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The Crystal Structure of *cis*-Dinitrotetraamminecobalt (III) Nitrate

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The crystal structure of *cis*-dinitrotetraamminecobalt(III) nitrate, $[Co(NO_2)_2(NH_3)_4]NO_3$, has been determined from three dimensional X-ray diffraction data. The dimensions of the orthorhombic unit cell are: $a=12.19$ Å, $b=7.18$ Å, $c=10.92$ 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 methods to $R=0.095$. The complex ion has a slightly distorted octahedral coordination, with six N atoms at 1.96 ± 0.02 Å. The complexes are tightly bound together by N–H···O interactions, thus forming a three-dimensional network.

In our series of investigations into the crystal structures of nitroamminecobalt(III) complexes,[1] the crystal structure of *cis*-dinitrotetraamminecobalt-(III) nitrate, $[Co(NO_2)_2(NH_3)_4]NO_3$, has been determined. In crystals of *trans*-$[Co(NO_2)_2(NH_3)_4]$-$NO_3\cdot H_2O$,[1] $[Co(NO_2)_3(NH_3)_3]$,[2] and $NH_4[Co-(NO_2)_4(NH_3)_2]$[3] in which all the complex ions (or molecules) possess at least a pair of nitro groups coordinated in *trans*-positions, the complex ions form a three-dimensional network connected by N–H···O interactions. Moreover, the arrangement of the cobalt atoms always exhibits a higher symmetry than that of the corresponding space groups.

It seemed that it would be of interest to investigate the crystal structure of a *cis*-form of dinitrotetraamminecobalt(III) salt and compare the results with those for the *trans*-form. In this paper, the crystal structure of *cis*-$[Co(NO_2)_2(NH_3)_4]NO_3$ will be reported on.

Experimental

The crystals were prepared by the method of Jörgensen.[4] Recrystallization from water containing a small amount of acetic acid yielded prismatic crystals. The unit-cell dimensions were determined from the 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,

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1) I. Oonishi, F. Muto and Y. Komiyama, This Bulletin, **42**, 2791 (1969).

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

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

4) S. M. Jörgensen, *Z. Anorg. Allg. Chem.*, **17**, 477 (1898).

Table 1. Crystal data

cis-$[Co(NO_2)_2(NH_3)_4]NO_3 \cdot H_2O$	
Orthorhombic	$a=12.19\pm0.02$ Å
	$b=7.18\pm0.01$
	$c=10.92\pm0.02$
	$Dx=1.95$ g·cm^{-3}
	$Dm=1.95$ g·cm^{-3}
	$Z=4$

Space group D_2^4-$P2_12_12_1$
Linear absorption coefficient for Ni$K\alpha$, $\mu=44.0$ cm^{-1}

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 *c*-axis (0 to 8th layers), the *a*-axis, and *b*-axis (0th layer). Ni$K\alpha$ radiation was used throughout. The intensities were estimated visually with a standard film strip and were converted to $|F_o(hkl)|^2$ and $|F_o(hkl)|$ by applying the usual Lorentz, polarization, and spot-shape corrections. 847 independent reflections were observed. This number is about two-thirds of those within the nickel sphere. The crystal used was a rod with the dimensions of $0.2\times0.15\times1.0$ mm. No correction was made for absorption or extinction.

Structure Analysis

At first, a three-dimensional Patterson synthesis was calculated. From the Patterson maps, the position of the Co atom and the approximate orientation of the complex ion were easily deduced, but those of the nitrate anion could not be fixed. The structure factors were calculated from the parameter values of the atoms of the complex ion. At this stage the discrepancy factor, *R*, was 0.35. Preliminary three-dimensional Fourier syntheses were calculated using all the $F(hkl)$'s except $|F_{obs.}|>2|F_{cal.}|$. From these Fourier maps, the positions of the nitrate ions were determined. The discrepancy factor calculated with the parameter values of all the atoms was 0.26.

