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The Molecular and Crystal Structure of *trans*-Dinitrotetramminecobalt(III) Nitrate Monohydrate

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The crystal structure of *trans*-dinitrotetramminecobalt(III) nitrate monohydrate $[Co(NO_2)_2(NH_3)_4]NO_3 \cdot H_2O$ has been determined from three dimensional X-ray diffraction data. The dimensions of orthorhombic unit cell are: $a = 10.02$ Å, $b = 6.02$ Å, $c = 16.84$ Å, and $Z = 4$. The space group is $P2_12_12_1$. The structure has been refined by the three dimensional Fourier and least-squares method to $R = 0.103$. The complex ion has a slightly distorted octahedral coordination with six N atoms at about 1.98 Å (two are N atoms of nitro groups and the others ammonium groups). The complexes are tightly bound together by N-H⋯O and O-H⋯O interactions, constructing a three dimensional network.

Crystal structures of various nitroammine-cobalt(III) complexes of the type, $[Co(NO_2)_m(NH_3)_{6-m}]^{3-m}$ have been determined, where $m = 1$,[1)] 3,[2)] 4,[3)] and 6.[4)] Nitropentamminecobalt(III) salts ($m = 5$) have not yet been synthesized, whereas for dinitrotetramminecobalt(III) complexes ($m = 2$) *cis*- and *trans*-isomers are well known.

However, no crystal structure analysis of these salts has yet been reported. Knowledge of the crystal structures of the whole series of nitroamminecomplexes evidently is an important basis for the understanding of the stereochemistry of nitroamminecomplexes and their structural principles. We have initiated a study of the structure of dinitrotetramminecobalt(III) nitrate.

The crystal structure of the *trans* form is reported in this paper. That of the *cis* form will be described in the following paper.

Experimental

The crystals were prepared by the method of Jörgensen.[5)]

Recrystallization from water containing a small amount of acetic acid yielded thin tabular or needle-like crystals, the latter being found to be twinned. The unit cell dimensions were determined from higher-order reflections of Weissenberg photographs (Ni$K\alpha$, $\lambda = 1.6591$Å). The systematic absences were: $h00$ for h odd, $0k0$ for k odd and $00l$ for l odd. Hence the space group was unequivocally determined. The crystal data are listed in Table 1. Sets of multiple film equi-inclination Weissenberg photographs were taken about the b-axis (0 to 5th layers), the a- and c-axes (0th layer). Ni$K\alpha$ radiation was used throughout. The intensities were estimated visually with a standard film strip and were converted to $|Fo(hkl)|^2$ and $|Fo(hkl)|$ by applying the usual Lorentz, polarization and spot shape corrections. 998 independent reflections were observed. They are about two-thirds of those within the nickel sphere. The crystal used was a rod 0.2 × 0.06 × 3.0 mm. No correction was made for absorption or extinction.

TABLE 1. CRYSTAL DATA

trans-$[Co(NO_2)_2(NH_3)_4]NO_3 \cdot H_2O$
Orthorhombic
$a = 10.02 \pm 0.02$ Å
$b = 6.02 \pm 0.01$
$c = 16.84 \pm 0.02$
$D_x = 1.84\ g \cdot cm^{-3}$
$D_m = 1.865\ g \cdot cm^{-3}$
$Z = 4$
Space group $D_2^4 - P2_12_12_1$
Linear absorption coefficient for Ni$K\alpha$,
$\mu = 40.8\ cm^{-1}$

Structure Analysis

At first Patterson projections $P(xz)$, $P(xy)$ were synthesized.

These led us to fix the position of Co at 0.2500, 0.0, 0.3750. Preliminary Fourier projections of electron density upon (010) and (001) were synthesized using $F(h0l)$s with $2h + l = 4n$ ($n = 0, 1, 2, 3, \cdots$) and $F(hk0)$s with $h + k = 2n$, respectively, the signs of which were calculated from the parameter values of the cobalt atom. Approximate orientations of

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1) F. A. Cotton and W. T. Edwards, *Acta Cryst.*, **B24**, 474 (1968).

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

3) Y. Komiyama, *ibid.*, **30**, 13 (1957).

4) M. Driel and H. J. Verweel, *Z. Krist*, **95**, 308 (1936).

5) S. M. Jörgensen, *Z. anorg. Chem.*, **17**, 477 (1898).

the complex ion could be assigned from these projections. They were in good accord with the conclusion drawn from Patterson projections $P(xz)$ and $P(xy)$. However, from the Fourier maps the atoms of nitrate ion and water molecule could not be fixed. Atomic parameters of nitrate ion were assigned by packing consideration. After inclusion of the parameters of the nitrate ion and the water oxygen atom in the structure factor calculation, considerable improvement was made in the agreement between the observed and calculated structure factors. Fourier projections of electron density upon (001) and (010) were then synthesized using all $F(hk0)$s and $F(h0l)$s, respectively, the signs of which were calculated from the parameter values of all the atoms. On the Fourier maps all the atoms were found on the expected location. At this stage the discrepancy factor R became 0.20. The structure thus obtained was refined by three dimensional difference synthesis with isotropic temperature factor to R=0.14, later by a block diagonal least-squares method with HBLS program written by T. Ashida.

