The Crystal Structure of Bromodinitro-triammine-cobalt(III)

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(Received July 20, 1957)

Bromodinitro-triammine-cobalt(III), [Co$(NH_3)_3(NO_2)_2$Br], can be prepared by treating chlorodinitro-triammine-cobalt(III), [Co$(NH_3)_3(NO_2)_2$Cl], with hydrobromic acid[1]. This suggests that the former is formed through a simple replacement reaction of chlorine atom in the latter with bromine atom. Kobayashi and his collaborators measured the absorption spectra of these coordination compounds[2], showing that the absorption curve of the bromo-compound is quite similar to that of the chloro-compound. However, the most interesting and instructive feature of a report is a remark regarding the configuration of these compounds; the presence of the third absorption band in any of them indicates that both of them should have two of the negative ligands in *trans*-position with respect to each other, on the basis of the Shibata and Tsuchida's hypothesis of the *trans* negative radicals[3].

The structure of chlorodinitro-triammine-cobalt(III) has been already analyzed by the present author and his co-workers[4], and it is known that this compound has a *trans*-dinitro-configuration. Taking this result together with the above-mentioned knowledge into consideration, one may assume that the bromo-compound also has the same configuration, i. e., the one illustrated in Fig. 1, (a).

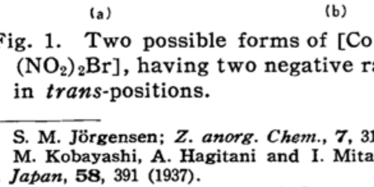

Fig. 1. Two possible forms of [Co$(NH_3)_3$$(NO_2)_2$Br], having two negative radicals in *trans*-positions.

However, one can not exclude the possibility of another configuration (b), since there is no evidence that no change in configuration has taken place at any stage of substitution reaction during the course of preparation from the chloro-compound. Therefore, an attempt was made to investigate the crystal structure of the bromo-compound by means of X-ray diffraction, which is the most powerful method in the direct determination of its configuration. Furthermore, the results of absorption measurement on the aqueous solution of this compound will be given, since the absorption curve previously reported was obtained by the photographic method.

Experimental

Bromodinitro-triammine-cobalt(III) [Co$(NH_3)_3$$(NO_2)_2$Br] has been prepared by Jörgensen's method. The crystals are monoclinic and dark red in color. Only thin tabular crystals were available. FeK_α radiation was used and a multiple-film technique was employed in taking Weissenberg photographs about the three principal axes.

The unit cell dimensions were calculated from high order reflections of some oscillation photographs taken for this measurement. They are:

$$a=12.06\pm0.04\ \text{Å},\quad b=10.30\pm0.02\ \text{Å},$$
$$c=6.85\pm0.02\ \text{Å and } \beta=105.6\pm3^\circ.$$

The observed density is 2.295 g./cc. at 8.5°C, which may be compared with a calculated value of 2.286 g./cc., assuming four formula units in the unit cell. The systematic absence of $(0k0)$ for k odd and $(h0l)$ for h, l odd shows that the space group is $C_{2h}^5-P2_1/n$. All the atoms are on the general positions. The relative intensities of the reflexions were estimated visually by comparison with a standard scale. The usual correction factors were applied by means of the chart given by Cochran[5]. No correction for absorption was made.

A temperature factor and a scale factor for converting the observed values of $|F_{\text{rel.}}|$ approximately into the absolute scale were calculated by Wilson's method[6]. The measurement of absorption spectrum of this complex was made over the wavelength range from 220 to 560 mμ

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[1] S. M. Jörgensen; *Z. anorg. Chem.*, **7**, 315 (1894).

[2] M. Kobayashi, A. Hagitani and I. Mita, *J. Chem. Soc. Japan*, **58**, 391 (1937).

[3] R. Tsuchida, "Colours and Structures of the Metallic Compounds" (1944), p. 96-113 (in Japanese).

[4] Y. Tanito, Y. Saito and H. Kuroya, This Bulletin, **26**, 420 (1953).

[5] W. Cochran, *J. Sci. Inst.*, **25**, 253 (1949).

