W. Cochran, *J. Sci., Inst.*, **25**, 253 (1949).

17) A. J. C. Wilson, *Acta Cryst.*, **2**, 318 (1949).

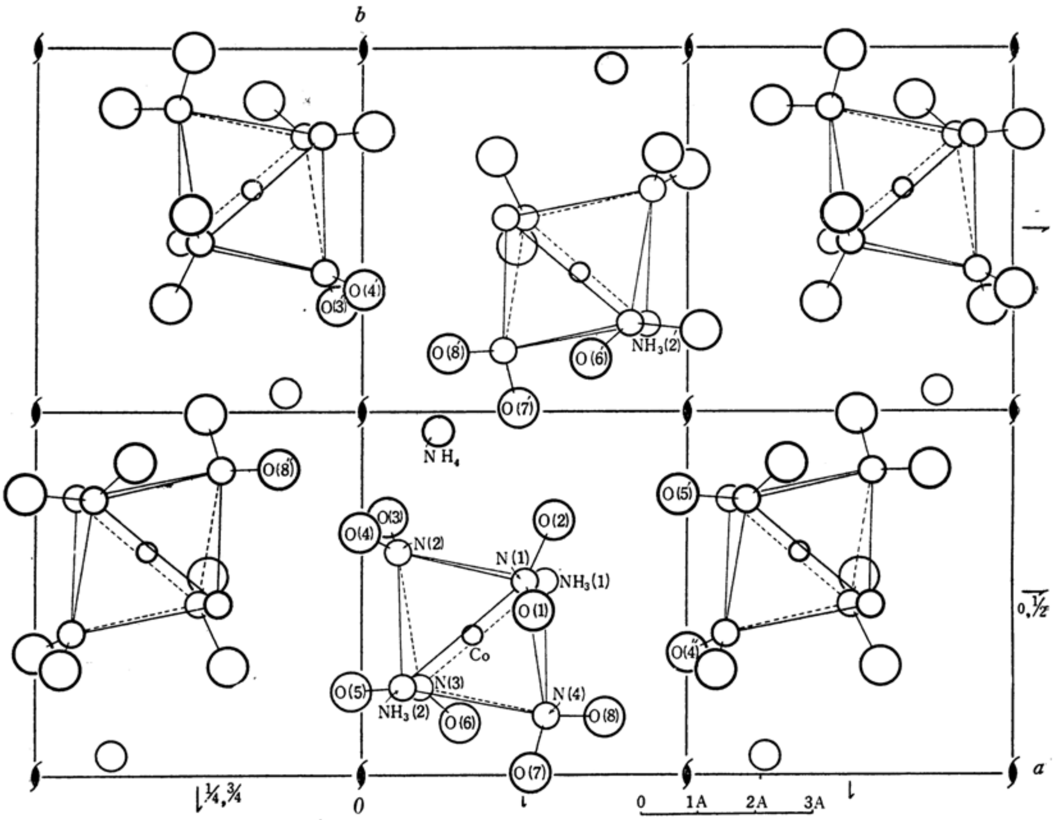


Fig. 3. Projection of the structure upon (001).

calculated on the basis of the atomic parameters in Table II are given in Table III. Two ammonia molecules are found to be co-ordinated to a cobalt atom in the *trans*-positions at the distance of 2.01 Å. Within the errors of the experiments this structure is exactly isotype to the corresponding potassium salt, and hence the detailed description of the structure will be discussed in the next section together with

TABLE II

FINAL PARAMETERS

	x/a	y/b	z/c
Co	0.1690	0.1915	0.2500
NH$_4$	0.117	0.473	0.695
NH$_3$(1)	0.279	0.265	0.064
NH$_3$(2)	0.059	0.118	0.436
N (1)	0.250	0.264	0.466
N (2)	0.056	0.305	0.234
N (3)	0.088	0.119	0.034
N (4)	0.281	0.078	0.266
O (1)	0.264	0.226	0.632
O (2)	0.293	0.350	0.442
O (3)	0.040	0.353	0.077
O (4)	−0.003	0.332	0.383
O (5)	−0.018	0.112	0.017
O (6)	0.150	0.070	−0.074
O (7)	0.260	0.005	0.376
O (8)	0.370	0.076	0.171