In this least-squares method anisotropic temperature factors were introduced and four cycles of refinement were carried out.

A weighting scheme was employed:

$w = 0.2$ if $F_o \leqq F_{\min.}$ (=4.0)

$w = 1.0$ if $F_{\min.} < F_o \leqq F_{\max.}$ (=100.0)

$w = F_o/F_{\max.}$ if $F_o > F_{\max.}$

The final discrepancy factor, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ was 0.103 for all the reflections. Atomic scattering factors were taken from International Tables for X-ray Crystallography.6)

Final atomic parameters and their standard deviations are summarized in Table 2. The observed and calculated structure factors are listed in Table 3.

Description of the Structure and Discussion

A perspective drawing of the complex ion, $[Co(NO_2)_2(NH_3)_4]^+$, is illustrated in Fig. 1. The bond lengths and bond angles with their e.s.d.'s calculated on the basis of the atomic parameters in Table 2 are listed in Table 4. A projection of the

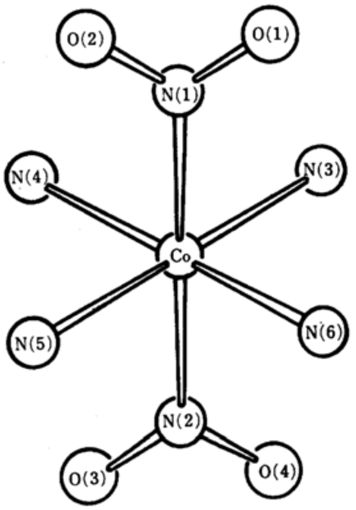

Fig. 1. A perspective drawing of the complex ion, $[Co(NO_2)_2(NH_3)_4]^+$.

Table 2. Atomic parameters and their e.s.d.'s* (10^4)

The expression of the anisotropic temperature factor is $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})]$.

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	2491(2)	0110(4)	3752(2)	60	207	26	−01	0	3
O (1)	3871(10)	3764(18)	4343(6)	74	188	27	−28	−31	−21
O (2)	3734(10)	3769(18)	3080(6)	69	180	28	−01	24	57
O (3)	1154(10)	−3553(18)	3149(6)	79	142	29	−70	24	41
O (4)	1211(10)	−3538(18)	4431(6)	66	204	19	−79	−10	−05
O (5)	1728(9)	3339(18)	1280(7)	7	318	34	−32	−03	14
O (6)	3450(9)	5489(16)	1281(8)	69	189	35	−29	−02	1
O (7)	3691(10)	1866(16)	1229(8)	104	197	30	19	4	30
O (8)	1221(10)	−1599(19)	1132(6)	78	273	27	23	10	−04
N (1)	3484(9)	2860(16)	3707(8)	26	98	28	−16	9	−22
N (2)	1497(9)	−2648(17)	3775(9)	25	126	30	29	−01	19
N (3)	3766(11)	−1092(19)	4518(6)	38	123	22	70	24	−34
N (4)	3601(11)	−1084(20)	2873(7)	55	117	23	50	−35	9
N (5)	1205(11)	1313(19)	2986(6)	53	70	4	8	−38	15
N (6)	1386(12)	1325(21)	4619(6)	57	145	21	53	15	−03
N (7)	2935(10)	3571(21)	1254(9)	65	274	21	29	3	−11

*e.s.d.'s in parentheses.

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6) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962), p. 202

TABLE 3. CALCULATED AND OBSERVED STRUCTURE FACTORS
Columns are l, F_o, F_c. Unobserved merked by *