[6] A. J. C. Wilson, *Acta Cryst.*, **2**, 318 (1949).

with Beckman Model DU spectro-photometer. Concentrations of aqueous solutions used for measurement were from 10^{-3} to 10^{-5} mol./l. The absorption maxima are:

λ_1(mμ)	log ε_1	λ_2(mμ)	log ε_2
457.5	2.15	334.0	2.59
λ_3(mμ)	log ε_3	λ_3(mμ)	log ε_3
252.0	4.12	237.0	4.16

and the absorption curve is shown in Fig. 2. It is interesting that the third absorption band is split into two maxima just as in the case of chlorodinitro-triammine-cobalt(III), $[Co(NH_3)_3(NO_2)_2Cl]$[7].

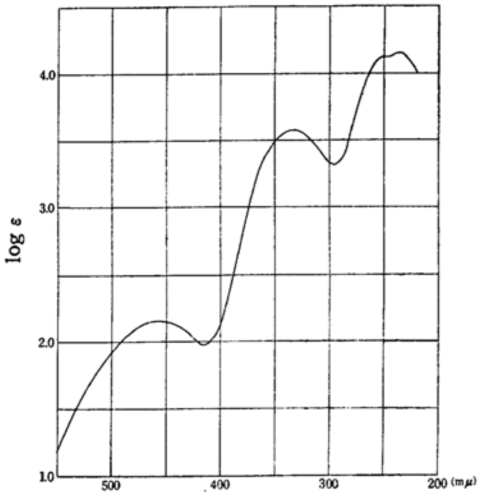

Fig. 2. Absorption spectrum of $[Co(NH_3)_3(NO_2)_2Br]$ in aqueous solution.

Determination of the structure

The Patterson projections $P(X, Y)$, $P(Y, Z)$ and $P(Z, X)$ were evaluated. These served for the purpose of determining the approximate parameters of cobalt and bromine atoms. These atoms were then used to fix the signs of the F values and successive Fourier syntheses were made. Approximate nitrogen positions were indicated in them, and inclusion of these in the preparation of the second synthesis resulted in positions leading to few further changes in sign. Then arranging the positions of oxygen atoms under an assumption that the two nitro-groups are in *trans*-coordination, F values were calculated. In any of such models, however, no good agreement was achieved between the observed and the calculated structure factors. Therefore, a model having a bromine atom and one of the nitro-groups in *trans*-coordination was adopted. This time the process of structure factor calculation and Fourier syntheses went on satisfactorily, thus allowing observed and calculated structure factors to be in comparatively good accord.

All the parameter values were refined by the usual procedure of successive approximations. The final parameters are listed in Table I. A final electron density projection along the *c*-crystal axis is shown in Fig. 3. The comparison of the observed structure factors with those calculated is given in Table II. The atomic scattering factors used for the calculation of the structure factors were those listed in the International Tables. A temperature factor was used in the form of $\exp-B(\sin\theta/\lambda)^2$, where B had the value 2.5 Å^2.

TABLE I

FINAL PARAMETERS

	x/a	y/b	z/c
Co	0.250	0.063	0
Br	0.124	0.125	0.225
N(1)	0.333	0.230	0.062
N(2)	0.350	0.015	−0.175
NH_3(1)	0.167	−0.104	−0.062
NH_3(2)	0.364	−0.015	0.236
NH_3(3)	0.136	0.141	−0.236
O(1)	0.412	0.246	0.220
O(2)	0.306	0.320	−0.057
O(3)	0.368	0.095	−0.300
O(4)	0.400	−0.092	−0.152

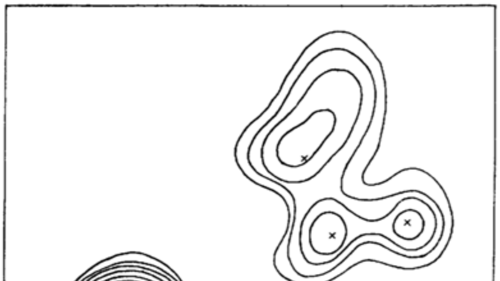

Fig. 3. Electron densities along the *c*-crystal axis of $[Co(NH_3)_3(NO_2)_2Br]$.
Contours are drawn at 2 e. Å^{-2} intervals, starting at two electron level and after 12 e. Å.$^{-2}$ level at intervals of 4 e. Å^{-2}. Atoms marked by crosses all belong to the same formula unit.