TABLE III

INTERATOMIC DISTANCES AND INTERBOND ANGLES

Co−NH$_3$(1)	2.01 Å	NH$_4$	···O(2)	3.08 Å
−NH$_3$(2)	2.01		···O(3)	3.15
−N(1)	1.96		···O(4)	3.10
−N(2)	1.96		···O(3')	2.99
−N(3)	1.96		···O(4')	3.11
−N(4)	1.96		···O(7')	3.24
			···O(8')	2.81
N(1)−O(1)	1.23		···O(8'')	3.02
−O(2)	1.23			
∠ONO	116°	NH$_3$(1)	···O(5')	2.86
		NH$_3$(1)	···O(1)	2.96
N(2)−O(3)	1.24	NH$_3$(2')	···O(5')	3.07
−O(4)	1.26			
∠ONO	118°	O(1)	···O(4'')	2.76
		O(2)	···O(6')	3.06
N(3)−O(5)	1.22	O(2)	···O(7')	3.00
−O(6)	1.20	O(3)	···O(7')	3.03
∠ONO	119°	O(3)	···O(8'')	2.72
N(4)−O(7)	1.23			
−O(8)	1.20			
∠ONO	118°			

those of other nitro-ammine-cobalt (III) complexes.

Discussions on the Structure of Nitro-ammine-cobalt (III) Complexes

General Features of Crystal Structure.—The crystal data of various nitro-ammine-cobalt(III) complexes are listed in Table IV.

It is worth while to point out that in all these structures the cobalt atoms always occupy the sets of positions having higher symmetry than the corresponding space group. The symmetries of the arrangement of cobalt atoms, are shown in Table V.

Crystals of trinitro-triammine-cobalt(III) $[Co(NH_3)_3(NO_2)_3]$9) and chlorodinitro-triammine-cobalt(III) $[Co(NH_3)_3(NO_2)_2Cl]$11) are molecular, while those of potassium and ammonium tetranitro-triammine-cobaltiate(III) $K[Co(NH_3)_2(NO_2)_4]$8), $NH_4[Co(NH_3)_2(NO_2)_4]$ are essentially ionic.

Characteristics of this structure seem to be the presence of spatial network consisting of the complex radicals. The binding force between the complex radicals is mainly due to the NH···O bonds between NH_3 and NO_2 groups.

Fig. 4 illustrates a network of complex radicals found in the structure of $[Co(NH_3)_3(NO_2)_3]$. It is perpendicular to the *a*-crystal axis. Each complex ion forms four hydrogen bonds with four neighboring complex radicals.

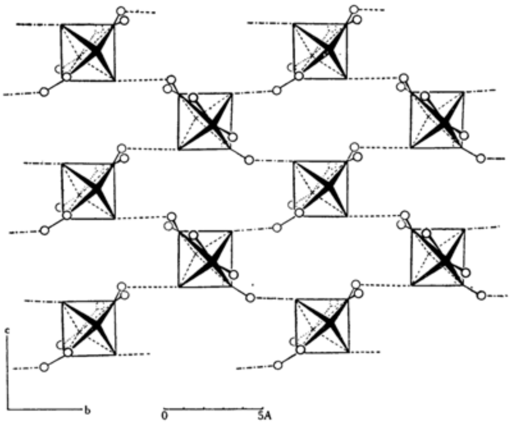


Fig. 4. Two dimensional network of complex radicals found in crystal of $[Co(NH_3)_3(NO_2)_3]$.
- - - -: linkages of 2.74 Å.
-·-·- : linkages of 2.78 Å.

Only one of the two oxygen atoms of NO_2 groups which are in the *trans*-positions with respect to each other is used to form a NH···O bond of 2.74 Å and 2.78 Å with NH_3 of the adjacent complex radicals, and the other oxygen atom is farther from its nearest NH_3 groups, (3.10 Å and 3.29 Å apart).

A similar type of network was found in the structure of $[Co(NH_3)_3(NO_2)_2Cl]$, which

TABLE IV

CRYSTAL DATA OF NITRO-AMMINE-COBALT(III) COMPLEXES

	Crystal System	Space Group	Lattice Constants *a*	*b*	*c*	*β*	*Z*
$[Co(NH_3)_3(NO_2)_3]$	Orthorhombic	$D_2^4-P2_12_12_1$	10.20 Å	11.77 Å	6.99 Å		4
$[Co(NH_3)_3(NO_2)_2Cl]$	Tetragonal	$C_{4h}^6-I4_1/a$	9.87		16.51		8
$[Co(NH_3)_3(NO_2)_2Br]$	Monoclinic	$C_{2h}^5-P2_1/n$	12.24	10.31	6.85	103.5°	4
$K[Co(NH_3)_2(NO_2)_4]$	Orthorhombic	$D_2^4-P2_12_12_1$	11.38	12.95	6.76		4
$NH_4[Co(NH_3)_2(NO_2)_4]$	Orthorhombic	$D_2^4-P2_12_12_1$	11.38	12.97	6.74		4