L	FO	FC
H,K=	0	0
2*	4	10
4	815	875
6*	7	24
8	278	293
10*	12	13
12	516	516
14*	14	14
16	263	259
18*	10	12
H,K=	1	0
1*	12	29
2	457	471
3*	7	15
4*	9	12
5*	10	4
6	333	272
7	50	46
8*	12	14
9*	10	16
10	61	71
11	17	24
12*	14	13
13	53	52
14	161	169
15	22	26
16*	14	2
17	20	19
18	51	36
19*	9	0
H,K=	2	0
0	632	632
1	47	56
2*	6	12
3	20	41
4	520	524
5	22	14
6*	9	10
7	105	105
8	418	407
9	25	17
10*	12	6
11*	14	20
12	268	255
13	47	55
14*	14	5
15*	14	0
16	133	123
17*	12	9
18*	10	3
19	22	23
H,K=	3	0
1	76	81
2*	15	58
3	35	16
4*	9	13
5	43	52
6	599	589
7	45	45
8*	15	31
9*	12	15
10	290	269
11*	14	2
12*	14	26
13	55	56
14	37	32
15*	15	18
16*	14	13
17	18	22
18	78	67
19*	7	11
H,K=	4	0
0	609	593
1	66	66
2*	9	9
3	35	24
4	110	115
5	91	84
6*	10	18
7	25	28
8	309	306
9	17	13
10*	14	13
11	20	18
12	45	54
13	18	18
14*	14	14
15*	14	2
16	18	0
17*	10	13
18*	9	11
19*	4	6
H,K=	5	0
1	43	40
2	177	166
3	24	16
4*	10	15
5	35	40
6	474	488
7*	12	3
8*	14	12
9*	14	3
10	165	175
11	38	35
12*	14	11
13	17	17
14	90	92
15	17	21
16*	10	4
17*	9	3
18	92	90
H,K=	6	0
0	30	56
1*	12	10
2*	12	15
3*	12	5
4	78	82
5	27	33
6	18	14
7	29	26
8*	14	13
9	22	26
10*	15	10
11*	14	1
12*	14	12
13*	14	9
14*	12	11
15*	10	7
16	76	64
17*	6	7
H,K=	7	0
1	29	29
2	338	319
3	29	37
4*	14	2
5	18	23
6	33	37
7*	14	1
8*	14	19
9*	14	5
10	74	69
11*	14	2
12*	14	14
13	22	23
14	148	147
15*	9	14
16*	6	9
H,K=	8	0
0	376	394
1*	14	11
2	18	7
3	48	53
4	141	131
5	30	33
6*	14	13
7*	14	3
8	25	15
9*	14	17
10*	14	15
11*	12	1
12	164	156
13*	9	1
14*	7	16
H,K=	9	0
1	20	15
2	214	207
3	33	31
4*	14	8
5	18	14
6	45	45
7*	14	5
8*	12	6
9*	12	16
10	145	128
11*	9	13
12*	7	4
H,K=	10	0
0	162	154
1	17	15
2*	12	7
3	22	25
4	145	128
5*	12	7
6*	12	4
7	25	26
8	146	146
9*	9	10
10*	7	0
H,K=	11	0
1*	14	24
2	87	72
3*	9	8
4*	9	0
5*	9	22
6	167	154
7*	6	2
8*	4	10
H,K=	0	1
1	55	87
2	377	404
3	84	85
4*	12	25
5	68	76
6	388	328
7	61	66
8*	12	32
9*	12	6
10	398	382
11	72	68
12	16	28
13	16	7
14	148	141
15	16	16
16	16	15
17	53	45
18	39	34
19*	10	1
H,K=	1	1
0	246	240
1	117	127
2	80	92
3	84	88
4	104	139
5	139	127
6	26	37
7	41	51
8	239	231
9	75	75
10	87	86
11	46	59
12	186	177
13	37	44
14	26	32
15*	15	11
16	46	31
17	51	53
18	44	45
19	17	17
H,K=	2	1
0	344	347
1	91	92
2	515	466
3	113	90
4	338	313
5	95	86
6	348	338
7	48	49
8	55	45
9	23	35
10	241	243
11	53	48
12	22	17
13*	15	7
14	142	146
15*	15	13
16	95	103
17	28	34
18	50	88
19*	8	10
H,K=	3	1
0	257	307
1	63	67
2	126	123
3	99	85
4	293	293
5	59	54
6	101	86
7	30	36
8	130	138
9	37	40
10	39	35
11	32	33
12	104	89
13	16	9
14	33	42
15	39	35
16	146	120
17	22	24
18	39	46
19	19	24
H,K=	4	1
0	21	13
1	26	29
2	371	360
3	44	43
4	86	53
5	43	41
6	278	284
7	19	15
8	48	50
9	39	40
10	97	90
11	33	36
12	33	27
13*	15	8
14	121	126
15	22	16
16	34	21
17	33	31
18	112	115
H,K=	5	1
0	266	284
1	17	11
2*	12	16
3	17	22
4	319	326
5	28	27
6	65	78
7	28	23
8	195	192
9	21	24
10	79	84
11	34	14
12	111	118
13*	15	6
14*	15	11
15	24	21
16	132	128
17	22	24
18	19	28
H,K=	6	1
0	150	136
1	35	34
2	144	133
3	45	45
4	140	123
5	46	48
6	148	165
7	16	11
8*	15	16
9	45	50
10	97	105
11	17	18
12	16	14
13	19	18
14	80	81
15	20	17
16	50	59
H,K=	7	1
0	229	219
1	19	20
2	70	64
3	37	40
4	204	218
5	21	18
6	79	75
7	17	9
8	203	209
9	22	27
10	17	8
11*	15	11
12	162	149
13	30	10
14	37	38
15*	14	19
16	52	60
H,K=	8	1
0	37	24
1	23	24
2	87	93
3	30	37
4	30	26
5	16	16
6	90	82
7	26	25
8	37	29
9	37	39
10	137	115
11*	14	6
12*	12	8