The structure thus obtained was refined by three-dimentional difference synthesis to $R=0.143$, and later again by a block-diagonal least-squares method using an HBLS-4 program written by T. Ashida. In this least-squares calculation, anisotropic temperature factors were introduced and six cycles of refinement were carried out. A weighting scheme employed was:

$\sqrt{w}=0.2$ if $F_0 \leqq F_{min.}$ $(=5.5)$

$\sqrt{w}=1.0$ if $F_{min.}<F_0 \leqq F_{max.}$ $(=100.0)$

$\sqrt{w}=F_{max.}/F_0$ if $F_0>F_{max.}$

The final discrepancy factor, $R=\sum||F_0|-|F_c||/\sum|F_0|$, was 0.095 for all the reflections. The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[5] The 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, *cis*-$[Co(NO_2)_2(NH_3)_4]^+$, is given in Fig. 1. The bond lengths and bond angles, with their e.s.d.'s

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

The expression of the 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	0973 (2)	0361 (3)	4599 (3)	27	91	64	4	5	−19
O(1)	0064 (12)	1262 (20)	2381 (13)	62	137	26	52	−31	−22
O(2)	1501 (9)	−0245 (19)	2143 (11)	32	169	22	−7	42	5
O(3)	2539 (9)	3064 (17)	5024 (12)	36	137	55	−101	43	−70
O(4)	3187 (9)	0785 (22)	4060 (12)	18	306	16	−50	18	−119
O(5)	2435 (12)	3949 (24)	2016 (17)	59	245	141	−100	−58	191
O(6)	3434 (13)	6148 (19)	2856 (13)	92	122	28	55	−14	−6
O(7)	4136 (13)	3997 (21)	1757 (15)	75	169	90	68	−8	−59
N(1)	0844 (9)	0500 (18)	2867 (13)	7	51	45	−18	−10	−61
N(2)	2406 (11)	1557 (20)	4549 (17)	28	132	70	−43	15	39
N(3)	1119 (12)	0229 (22)	6427 (13)	51	133	11	−18	21	−71
N(4)	−0498 (9)	−0864 (19)	4700 (17)	5	113	93	−23	24	−71
N(5)	0259 (11)	2828 (19)	4762 (19)	41	56	102	49	−2	−116
N(6)	1657 (11)	−2150 (19)	4367 (15)	35	68	42	28	35	30
N(7)	3305 (11)	4671 (22)	2223 (14)	30	106	42	−9	0	19