TABLE V

FSEUDO-SYMMETRIES OF THE ARRANGEMENT OF COBALT ATOMS

	x/a	*y/b*	*z/c*	
$[Co(NH_3)_3(NO_2)_3]$	0.0686	1/4	1/4	$D_{2h}^{17}-Bbmm$
$[Co(NH_3)_3(NO_2)_2Cl]$	0	0	0.267	$D_{4h}^{19}-I4_1/amd$
$[Co(NH_3)_3(NO_2)_2Br]$	1/4	*y*	0	$C_{2h}^{6}-A2/n$
$K[Co(NH_3)_2(NO_2)_4]$	0.1690	0.1915	1/4	$D_{2h}^{16}-Pbnm$
$NH_4[Co(NH_3)_2(NO_2)_4]$	〃	〃	〃	〃

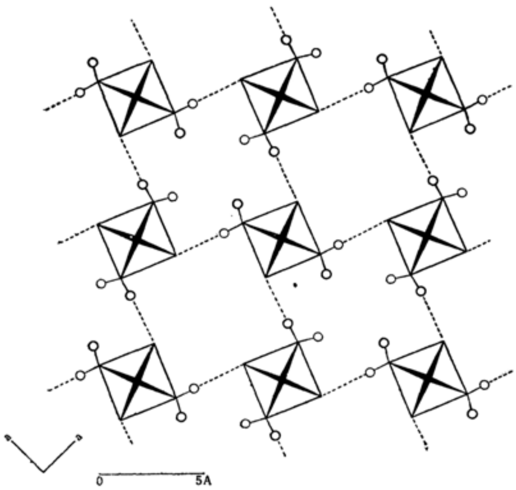
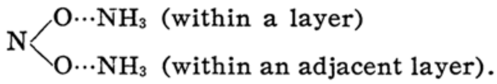


Fig. 5. Two dimensional network of complex radicals found in crystal of $[Co(NH_3)_3(NO_2)_2Cl]$.
- - - - : linkages of 2.84 Å.

is shown in Fig. 5. The network is perpendicular to the *c*-crystal axis. Each complex ion is held together by a hydrogen bond of 2.84 Å, the mode of binding being essentially similar to that illustrated in Fig. 4. However, in the structure of $[Co(NH_3)_3(NO_2)_2Cl]$ these networks are held together by another NH···O bond between NO_2 and NH_3 of complex radical belonging to the adjacent layers, forming a three-dimensional network.

Thus, both of the oxygen atoms in the nitro-group are used to form NH···O bonds as follows:



$$N\begin{cases} O\cdots NH_3 \text{ (within a layer)} \\ O\cdots NH_3 \text{ (within an adjacent layer).} \end{cases}$$

In Fig. 6 is shown a network which is found in crystals of $K[Co(NH_3)_2(NO_2)_4]$ and $NH_4[Co(NH_3)_2(NO_2)_4]$. The plane of the network is perpendicular to the *b*-crystal axis. NH···O hydrogen bonds which are responsible for binding the complex anions with each other in a single layer are 2.87 Å and 2.97 Å.

It is interesting that the arrangement of cobalt atoms only in the network is remarkably similar to that found in the structures of $[Co(NH_3)_3(NO_2)_3]$, except that the orientation of octahedra consisting of

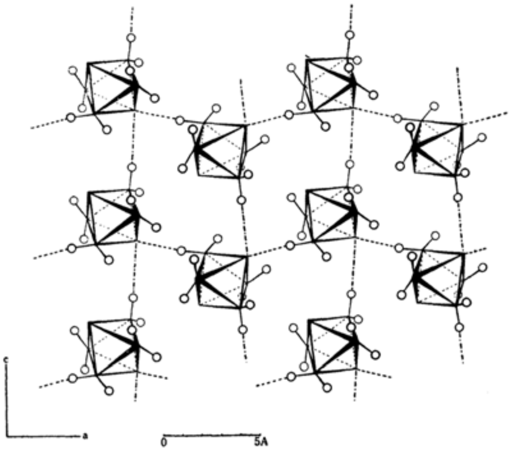


Fig. 6. Two dimensional network of complex radicals found in crystals of $K[Co(NH_3)_2(NO_2)_4]$ and $NH_4[Co(NH_3)_2(NO_2)_4]$.
- - - -: linkages of 2.87 Å.
-·-·- : linkages of 2.97 Å.