13	19	19
14	52	50
H,K=	9	1
0	133	154
1*	15	13
2	48	65
3	17	19
4	111	104
5	16	10
6	106	91
7	19	20
8	117	104
9*	14	11
10	79	75
11*	10	11
12	101	93
H,K=	10	1
0	43	54
1	21	20
2	124	116
3*	14	4
4	52	54
5	19	17
6	70	72
7	23	24
8	24	21
9*	8	10
10	68	72
H,K=	11	1
0	64	74
1*	10	6
2*	10	11
3*	14	18
4	66	60
5*	8	7
6*	15	11
H,K=	0	2
0	35	64
1	62	70
2*	4	10
3	57	53
4	78	93
5*	8	1
6	18	9
7	93	95
8	109	118
9	22	16
10*	13	13
11*	13	0
12	69	75
13	41	35
14*	14	11
15	23	18
16	43	40
17*	11	1
18*	9	3
19*	6	17
H,K=	1	2
0	361	348
1	140	123
2	241	250
3	76	71
4	190	179
5	66	64
6	215	231
7	30	85
8	273	275
9	27	34
10	140	169
11	31	22
12	39	42
13	48	63
14	97	95
15	22	16
16	23	25
17	20	19
18	57	58
19*	13	13
H,K=	2	2
0	241	252
1	55	44
2	644	584
3	39	38
4	217	228
5	78	67
6	228	202
7	70	64
8	152	177
9	36	31
10	41	49
11*	14	15
12	123	123
13*	15	15
14	138	155
15*	15	7
16	81	78
17*	11	7
18*	9	5
19*	4	6
H,K=	3	2
0	283	258
1	91	93
2	278	296
3	60	59
4	220	181
5	84	79
6	217	226
7	23	28
8	241	216
9	34	32
10	151	162
11	57	55
12	60	55
13*	14	14
14	121	120
15	43	41
16*	13	6
17	16	11
18	69	71
H,K=	4	2
0	369	383
1	49	45
2	32	35
3	49	48
4	306	333
5	17	23
6	30	32
7	76	64
8	226	233
9	17	19
10	63	68
11	22	19
12	161	166
13	27	20
14*	13	13
15*	13	18
16	109	109
17*	9	4
18*	11	14
H,K=	5	2
0	219	199
1	25	22
2	283	292
3	74	67
4	91	78
5	18	25
6	222	238
7	20	26
8	192	189
9	39	40
10	170	172
11	25	26
12*	14	18
13*	14	3
14	124	120
15	32	31
16	18	30
17*	6	10
H,K=	6	2
0	219	238
1	79	63
2	299	271
3	23	21
4	194	225
5	48	53
6	112	114
7	21	22
8	166	181
9*	14	9
10	30	28
11	21	27
12	123	125
13	23	22
14	114	110
15*	9	6
16	74	77
H,K=	7	2
0	93	87
1	30	31
2	184	190
3	39	43
4	126	111
5	17	19
6	165	172
7	20	12
8	116	114
9	22	22
10	135	129
11	29	22
12	36	37
13	27	21
14	78	77
15*	11	12
H,K=	8	2
0	116	118
1	32	35
2	51	48
3	22	29
4	100	104
5	36	39
6	34	45
7	20	18
8	98	91
9	34	33
10	91	84
11	18	23
12	62	63
13*	8	12
14*	4	16
H,K=	9	2
0	116	113
1*	14	11
2	67	71
3	30	38
4*	15	7
5	20	27
6	58	61
7	29	28
8	67	67
9	20	24
10	48	49
11*	15	16
12	17	26
H,K=	10	2
0	81	68
1	18	19
2	60	60
3	44	54
4	65	61
5*	11	2
6	89	87
7	17	22
8	51	48
9	22	29
H,K=	11	2
0	67	63
1*	8	4
2	32	30
3	23	30
4	20	19
5*	11	15
H,K=	0	3
1	88	98
2	399	421
3	110	93
4*	11	20
5	73	75
6	270	264
7	45	53
8*	13	27
9	48	52
10	120	106
11*	13	0
12*	14	17
13	46	44
14	140	140
15	26	34
16	20	19
17	16	9
18	86	104
H,K=	1	3
0	273	305
1	36	28
2*	8	13
3	58	42
4	286	276
5	23	14
6	23	23
7	26	33
8	150	141
9	26	30
10	71	76
11	34	33
12	117	108
13*	14	11
14	19	21
15	31	28
16	137	124
17	29	32
18	19	30
H,K=	2	3
0	164	153
1	43	48
2	199	183
3	43	46
4	61	52
5	55	55
6	181	184
7	31	38
8	117	114
9	31	42
10	135	126
11	34	32
12	117	114
13	35	34
14	85	82
15	19	22
16	16	16
17*	14	11
18	26	47
H,K=	3	3
0	251	247
1	65	66
2	28	37
3	78	77
4	268	264
5	61	43
6	24	10
7	66	68
8	285	270
9	70	63
10	83	82
11	29	41
12	172	165
13	35	32
14	26	17
15	28	34
16	64	55
17*	13	21
H,K=	4	3
0	75	83
1	32	28
2*	13	20
3	28	29
4	45	45
5	16	19
6	78	81
7	26	31
8	31	37
9*	12	7
10	122	124
11	28	27
12	26	25
13*	12	15
14	38	29
15*	14	11
16*	8	13
17*	4	9
H,K=	5	3
0	194	198
1	61	62
2	31	35
3	36	44
4	149	159
5	38	41
6	29	30
7	38	44
8	157	163
9	38	47
10	24	30
11	23	18
12	115	118
13	38	38
14*	9	14
15	23	17
16	31	31
H,K=	6	3
0	85	71
1	18	6
2	175	166
3	31	25
4	22	24
5	16	12
6	107	97
7*	14	11
8	48	57
9	23	23
10	95	91
11	23	21
12	75	73
13*	9	17
14	70	62
15*	14	19