* e.s.d.'s in parentheses

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

TABLE 3. OBSERVED AND CALCULATED STRUCTURE FACTORS

Columns are k, F_o, F_c. Unobserved marked by *

K FO FC	K FO FC	K FO FC	K FO FC	K FO FC	K FO FC	K FO FC	K FO FC
H,L= 0 0	H,L= 14 0	2* 36 15	3 109 115	H,L= 8 3	0 264 269	7 78 107	2 361 368
2 872 943	0 209 226	3 187 178	4 127 147	0 55 57	1 235 242	H,L= 7 5	3 69 74
4 173 155	1 44 30	4* 29 32	5 122 144	1 395 402	2 224 242	0 178 154	4 150 133
6 54 0	2 92 71	5 129 127	6 176 181	2 199 205	3 125 121	1 184 180	5 63 47
8 40 44	H,L= 0 1	H,L= 12 1	H,L= 10 2	3 172 165	4 59 42	2 200 161	6 66 62
H,L= 1 0	1 411 377	0 217 232	0 139 140	4 55 61	5 57 58	3 175 162	H,L= 8 6
1 443 404	2 111 115	1 65 54	1 114 137	5 66 43	6 81 90	4 83 93	0 114 113
2 243 277	3 190 191	2 168 161	2 284 289	6 60 56	7 70 69	5 160 166	1 81 93
3 491 449	4* 29 9	3 100 113	3 104 118	H,L= 9 3	H,L= 8 4	6 41 14	2 189 188
4 393 415	5 301 313	4 150 145	4 144 166	0* 36 32	0 147 150	H,L= 8 5	3 51 14
5 228 227	6 61 57	H,L= 13 1	5* 33 23	1 62 50	1 65 64	0 210 199	4 145 160
6 189 183	7 309 319	0 96 105	6* 36 38	2 121 125	2 143 136	1 243 254	5 63 60
7* 36 13	8* 38 39	1 56 57	H,L= 11 2	3 63 71	3 165 151	2 207 194	6 153 185
8 221 236	H,L= 1 1	2 91 87	0 42 22	4 79 76	4 97 98	3 184 191	H,L= 9 6
H,L= 2 0	0 254 222	3 100 109	1 66 65	5 67 74	5 118 125	4* 35 15	0 221 202
0 55 75	1 648 633	H,L= 14 1	2 73 51	6 123 122	6 167 167	5 86 82	1 240 66
1 95 87	2 417 404	0 212 230	3 128 137	H,L= 10 3	H,L= 9 5	6 44 27	2 238 236
2 211 236	3 529 462	1 147 152	4 87 90	0 42 39	0 75 77	H,L= 9 5	3 76 58
3 393 370	4 474 447	2 96 102	5 76 93	1 100 89	1 201 215	0 253 258	4 117 122
4 130 97	5 140 112	H,L= 0 2	H,L= 12 2	2 59 45	2 172 168	1 60 37	5 131 123
5 245 243	6 64 64	0 317 259	0 44 36	3 116 131	3 177 170	2 216 198	H,L= 10 6
6 96 74	7 53 43	1 548 574	1 127 140	4 100 88	4 62 54	3 119 131	0 58 33
7 189 198	8 140 152	2 401 375	2* 36 35	5 152 159	5 161 174	4 88 64	1 211 216
8* 24 3	H,L= 2 1	3* 28 24	3 58 47	H,L= 11 3	6* 31 28	5 179 179	2 61 38
H,L= 3 0	0 671 754	4 376 362	4 71 78	0 55 47	H,L= 10 4	H,L= 10 5	3 247 216
1 689 727	1 636 641	5 54 45	H,L= 13 2	1 126 123	0* 38 20	0 139 137	4 64 70
2 258 237	2 361 398	6 63 61	0 133 123	2 135 135	1 124 127	1 58 48	H,L= 11 6
3 571 562	3 179 148	7 76 75	1 216 230	3 82 76	2 90 80	2 204 188	0 122 108
4 58 46	4 342 362	8 112 105	2 71 85	4 138 142	3 156 150	3 83 83	1 78 60
5 288 281	5 188 184	H,L= 1 2	3 136 151	5 90 89	4 72 72	4 207 199	2 145 131
6 157 163	6 93 93	0 190 222	H,L= 14 2	H,L= 12 3	5 67 60	5 67 67	3 179 178
7* 34 5	7 64 49	1 565 530	0 209 212	0 133 128	H,L= 11 4	H,L= 11 5	4 110 96
8 60 63	8 58 60	2 313 224	1 68 87	1 113 121	0* 36 29	0 179 159	H,L= 12 6
H,L= 4 0	H,L= 3 1	3 179 182	2 63 68	2 75 69	1 53 45	1 116 103	0 61 70