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[7] Y. Komiyama, This Bulletin, **30**, 13 (1957) Fig. 9.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS

hkl	F_o	F_c
200	33.5	−34.0
400	35.7	−34.8
600	12.7	− 8.6
800	30.6	29.4
1000	6.4	− 8.5
020	16.6	16.7
040	24.1	−23.8
060	14.2	−14.2
080	10.5	8.9
0100	5.2	− 2.1
110	4.9	5.3
120	35.9	−34.6
130	22.0	−22.6
140	19.3	−18.3
150	12.1	−10.3
160	—	3.3
170	12.1	10.8
180	1.6	0.2
190	2.7	2.3
1100	3.5	− 3.3
210	9.5	− 7.7
220	13.7	−14.6
230	23.2	−25.4
240	—	0.8
250	20.2	21.2
260	5.3	5.8
270	10.0	6.8
280	12.0	10.1
290	7.9	− 8.4
2100	4.1	3.6
310	7.5	− 7.4
320	11.2	− 7.8
330	25.2	24.8
340	19.5	21.3
350	12.2	12.2
360	20.8	20.7
370	10.0	− 8.7
380	3.0	− 1.0
390	1.7	− 1.5
3100	9.6	−11.3
410	11.6	− 8.2
420	6.4	7.0
430	6.7	− 5.9
440	17.3	20.6
450	—	1.3
460	4.5	− 4.9
470	1.6	− 0.5
480	26.6	−25.2
490	—	2.9
510	2.5	− 1.9
520	10.4	6.6
530	10.4	12.1
540	13.3	−14.2
550	4.2	6.1
560	17.2	−17.7
570	7.7	− 8.6
580	—	− 0.4
590	3.2	− 3.9
610	18.9	18.1
620	6.9	− 7.7
630	12.5	12.5
640	1.7	0.6
650	13.5	−14.2
660	8.6	8.4
670	6.5	− 5.5
680	9.2	7.5
710	3.9	4.6
720	24.7	24.4
730	11.9	−11.9
740	8.8	9.0
750	9.1	−10.7
760	4.0	− 4.6
770	2.8	5.3
780	2.2	0.6
810	1.6	3.3
820	13.9	13.9
830	4.8	4.3
840	11.1	−15.0
850	—	1.5
860	2.3	− 5.6
870	—	− 3.0
910	5.9	4.5
920	19.1	−20.2
930	6.7	− 5.9
940	9.1	− 8.5
950	1.3	− 1.3
960	—	3.1
1010	9.8	−12.3
1020	9.7	− 9.2
1030	3.1	− 5.5
1040	2.0	− 1.5
1050	8.0	− 7.5
1110	—	− 2.4
1120	1.9	− 1.8
1130	5.2	6.1
1140	1.3	5.2
002	17.2	−18.0
004	29.1	32.8
006	—	− 1.0
011	35.0	32.6
012	17.6	−13.7
013	6.2	3.9
014	7.6	10.3
015	11.9	16.0
016	4.6	− 7.5
021	25.6	−26.7
022	5.0	5.3
023	2.4	− 6.4
024	7.1	6.4
025	9.2	− 9.7
026	4.1	7.5
031	6.5	8.9
032	9.7	− 9.5
033	12.0	9.7
034	2.2	6.8
035	4.2	− 1.4
036	3.3	− 4.5
041	5.7	3.7
042	14.1	17.2
043	5.0	0.4
044	10.0	−10.1
045	0.6	2.6
046	3.3	4.9
051	15.5	−12.0
052	1.7	0.4
053	2.4	− 3.8
054	7.6	− 6.6
055	5.4	− 5.4
061	20.0	16.7
062	10.0	− 8.0
063	13.2	−12.5
064	5.8	− 5.1
065	2.4	5.2
071	10.6	−10.2
072	10.7	10.9
073	19.4	−14.0
074	4.0	− 4.7
081	3.0	3.9
082	30.4	−24.9
083	5.1	0.8
084	3.3	2.7
091	3.7	− 2.4
092	1.7	− 0.6
093	8.6	− 8.6
0101	6.6	− 7.2
101	13.5	−14.5
$10\bar{1}$	6.7	5.8
103	8.3	14.2
$10\bar{3}$	20.9	−20.6
105	—	− 1.5
$10\bar{5}$	20.7	14.5
202	33.3	−34.2
$20\bar{2}$	12.9	−16.0
204	4.4	− 3.8
$20\bar{4}$	25.7	−22.4
206	7.8	−10.7
$20\bar{6}$	2.2	− 2.0
301	12.1	−13.3
$30\bar{1}$	15.5	22.8
303	19.4	18.6
$30\bar{3}$	10.1	− 9.3
305	12.8	−15.9
$30\bar{5}$	7.4	4.8
402	43.6	45.6
$40\bar{2}$	51.6	52.8
404	3.7	− 2.6
$40\bar{4}$	1.5	− 2.8
$40\bar{6}$	12.4	11.5
501	3.2	3.5
$50\bar{1}$	9.5	−10.7
503	4.6	− 6.7
$50\bar{3}$	11.3	10.1
505	2.0	0.9
$50\bar{5}$	14.4	−12.4
602	1.3	− 3.6
$60\bar{2}$	13.7	−13.9
604	14.6	−15.6
$60\bar{4}$	—	− 1.7
$60\bar{6}$	11.5	−12.9
701	18.8	15.8
$70\bar{1}$	10.7	− 8.9
703	12.7	−11.9
$70\bar{3}$	5.2	4.8
$70\bar{5}$	1.9	− 2.6
802	7.7	− 5.3
$80\bar{2}$	15.7	−12.4
$80\bar{4}$	18.4	18.2
$80\bar{6}$	2.0	2.5
901	4.5	− 4.9
$90\bar{1}$	6.9	7.0
903	3.3	− 0.2
$90\bar{3}$	8.1	− 6.8
$90\bar{5}$	13.9	11.1
1002	9.9	− 9.3
$100\bar{2}$	3.2	− 5.0
$100\bar{4}$	13.1	−15.2
1101	9.4	− 9.0
$110\bar{1}$	9.2	4.3
$110\bar{3}$	4.4	− 3.3
$120\bar{2}$	18.2	18.3