H,K=	7	3
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4	61	74
5	27	28
6	19	14
7	43	48
8	32	28
9	31	25
10	36	45
11	31	32
12	38	35
13	21	25
14*	4	2
H,K=	8	3
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2	184	195
3	38	40
4	49	53
5	29	29
6	160	147
7	38	39
8	43	47
9	24	26
10	107	85
11*	8	14
12	24	36
H,K=	9	3
0	55	53
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2*	11	18
3	26	26
4	76	75
5	36	38
6	16	13
7	31	35
8	61	52
9*	11	7
10*	6	9
H,K=	10	3
0*	10	5
1	24	30
2	96	94
3*	14	12
4	16	21
5	26	31
6	113	116
7*	13	31
H,K=	0	4
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3	74	78
4	247	239
5	104	118
6*	9	7
7	106	115
8	329	307
9	83	76
10*	12	10
11	40	36
12	37	29
13	23	26
14*	10	7
15*	15	7
16	38	36
H,K=	1	4
0*	4	4
1	34	40
2	172	144
3*	13	5
4*	13	14
5	43	38
6	369	377
7	43	34
8	19	24
9	34	25
10	178	178
11	19	16
12*	10	8
13	18	16
14	54	56
15*	13	11
16*	12	13
H,K=	2	4
0	170	168
1	82	77
2	106	103
3	81	69
4	203	166
5	85	79
6	51	54
7	43	44
8	123	115
9	49	54
10	26	30
11	29	33
12	70	78
13	27	32
14	29	40
15	26	29
16	54	64
H,K=	3	4
0*	12	16
1	78	63
2	280	268
3	35	34
4	19	11
5	23	13
6	23	16
7	21	19
8	16	8
9	26	21
10	73	69
11	16	9
12	18	11
13	30	32
14	121	121
15*	12	7
H,K=	4	4
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1	62	53
2*	10	10
3	29	36
4	68	61
5*	14	21
6	16	16
7	19	22
8	35	45
9	17	13
10	17	16
11	19	19
12	108	121
13	21	20
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15*	14	25
H,K=	5	4
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2	162	160
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4	18	25
5	37	39
6	23	36
7*	15	11
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9	21	25
10	55	65
11	27	38
12*	8	13
13	23	29
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H,K=	6	4
0	97	90
1	26	28
2	43	56
3	19	19
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5	27	37
6	29	34
7	17	11
8	89	86
9	21	21
10	20	19
11	18	18
12	76	72
13*	6	9
H,K=	7	4
0*	12	10
1	17	13
2	23	20
3	38	44
4	16	12
5	34	43
6	161	143
7	42	47
8	17	8
9	38	45
10	93	91
11	18	23
12*	2	9
H,K=	8	4
0*	10	14
1*	10	16
2*	10	20
3	31	40
4	120	122
5	24	17
6	26	24
7	24	27
8	169	155
H,K=	9	4
0*	15	17
1*	14	14
2	46	54
3	24	34
4	19	21
5	18	26
6	134	137
7	17	28
H,K=	0	5
1	52	55
2	61	60
3	76	68
4*	12	4
5	78	64
6	102	99
7	74	67
8	17	6
9	19	14
10	19	4
11	39	43
12*	14	5
13	17	8
14	16	22
H,K=	1	5
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1*	12	28
2	25	29
3	16	18
4	142	134
5	19	16
6	68	57
7	23	22
8	71	82
9	16	18
10	54	64
11	30	37
12	34	29
13*	10	12
14*	10	14
H,K=	2	5
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1	56	54
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3	65	55
4	28	32
5	52	52
6	109	100
7	47	41
8	25	28
9	39	41
10	53	70
11	34	34
12	19	16
13	23	23
14	32	54
H,K=	3	5
0	120	122
1	32	34
2	41	59
3	30	27
4	93	80
5	23	23
6	72	59
7	32	27
8	80	84
9	21	24
10	58	71
11	43	47
12	69	94
13*	14	17
H,K=	4	5
0	21	23
1	39	32
2	144	156
3	30	24
4*	12	6
5	18	16
6	76	95
7	18	9
8*	12	10
9	43	44
10	100	139
11	19	11
12*	8	4
H,K=	5	5
0	133	141
1	54	56
2	19	17
3	41	43
4	95	86
5	41	42
6	23	22
7	34	29
8	104	93
9	32	39
10	23	25
11	34	45
H,K=	6	5
0	25	18
1	21	10
2	124	107
3*	12	0
4*	12	7
5*	12	9
6	107	85
7	19	5
8	30	26
9	16	13
10	74	78
H,K=	7	5
0	87	91
1	38	38
2	28	37
3	49	50
4	111	102
5	36	38
6	16	23
7	28	31
8	72	77
H,K=	8	5
0	43	46
1*	14	14
2	45	39
3*	8	7
4	19	19
5*	10	15