0 415 380	0 462 395	4 203 170	H,L= 0 3	3 144 146	2 156 161	2 156 146	1 126 118
1 420 354	1 46 44	5 130 133	1 495 541	4 86 96	3 75 67	3 92 85	2 49 54
2 781 827	2 337 323	6 120 135	2* 38 70	H,L= 13 3	4 141 143	4 81 84	H,L= 0 7
3 253 250	3 137 111	7 82 87	3 199 183	0* 38 17	5 78 83	H,L= 12 5	1 240 194
4 408 399	4 434 435	8 131 161	4 310 315	1 45 12	H,L= 12 4	0 170 173	2 78 94
5 402 406	5 231 215	H,L= 2 2	5 63 62	2 49 60	0 159 148	1 181 170	3 98 97
6 47 34	6 298 303	0 101 66	6 172 180	3 55 51	1 63 54	2 139 123	4 176 141
7 227 221	7 62 74	1 69 53	7 92 88	H,L= 14 3	2 67 74	3 157 125	5 91 70
8* 20 21	8 131 139	2 392 368	H,L= 1 3	0 138 125	3* 26 27	H,L= 13 5	6 212 203
H,L= 5 0	H,L= 4 1	3 359 338	0 254 232	1 79 78	4 94 109	0* 36 28	7 55 62
1 293 220	0 466 466	4 231 207	1 450 451	H,L= 0 4	H,L= 13 4	1 61 52	H,L= 1 7
2 397 398	1 289 258	5 273 275	2 324 278	0 869 960	0 252 263	H,L= 0 6	0 193 300
3 70 57	2 428 381	6 120 133	3 297 300	1 972 595	1 66 73	1 494 529	1 121 83
4 400 418	3 405 409	7 204 196	4 175 172	2 150 164	2 127 111	2 93 73	2 286 316
5 74 67	4 202 177	8 76 102	5 55 53	3 224 222	H,L= 0 5	3 402 317	3 162 131
6 303 332	5 283 281	H,L= 3 2	6* 38 41	4 79 67	1* 35 33	4 44 57	4 227 226
7 106 126	6* 36 33	0 88 34	7* 38 24	5 165 147	2 415 380	5 157 126	5 70 51
8 91 107	7 140 142	1 130 170	8 72 85	6 59 30	3 296 318	6 49 34	6 57 41
H,L= 6 0	8* 20 16	2 381 351	H,L= 2 3	7* 33 17	4 284 296	7 46 43	7 87 104
0 369 382	H,L= 5 1	3 246 246	0 209 252	H,L= 1 4	5 169 149	H,L= 1 6	H,L= 2 7
1 100 63	0 49 16	4 163 154	1 314 259	0 824 806	6 75 79	0 179 234	0 102 77
2 311 319	1 652 669	5 157 163	2 383 363	1 168 113	7 125 162	1 175 187	1 312 361
3 126 117	2 192 209	6 49 27	3 101 83	2 297 299	H,L= 1 5	2 61 55	2 150 113
4 72 75	3 462 450	7* 38 24	4 164 151	3 174 164	0 785 826	3 276 293	3 173 177
5 137 133	4 176 165	8* 28 34	5 176 175	4 186 178	1 153 112	4 100 70	4 85 93
6 67 62	5 131 136	H,L= 4 2	6 86 80	5 104 100	2 391 383	5 259 255	5 87 61
7 98 107	6 45 47	0 139 78	7 41 26	6 94 81	3 251 240	6 76 62	6 76 62
H,L= 7 0	7* 29 23	1 347 301	8* 21 15	7 138 140	4 234 217	7 204 196	7 50 30
1 390 435	8 44 59	2 332 332	H,L= 3 3	H,L= 2 4	5 169 152	H,L= 2 6	H,L= 3 7
2 149 134	H,L= 6 1	3 189 169	0 210 213	0 112 106	6* 36 12	0 75 42	0 197 211
3 384 398	0 332 337	4 158 147	1 114 111	1 209 210	7 116 153	1 141 145	1 135 133
4 95 90	1 296 266	5 146 138	2 162 162	2 273 260	H,L= 2 5	2 192 173	2 109 113
5 113 119	2 396 372	6 103 113	3 176 173	3 303 272	0 63 140	3 242 218	3 279 293
6 152 172	3 89 87	7 68 61	4 135 122	4 258 262	1 603 567	4 349 340	4 83 89
7* 37 11	4 93 85	8* 28 33	5 236 244	5 106 96	2 179 180	5 76 80	5 286 252
H,L= 8 0	5 139 160	H,L= 5 2	6 148 137	6 101 91	3 335 360	6 293 244	6 83 42
0 162 151	6 243 239	0 117 97	7 90 96	7 63 39	4 156 166	7 66 39	7 102 108
1 66 46	7 230 221	1 187 174	8 67 70	8 107 113	5 240 218	H,L= 3 6	H,L= 4 7