TABLE VI

THE INTERATOMIC DISTANCES BETWEEN COBALT AND ITS LIGAND ATOMS

	Co—NH_3	In *trans*-coordination with respect to	Co—NO_2	In *trans*-coordination with respect to	Co—Cl	In *trans*-coordination with respect to
$[Co(NH_3)_3(NO_2)_3]$	1.98 Å	NH_3	1.96 Å	NH_3		
	1.99	〃	1.97	NO_2		
	1.97	NO_2	1.97	〃		
$[Co(NH_3)_3H_2OCl_2]$	1.96	NH_3			2.33 Å	Cl
$[Co(NH_3)_3(NO_2)_2Cl]$	1.99	NH_3	1.99	NO_2	2.30	NH_3
	1.90	Cl				
$K[Co(NH_3)_2(NO_2)_4]$	2.00	NH_3	1.96	NO_2		
	2.00	〃	1.96	〃		
			1.96	〃		
			1.96	〃		
$NH_4[Co(NH_3)_2(NO_2)_4]$	2.01	NH_3	1.96	NO_2		
	2.01	〃	1.96	〃		
			1.96	〃		
			1.96	〃		

six nitrogen atoms around each cobalt atom is slightly different from that of $[Co(NH_3)_3(NO_2)_3]$, and that the mode of binding is different. In case of $[Co(NH_3)_3(NO_2)_3]$ one ammonia group is used to form NH···O hydrogen bond with only one nitro-group, but in Erdmann's salt one ammonia group is bound to the two oxygen atoms of NO_2 groups belonging to different complex anions.

Potassium and ammonium ions are distributed between these networks. Hence the distances between the layers, 6.48 Å and 6.49 Å, are longer than the corresponding one, 5.10 Å, found in the crystals of $[Co(NH_3)_3(NO_2)_3]$.

Two nitro-groups which are in the *trans*-co-ordination seem to be more likely to form NH···O bonds than the case in which a nitro-group and other ligand are co-ordinated to the central cobalt atom in the *trans*-positions with respect to each other.

The interatomic distances between cobalt and its ligand atoms found in these four nitro-ammine-cobalt (III) complexes as well as dichrochloride $[Co(NH_3)_3H_2OCl_2]Cl$[10] are tabulated in Table VI.

The Shape of Nitro-groups in Nitro-ammine-cobalt (III) Complexes.—There have been no accurate data available for the shape and size of nitro-groups in nitro-ammine-cobalt(III) complexes. The present investigation provides the results shown in Table VII. The average of these values are: N—O=1.23_3 Å, ∠ONO=119.3°. Such a shape and size are not very different from those found in various inorganic[6,7,19] and organic[20] compounds.

TABLE VII

THE SHAPE OF NITRO-GROUPS IN NITRO-AMMINE-COBALT(III) COMPLEXES

	N—O		∠ONO
$[Co(NH_3)_3(NO_2)_3]$	1.24 Å	1.25 Å	127°
	1.25	1.27	119°
	1.25	1.27	121°
$[Co(NH_3)_3(NO_2)_2Cl]$	1.22	1.24	119°
$K[Co(NH_3)_2(NO_2)_4]$	1.23	1.24	115°
	1.21	1.26	116°
	1.20	1.22	118°
	1.20	1.23	124°
$NH_4[Co(NH_3)_2(NO_2)_4]$	1.23	1.23	116°
	1.24	1.26	118°
	1.20	1.22	119°
	1.20	1.23	118°

Relation between Absorption Spectra of Aqueous Solution and Configuration of the Complex Radicals

A number of studies have been made on the relation between the structures of nitro-ammine-complexes of cobalt(III) and their absorption spectra in solution. These results are summarized as follows:

1) The special absorption band of nitro-radical appears in the region from 350 to 330 mμ ($\nu=86\sim90\times10^{13}$ sec.$^{-1}$). Since this band is extremely bathochromic, the second absorption band found in ordinary cobalt (III) complexes is strongly masked. Thus the absorption curves are usually observed which are quite different from those obtained in case of $[Co(NH_3)_6]^{+3}$, $[Co\ en_3]^{3+}$ and $[Co(NH_3)_5Cl]^{++}$.