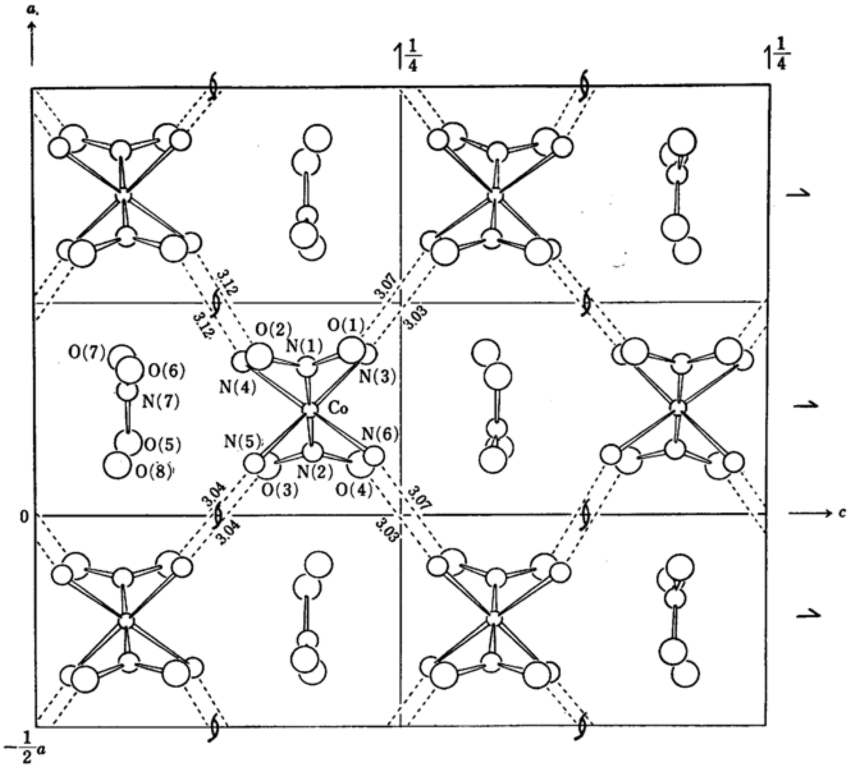

Fig. 2. Projection of the unit cell contents on the (010) plane.

Table 4. Bond distances and angles and their standard deviations

Co—N(1)	1.933(11) Å	N(1)-Co-N(3)	90.4(5)°
N(2)	1.937(11)	N(1)-Co-N(4)	89.6(5)
NH_3(3)	1.954(11)	N(1)-Co-N(5)	89.7(5)
NH_3(4)	1.986(12)	N(1)-Co-N(6)	90.0(5)
NH_3(5)	1.963(12)	N(2)-Co-N(3)	90.3(5)
NH_3(6)	1.973(12)	N(2)-Co-N(4)	89.6(5)
N(1)—O(1)	1.262(16)	N(2)-Co-N(5)	89.6(5)
O(2)	1.215(16)	N(2)-Co-N(6)	90.8(5)
N(2)—O(3)	1.235(17)	N(3)-Co-N(4)	89.5(5)
O(4)	1.260(17)	N(3)-Co-N(6)	90.9(5)
N(1)—NH_3(3)	2.758(16)	N(4)-Co-N(5)	90.6(5)
NH_3(4)	2.761(16)	N(5)-Co-N(6)	88.9(5)
NH_3(5)	2.749(15)	O(1)-N(1)-O(2)	118.7(10)
NH_3(6)	2.762(16)	Co-N(1)-O(1)	119.6(10)
N(2)—NH_3(3)	2.758(15)	Co-N(1)-O(2)	121.7(10)
NH_3(4)	2.764(16)	O(3)-N(2)-O(4)	119.8(10)
NH_3(5)	2.746(16)	Co-N(2)-O(3)	120.2(10)
NH_3(6)	2.784(16)	Co-N(2)-O(4)	120.0(10)
NH_3(3)-NH_3(4)	2.775(16)	O(5)-N(7)-O(6)	120.6(11)
NH_3(4)-NH_3(5)	2.808(16)	O(5)-N(7)-O(7)	119.9(12)
NH_3(5)-NH_3(6)	2.756(15)	O(6)-N(7)-O(7)	119.5(10)
NH_3(3)-NH_3(6)	2.798(16)		
N(7)—O(5)	1.218(14)		
O(6)	1.265(16)		
O(7)	1.277(16)		
O(5)—O(6)	2.157(14)		
O(7)	2.160(14)		
O(6)—O(7)	2.196(15)		