2 80 75	H,L= 7 1	2 219 223	H,L= 4 3	H,L= 3 4	6 76 61	0 399 446	0 102 94
3 270 246	0* 29 5	3 258 277	0 165 111	0 254 258	7* 29 16	1 109 114	1 137 149
4 47 12	1 250 247	4 189 194	1 373 390	1 382 379	H,L= 3 5	2 384 424	2 197 190
5 310 328	2 159 151	5 130 139	2 73 76	2 311 305	0* 26 8	3 298 293	3 208 184
6 105 102	3 171 155	6 201 209	3 328 327	3 137 123	1 92 85	4 259 225	4 171 152
7 265 282	4 117 128	7 90 118	4 236 266	4 252 259	2 210 185	5 116 121	5 83 80
H,L= 9 0	5 64 65	H,L= 6 2	5 128 118	5 69 69	3 238 240	6* 37 11	6 128 113
1 304 313	6 196 202	0 560 531	6 141 141	6 110 122	4 204 191	7 63 61	H,L= 5 7
2 325 311	7* 24 18	1 271 281	7 63 63	7 59 40	5 307 301	H,L= 4 6	0 210 193
3 106 98	H,L= 8 1	2 309 324	8 50 76	H,L= 4 4	6 139 112	0* 29 43	1 193 160
4 146 149	0 416 430	3 106 114	H,L= 5 3	0 162 127	7 145 176	1 226 234	2 255 252
5 81 71	1 168 168	4 90 101	0 317 313	1 347 374	H,L= 4 5	2 218 205	3 96 101
6 149 132	2 458 480	5 109 114	1 226 241	2 357 355	0 188 182	3 252 245	4 160 157
H,L= 10 0	3* 36 17	6 131 156	2 250 272	3 232 242	1 148 134	4 228 212	5 68 33
0 137 125	4 72 80	7 87 92	3 205 198	4 218 209	2 91 73	5 146 138	6 74 76
1 150 132	5 45 39	H,L= 7 2	4 111 113	5 202 191	3 257 250	6 180 163	H,L= 6 7
2 296 290	6 66 58	0 50 25	5 93 83	6 112 117	4 247 263	7 47 40	0 72 52
3* 37 7	7 62 66	1 306 313	6* 36 24	7 82 91	5 98 87	H,L= 5 6	1 162 157
4 152 150	H,L= 9 1	2 106 131	7 49 46	H,L= 5 4	6 207 188	0 49 40	2 176 159
5* 30 19	0 175 147	3 119 132	H,L= 6 3	0 50 32	7 51 50	1 128 111	3 108 90
6* 20 15	1 243 256	4 84 89	0 126 124	1 47 52	H,L= 5 5	2 117 112	4 85 89
H,L= 11 0	2 143 153	5 42 50	1 239 244	2 152 120	0 353 368	3 256 239	5 76 60
1 156 163	3 238 236	6 84 82	2 267 274	3 187 159	1 235 193	4 133 118	6 139 138
2 188 191	4 100 117	7 42 47	3 133 142	4 218 209	2 443 485	5 233 216	H,L= 7 7
3 78 67	5 144 154	H,L= 8 2	4 84 60	5 205 222	3 113 112	6 69 91	0 150 157
4 239 259	6 182 193	0 44 26	5 65 57	6 135 139	4 238 243	7 143 169	1 169 181
5* 24 22	H,L= 10 1	1 168 136	6* 33 21	7 169 153	5 83 106	H,L= 6 6	2 104 103
H,L= 12 0	0 53 2	2 100 110	7 113 109	H,L= 6 4	6 67 68	0 348 352	3 180 209
0 364 354	1 146 140	3 141 144	H,L= 7 3	0 131 127	7* 23 12	1 465 506	4 89 72
1 52 32	2 116 107	4 108 117	0 149 151	1 100 87	H,L= 6 5	2 66 52	5 104 94
2 114 123	3 229 234	5 41 29	1 107 112	2 107 94	0 58 36	3 174 146	H,L= 8 7
3 45 16	4 93 109	6 106 132	2 103 125	3 202 201	1 297 296	4 76 71	0 111 114
4* 34 48	5 234 238	7 85 85	3 48 26	4 87 93	2 188 178	5* 39 4	1 266 275
H,L= 13 0	6 53 75	H,L= 9 2	4 82 98	5 135 141	3 220 198	6 141 145	2 98 90
1 246 234	H,L= 11 1	0 184 174	5 70 70	6 85 83	4 159 143	H,L= 7 6	3 148 133
2 73 75	0* 36 2	1 233 248	6 140 150	7 53 50	5 89 78	0 339 370	4 63 42
3 149 143	1 131 139	2 212 210	7 110 119	H,L= 7 4	6 241 245	1 78 76	5 68 62