2) When two nitro-groups enter into combination to the central cobalt atom in *trans*-positions, the third absorption band appears at approximately 250 mμ ($\nu\simeq120\times10^{13}$ sec.$^{-1}$)[21–23]. For instance see Figs.

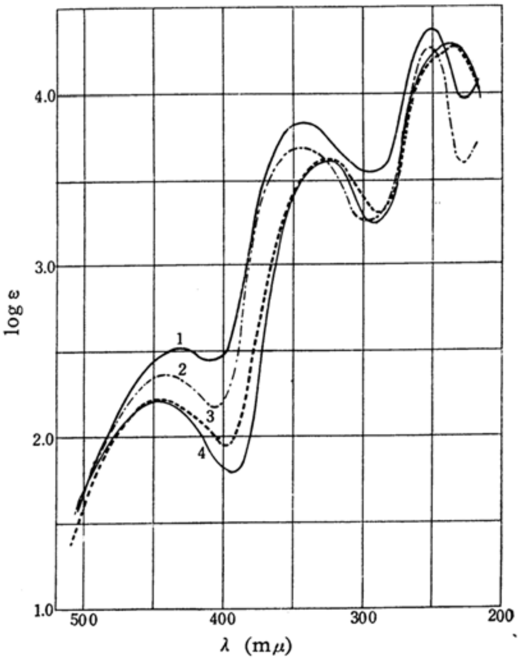


Fig. 7. Absorption spectra of *trans*- and *cis*-$[Co(NH_3)_4(NO_2)_2]^+$ in aqueous solutions. 1 and 2: *trans*-isomor, 3 and 4: *cis*-isomer, 2 and 4: obtained by M. Linhard.

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18) To be published shortly.

19) Van Driel, M. and Vermeel, H. J., *Z. Krist.*, **A. 95**, 308 (1936); Gene B. Carpenter, *Acta Cryst.*, **5**, 132 (1952); Mary R. Truter, ibid., **7**, 73 (1954).

20) S. C Abrahams and J. Monteath Robertson, ibid., **1**, 252 (1948); D. June Sutor, F. J. Llewellyn and H. S. Maslen, ibid., **7**, 145 (1954); D. June Sutor, L. D. Calvert and F. J. Llewellyn, ibid., **7**, 767 (1954).

21) R. Tsuchida, "Colours and Structures of the Metallic Compounds" (1944), p 96-113.

22) H. Kuroya and R. Tsuchida, This Bulletin, **15**, 427 (1940).

23) M. Linhard and M. Weigel, *Z. anorg. allgem. Chem.*, **267**, 113 (1950).

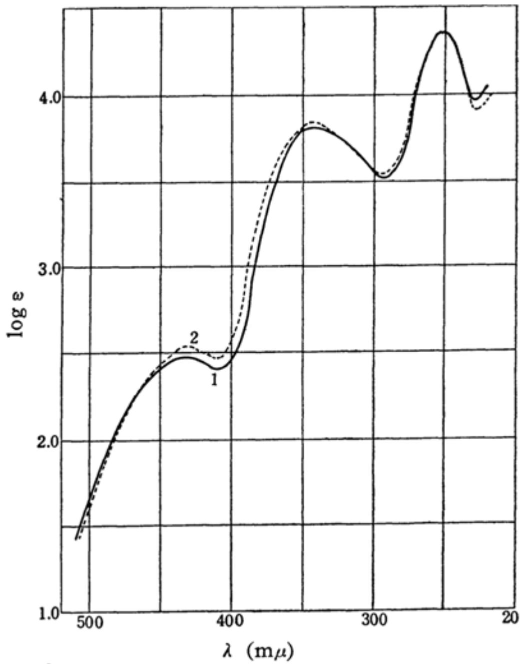

Fig. 8. Absorption spectra of [$Co(NH_3)_3(NO_2)_3$] in aqueous solution.
2: obtained by M. Linhard.