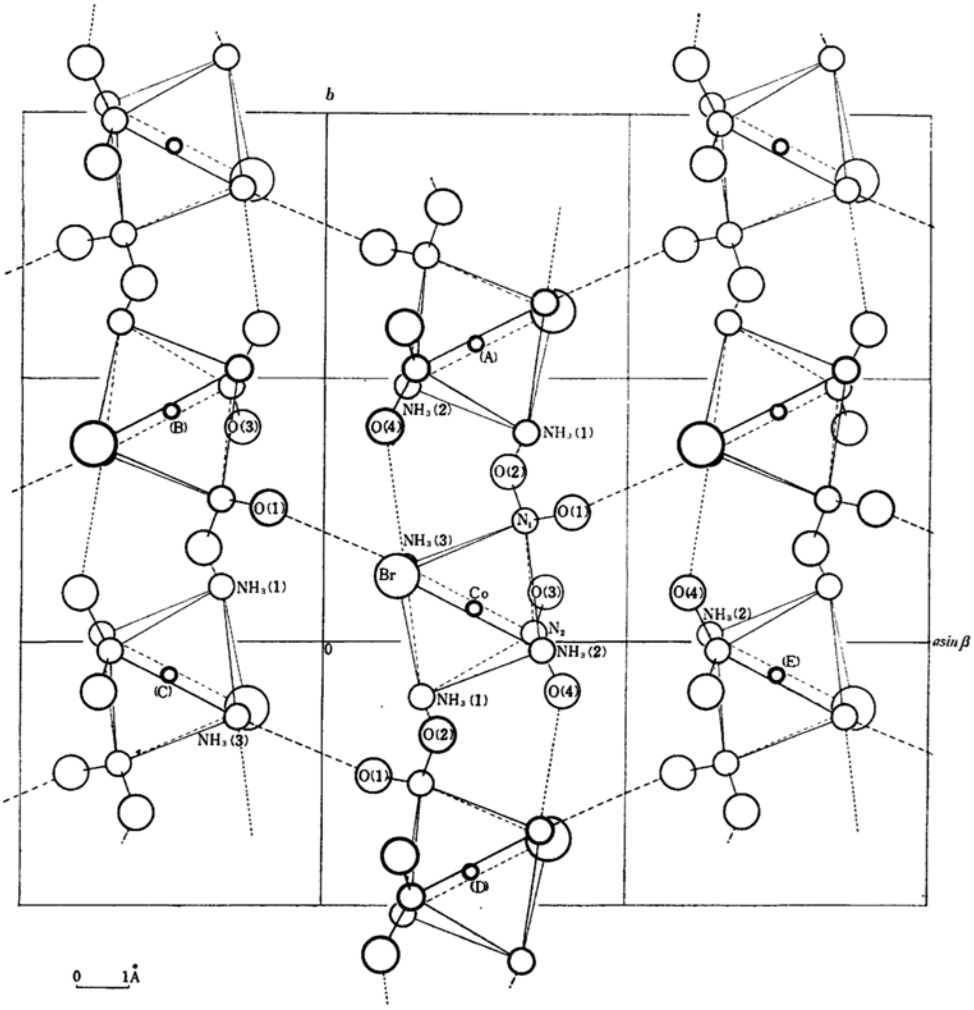

Fig. 4. Projection of the structure upon a plane normal to the c-crystal axis.

The reliability factors $R=\sum||F_o|-|F_c||/\sum|F_o|$ are 0.114, 0.198 and 0.133 for ($hk0$), ($0kl$) and ($h0l$) respectively. The higher value of R for ($0kl$) may be attributed to the less accurate values due to the absorption. The weighted mean value of R is 0.147 for which only observed reflections up to $\sin\theta/\lambda=0.500$ have been used.

Description of the Structure

The structure projected upon a plane normal to the c-crystal axis is shown in Fig. 4, which correspounds to Fig. 3. The crystal consists of bromodinitro-triammine-cobalt(III) $[Co(NH_3)_3(NO_2)_2Br]$ molecules. Two nitro-groups are coordinated to a cobalt atom in *cis*-position and one of them is in *trans*-coordination with respect to the bromine atom, making a remarkable difference from the configuration of the chloro-compound. The six ligands form a distorted octahedron around the central cobalt atom.

The interatomic distances and the interbond angles calculated on the basis of the atomic parameters in Table I are given in Table III. These interatomic distances and the bond angles are in good agreement with those found in the various complexes of cobalt(III), except the cobalt-bromine and other related distances.

The distances of approach between the nitrogen atom of an ammonia molecule and the oxygen atom of the nitro-group of an adjacent molecule are found to be 2.83, 2.86 and 2.88 Å. These short distances suggest the presence of hydrogen bonding between them. By these NH···O bonds, the complex radicals are held together, forming a layer parallel to the b-crystal