Table 4. Bond distances and angles and their standard deviations*

Co–N(1)	1.900 (15) Å	N(1)–Co–N(2)	91.3 (7)°
N(2)	1.948 (14)	N(1)–Co–N(4)	90.2 (6)
NH_3(3)	2.006 (14)	N(1)–Co–N(5)	90.4 (7)
NH_3(4)	1.999 (12)	N(1)–Co–N(6)	87.5 (6)
NH_3(5)	1.981 (14)	N(2)–Co–N(3)	88.2 (7)
NH_3(6)	2.003 (14)	N(2)–Co–N(5)	90.1 (6)
N(1)–O(1)	1.218 (19)	N(2)–Co–N(6)	91.1 (6)
O(2)	1.246 (17)	N(3)–Co–N(4)	90.2 (7)
N(2)–O(3)	1.211 (20)	N(3)–Co–N(5)	89.5 (7)
O(4)	1.224 (19)	N(3)–Co–N(6)	92.6 (6)
N(1)–N(2)	2.753 (20)	N(4)–Co–N(5)	89.7 (6)
NH_3(4)	2.764 (21)	N(4)–Co–N(6)	89.1 (5)
NH_3(5)	2.754 (22)	O(1)–N(1)–O(2)	114.7 (14)
NH_3(6)	2.699 (19)	Co–N(1)–O(1)	121.4 (11)
N(2)–NH_3(3)	2.752 (22)	Co–N(1)–O(2)	123.8 (10)
NH_3(5)	2.782 (19)	O(3)–N(2)–O(4)	119.2 (14)
NH_3(6)	2.821 (20)	Co–N(2)–O(3)	120.1 (11)
NH_3(3)–NH_3(4)	2.839 (21)	Co–N(2)–O(4)	120.7 (12)
NH_3(5)	2.809 (22)	O(5)–N(7)–O(6)	124.7 (16)
NH_3(6)	2.900 (21)	O(5)–N(7)–O(7)	118.5 (17)
NH_3(4)–NH_3(5)	2.808 (19)	O(6)–N(7)–O(7)	116.7 (14)
NH_3(6)	2.808 (18)		
N(7)–O(5)	1.202 (21)		
O(6)	1.275 (21)		
O(7)	1.232 (21)		
O(5)–O(6)	2.195 (22)		
O(7)	2.092 (22)		
O(6)–O(7)	2.135 (21)		

* e.s.d.'s $\times 10^3$ are given in parentheses

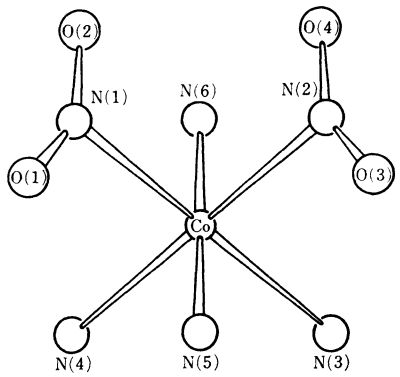

Fig. 1. A perspective drawing of the complex ion, *cis*-$[Co(NO_2)_2(NH_3)_4]^+$

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

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 *cis*-positions. The distortion of the coordinated octahedron is more marked than that of the *trans* isomer described in a previous paper.[1] For example, the N(1)–Co–N(6), N(2)–Co–N(3), N(3)–Co–N(6), and N(1)–Co–N(2) angles are 87.5, 88.2, 92.6, and 91.3° respectively. This is partly due to the repulsion of the two nitro groups in *cis*-positions. However, in the *trans* isomer[1] the greatest deviation of N–Co–N angles from 90° are 1.1°; the other deviations are within 1°. Two nitro groups are inclined in the direction opposite to the mean plane consisting of N(1), N(2), N(3), and N(4), with angles of 60 and −64° respectively. Such an inclination in the opposite direction of the nitro groups is also found in $[Co(NO_2)_3(NH_3)_3]$,[2] where the inclination angles are −16, 13, and 18° to the mean plane, consisting of four nitrogen atoms of three nitro groups and one ammonia molecule respectively. In Table 6 the distances between the central cobalt atom and the ligand atoms in various complex ions are compared. The distances are in agreement with those found in the related compounds. Generally