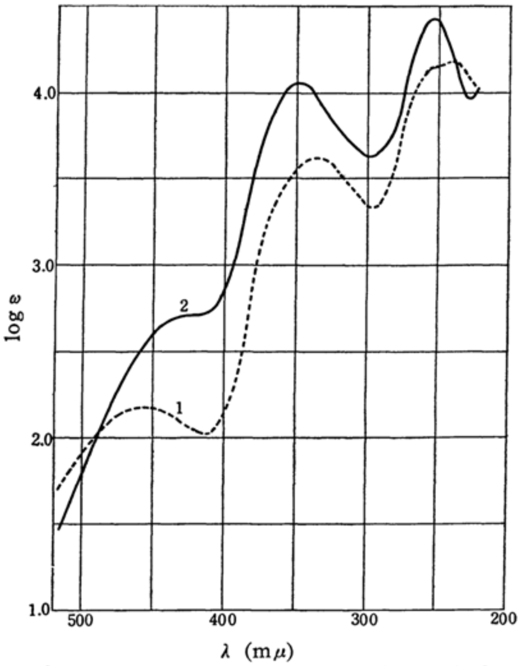

Fig. 9. Absorption spectra of [$Co(NH_3)_3(NO_2)_2Cl$] (1) and [$Co(NH_3)_2(NO_2)_4$]$^-$ (2) in aqueous solutions.

7, 8 and 9. This fact has been a part of the basis of "*trans*-negative radical hypothesis". This hypothesis states that the third band appears when two negative ligands are in the *trans*-co-ordination with respect to each other. It turned out later that even when two nitro-groups or some other negative radicals are co-ordinated even in the *cis*-positions, similar third band can still be observed, but in this case the absorption maximum is very much shifted towards shorter wave lengths[24]. Therefore the "*trans*-negative radical hypothesis" should be stated as follows: the third band appears in the region near 250 mμ when two negative radicals are co-ordinated in the *trans*-positions.

The author has measured the absorption spectra of the following complex compounds: (A) [$Co(NH_3)_3(NO_2)_3$], (B) [$Co(NH_3)_3(NO_2)_2Cl$], (C) K[$Co(NH_3)_2(NO_2)_4$], (D) *cis*[$Co(NH_3)_4(NO_2)_2$]NO_3 and (E) *trans* [$Co(NH_3)_4(NO_2)_2$]Cl.

Among these the crystal structures of (A), (B) and (C) have been determined by the present author. The absorption spectra of (D) and (E) were measured merely for reference. The results obtained are shown in Figs. 7, 8 and 9. All these curves were in good accord with those observed by other investigators. For comparison, the corresponding curves obtained by Linhard[23] are inserted in Figs. 7 and 8.

The X-ray evidence revealed that in (A) three nitro-groups are in the *trans-cis*-positions, and in (B) and (C) two nitro-groups are found to be in the *trans*-co-ordination. Corresponding to these configurations, the third bands appear at about 250 mμ in the absorption spectra of these compounds, as in the case of (E).

On the other hand, in (D), where two nitro-groups are in the *cis*-positions, the third band appears in the region of far shorter wave-lengths. Thus the "*trans*-negative radical hypothesis" was indeed confirmed, since the configurations of these nitro-complexes was established by the present investigation.

In view of this result a different configuration would be assigned to [$Co(NH_3)_3(NO_2)_3$] prepared by Sueda[25], as the absorption curve is different from the one shown in Fig. 6. [$Co(NH_3)_3(NO_2)_2Br$][26] shows similar absorption spectra to [$Co(NH_3)_3(NO_2)_2Cl$]. Since the configuration of the latter has been established, the configuration of the former is expected to be a *trans*-form with respect to two nitro-groups. The crystal structure analysis is

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[24] F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950).

[25] H. Sueda, *J. Chem. Soc. Japan*, **59**, 47 (1938).

[26] M. Kobayashi, A. Hagitani and I. Mita, ibid., **58**, 391 (1937).

now being continued by the present author. The result will be published soon.

Summary

$NH_4[Co(NH_3)_2(NO_2)_4]$ belongs to the space group $P2_12_12_1$, with four formula units per unit cell. All the atomic coordinates were determined by the method of two-dimensional Fourier series. The structure is found to be isotype to $K[Co(NH_3)_2(NO_2)_4]$. Two ammonia groups are co-ordinated to the central cobalt atom in the *trans*-positions.

General features of the structures of various nitro-ammine-cobalt(III) complexes were discussed. The absorption spectra of these complexes were reexamined in their aqueous solutions. Results are briefly discussed in relation to their steric configurations.

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Institute of Polytechnics
Osaka City University, Osaka