TABLE 5. INTERMOLECULAR CONTACTS NOT EXCEEDING 3.5 Å

N(1)—O(3) (1′)	3.315(14) Å	N(6)—O(6) (3+1″)	3.398(16) Å
O(4) (1′)	3.372(14)	O(7) (3)	3.323(16)
O(6) (4+1″)	3.388(13)	O(8) (4)	3.160(15)
N(2)—O(1) (1″)	3.352(14)	N(7)—O(2) (1)	3.180(18)
O(2) (1″)	3.323(14)	O(4) (3)	3.187(17)
O(5) (4+1″)	3.287(12)	O(8) (1′)	3.383(16)
N(3)—O(1) (1″)	3.113(16)	O(1)—O(4) (1′)	3.125(14)
O(4) (1″)	3.031(14)	O(8) (3)	3.283(15)
O(5) (3+1″)	3.298(16)	O(6) (4)	3.493(14)
O(6) (4+1″)	3.240(15)	O(7) (4)	3.222(14)
O(7) (4+1″)	3.096(15)	O(2)—O(3) (1′)	3.048(14)
O(8) (3)	3.163(15)	O(6) (1)	3.213(16)
N(4)—O(2) (1″)	3.121(16)	O(7) (1)	3.321(16)
O(2) (4+1″)	3.117(15)	O(7) (4)	3.389(14)
O(6) (1″)	3.386(16)	O(3)—O(5) (4+1″)	3.250(14)
O(6) (4+1″)	3.414(15)	O(8) (4+1″)	3.239(15)
O(7) (1″)	3.290(17)	O(4)—O(6) (3)	3.347(16)
O(7) (4+1″)	3.342(15)	O(7) (3)	3.193(16)
N(5)—O(3) (1′)	3.103(16)	O(5) (4+1″)	3.373(14)
O(3) (4)	3.041(15)	O(8) (4+1″)	3.199(14)
O(5) (1)	3.164(16)	O(5)—O(8) (1)	3.026(15)
O(8) (4)	3.114(15)	O(8) (1′)	3.099(15)
N(6)—O(1) (2)	3.068(15)	O(6)—O(8) (1′)	2.851(14)
O(4) (1′)	3.114(17)	O(7)—O(8) (1′)	3.241(14)

1)	x,	y,	z
1′)	x,	$1+y$,	z
1″)	x,	$-1+y$,	z
2)	$1/2+x$,	$1/2-y$,	$-z$
3)	$1/2-x$,	$-y$,	$1/2+z$
4)	$-x$,	$1/2+y$,	$1/2-z$

e.s.d.'s in parentheses

contents of one unit cell onto the (010) plane is presented in Fig. 2, and important intermolecular contacts (*i. e.*, those$\leq$3.5 Å) are listed in Table 5. The interatomic distances and bond angles were calculated by using program RSDA-4 written by T. Sakurai (1965).

The cobalt atoms are surrounded by nitrogen atoms of two nitro groups and of four ammonia molecules, which form a slightly distorted octahedron. Two nitrogen atoms of nitro groups are coordinated to a cobalt atom in *trans* positions.

The complex ion has an approximate symmetry *mmm*, with the first mirror containing the two nitro groups, the second containing N(3), N(4), N(5), and N(6), and the last perpendicular to the other two mirrors. In Table 6 are compared the distances between cobalt and ligand atoms and N–O distances in various complex ions. The distances are in agreement with those found in the related compounds. It is to be noted here that the Co–NO_2 distances are likely to increase with increase in number of the nitro groups. This may be partly due to the steric hindrance. Generally, the Co–N distances in Co–NH_3 seem to be longer than that in Co–NO_2.

TABLE 6. COMPARISON OF BOND LENGTHS IN VARIOUS NITROAMMINE COMPLEXES

	Co–NO_2	Co–NH_3	N–O
$[Co(NO_2)(NH_3)_5]^{2+}$ 1)	1.921 Å	1.977 Å	1.161 Å
trans-$[Co(NO_2)_2(NH_3)_4]^+$	1.935	1.969	1.243
$[Co(NO_2)_3(NH_3)_3]$ 2)	1.97	1.98	1.26
$[Co(NO_2)_4(NH_3)_2]^-$ 3)	1.96	1.98	1.23
$[Co(NO_2)_6]^{3-}$ 4)	2.03		1.11