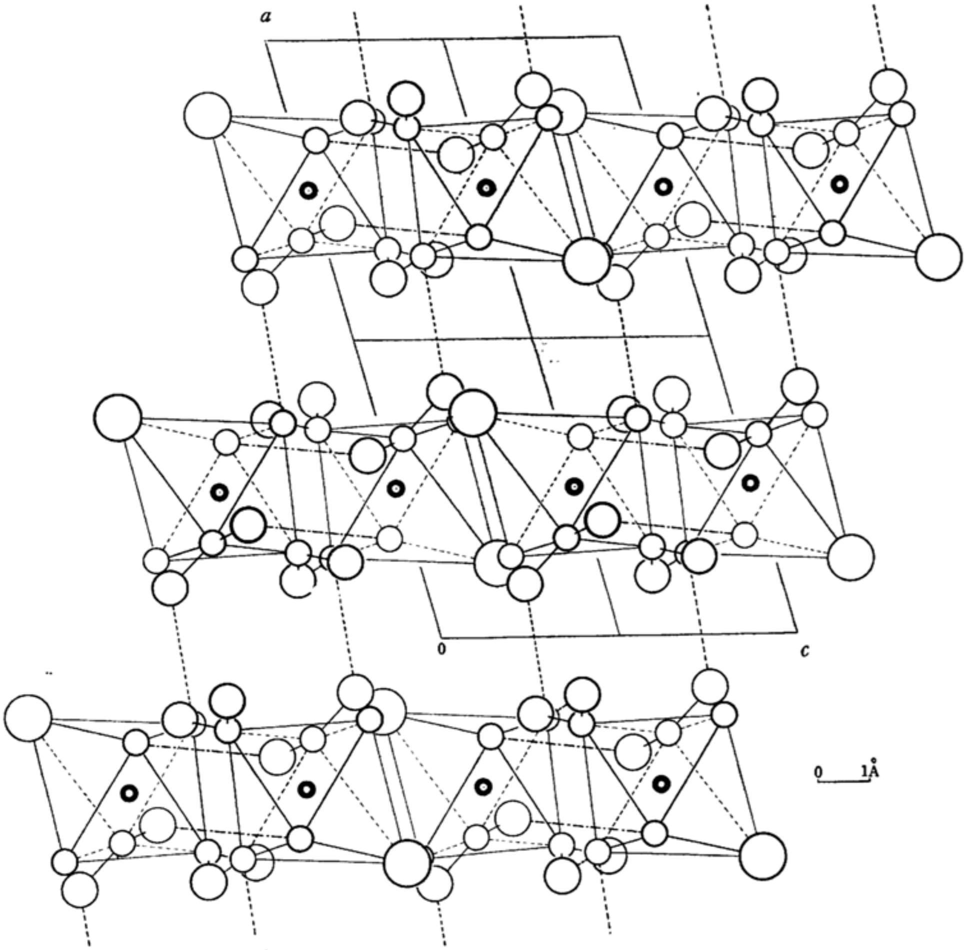

Fig. 5. Structure of $[Co(NH_3)_3(NO_2)_2Br]$, showing layers parallel to the *b*-crystal axis in double sheet.
----: linkages of 2.83 Å. ------: linkages of 2.86 Å. ---: linkages of 2.88 Å.

TABLE III

INTERATOMIC DISTANCES AND INTERBOND ANGLES

Co	—Br	2.45 Å
	—N(1)	1.98 Å
	—N(2)	1.98 Å
	—NH_3(1)	1.98 Å
	—NH_3(2)	1.99 Å
	—NH_3(3)	1.99 Å
N(1)	—O(1)	1.25 Å
	—O(2)	1.22 Å
∠O(1)N(1)O(2)		118°
N(2)	—O(3)	1.25 Å
	—O(4)	1.24 Å
∠O(3)N(2)O(4)		121°
NH_3(1)	...O(2)(D−)	2.83 Å
NH_3(3)	...O(4)(A−)	2.86 Å
NH_3(3)	...O(1)(B−)	2.88 Å
O(1)	...NH_3(1)(A)	3.16 Å
O(3)	...NH_3(1)(A−)	3.23 Å
O(3)	...NH_3(2)(E)	3.25 Å
O(3)	...NH_3(2)(−)	3.40 Å
O(2)	...O(4)(A−)	2.88 Å
O(1)	...O(4)(E)	2.90 Å
O(4)	...O(4)(E)	3.32 Å
Br	...NH_3(1)(C)	3.39 Å
	...NH_3(2)(A)	3.72 Å
	...NH_3(1)(A)	4.04 Å
	...NH_3(3)(C)	4.18 Å
	...O(3)(+)	3.76 Å
	...O(1)(B−)	3.94 Å
	...O(3)(B)	4.19 Å
	...O(1)(D)	3.95 Å
	...O(2)(D)	3.84 Å
Br	...Br	4.48 Å

axis in double sheet as shown in Fig. 5. The closest approach between the adjacent layers are seen between bromine and nitrogen atoms of ammonia molecules with distances 3.39, 3.72, 4.04 and 4.18 Å. General characteristics of the structure containing such net works were also found in the structure of the cobalt(III) complexes previously reported by us[8].

It is interesting that the configuration of this bromo-complex is entirely different from that expected from the similarity of absorption spectra of the chloro- and bromo-complexes.

Summary

The crystal structure of bromodinitrotriammine-cobalt(III) $[Co(NH_3)_3(NO_2)_2Br]$ is monoclinic, with four formula units in a cell of dimensions; a=12.06 Å, b=10.30Å, c=685 Å and β=105.6°. The space group is $C_{2h}^5-P2_1/n$. The determination of atomic parameters was made by Fourier methods.

The configuration of the complex molecule is described. One nitro-group is found to be in *trans*-position with respect to bromine atom and in *cis*-position to the other nitro-group.

The absorption spectrum of this complex was re-examined in aqueous solution.

The author expresses his hearty thanks to Professors H. Kuroya and Y. Saito of this University for encouragement and valuable discussion. Part of the cost of this study has been defrayed from a Grant of the Ministry of Education.

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[8] Y. Tanito, Y. Saito and H. Kuroya, This Bulletin, **25**, 188, 328 (1952); **26**, 420 (1953). Y. Komiyama, ibid., **29**, 300 (1956); **30**, 13 (1957).