Nitrate ion has an approximate three fold axis and N atom is 0.034 Å apart from the plane composed of three O atoms. The structure is built up of complex cations $[Co(NO_2)_2(NH_3)_4]^+$, nitrate ions and water molecules, thus being essentially ionic. The arrangement of the cobalt atoms themselves has approximately the symmetry D_{2h}^{25}-*Immm*. This characteristic feature seems to be mainly due to the presence of spatial network consisting of the complex ions. The water molecules and nitrate ions also appear to play an important role. The binding force between complex ions is mainly due to the N–H···O interactions between NH_3 and NO_2 groups. Figure 3 illustrates a network of the

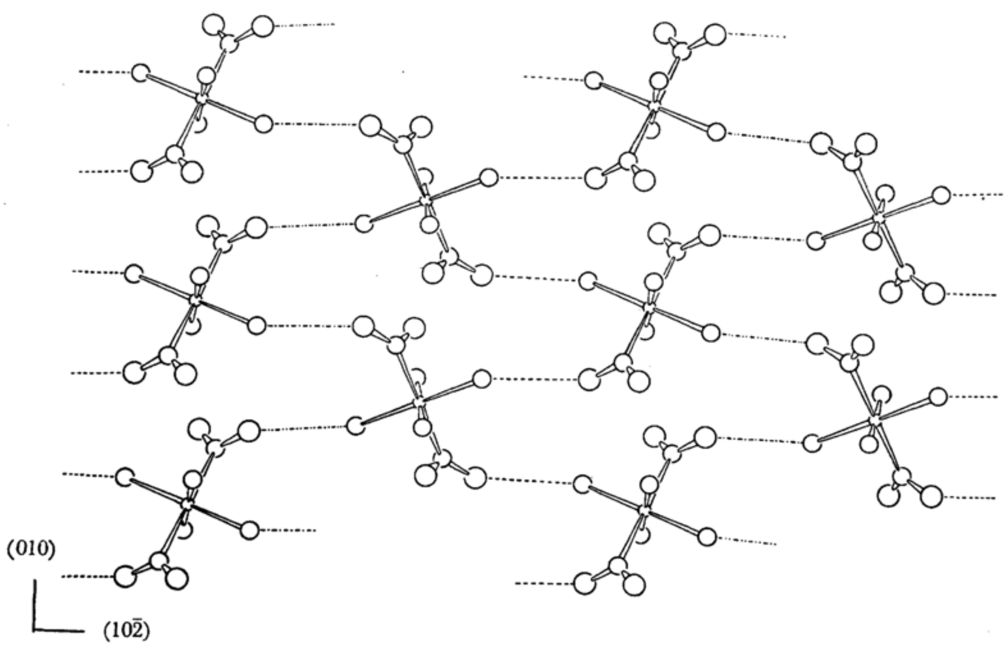

Fig. 3. Two dimensional network of complex ions found in crystal of $[Co(NO_2)_2(NH_3)_4]NO_3 \cdot H_2O$.
----: linkages of 3.041 Å; —·—: linkages of 3.068 Å; —··—: linkages of 3.031 Å

complex ions found in this structure. Each complex ion forms four N–H···O bonds with four neighboring complex ions in a similar manner to that of binding found in the structure of $[Co(NO_2)_3(NH_3)_3]$. One of the two oxygen atoms of NO_2 groups is used to form N–H···O bonds of 3.068 Å, 3.031 Å, and 3.041 Å with NH_3 of the adjacent complex ions, thus two dimensional network parallel to the plane (10$\bar{2}$) being formed. At the same time the other oxygen atom is used to form another network with N–H···O distances of 3.068 Å, 3.031 Å, and 3.117 Å in the latter, parallel to the plane (102).

Thus these layers form a three dimensional network.

The distances between two layers parallel to (10$\bar{2}$) and (102), 6.45 Å, and 6.44 Å, respectively are the same as the corresponding ones, 6.48 Å, and 6.49 Å found in the crystals of $NH_4[Co(NO_2)_4(NH_3)_2]$, but longer than that in $[Co(NO_2)_3(NH_3)_3]$ (5.10 Å). In this three dimensional network four oxygen atoms of each complex form weak N–H···O bonds with four NH_3 groups of upper and lower complex ions in the direction of the *b*-axis (3.103 Å, 3.113 Å, 3.114 Å, and 3.121 Å). This fact seems to account for the tendency for the crystal to grow along the *b*-axis. Water molecules form O–H···O hydrogen bond with oxygen of upper and lower nitrate ions in the direction of the *b*-axis (3.026 Å, and 2.851 Å). The water molecules and nitrate ions form N–H···O bond with NH_3 groups of complex ions (3.160 Å, 3.114 Å, 3.096 Å, *etc.*). These facts seem to support the conclusion drawn by Komiyama[3] that two nitro groups in *trans*-position are more likely to form N–H···O bonds than those nitro groups which are coordinated to the central cobalt atom in *trans*-positions with respect to different ligands.

The numerical calculations were carried out on the HITAC 5020 at the Computation Center, the University of Tokyo.

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