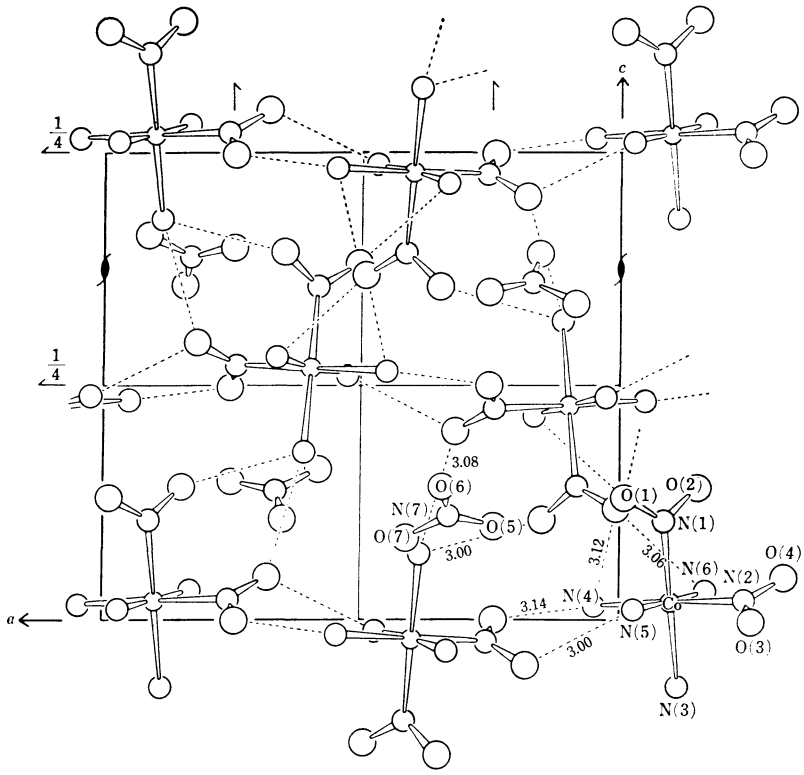

Fig. 2. Projection of the unit cell contents on the (010) plane.

TABLE 5. INTERMOLECULAR CONTACTS NOT EXCEEDING 3.5 Å

N(1)-O(5)(1)	3.280 (21) Å	N(7)-O(3)(1)	3.400 (20) Å
N(2)-O(2)(3)	3.129 (22)	O(3)(3)	3.077 (20)
O(5)(1)	3.256 (26)	O(4)(1)	3.439 (21)
N(3)-O(2)(3)	3.004 (18)	O(1)-O(5)(1)	3.498 (22)
O(4)(3+1′)	3.084 (19)	O(2)(4)	3.194 (19)
O(6)(3)	3.082 (21)	O(2)-O(3)(3)	3.289 (18)
O(7)(2)	3.176 (21)	O(4)(3+1′)	3.411 (18)
O(7)(3+1′)	3.071 (21)	O(3)-O(5)(1)	3.348 (23)
N(4)-O(1)(4+1′)	3.115 (22)	O(5)(3)	3.055 (22)
O(3)(2)	3.140 (17)	O(6)(1)	3.420 (19)
O(5)(4+1′)	3.018 (22)	O(6)(3)	3.360 (20)
O(6)(2+1′)	2.976 (23)	O(7)(3)	3.493 (20)
N(5)-O(2)(4)	3.294 (21)	O(4)-O(5)(1)	3.313 (23)
O(3)(2)	3.385 (18)	1) x, y, z	
O(4)(2)	3.004 (19)	1′) x, $-1+y$, z	
N(6)-O(1)(4+1′)	3.058 (21)	2) $1/2+x$, $1/2-y$, $-z$	
O(5)(3+1′)	3.355 (24)	3) $1/2-x$, $-y$, $1/2+z$	
O(6)(1′)	2.984 (20)	4) $-x$, $1/2+y$, $1/2-z$	
O(7)(3+1′)	3.083 (22)		

e.s.d.'s $\times 10^3$ in parentheses

the distances of Co–N (NH_3) seem to be longer than those of Co–N (NO_2). An inspection of Table 6 would seem to support in the previous paper[1] that the distances of Co–N (NO_2) increase with an increase in the number of nitro groups. In Table 7 the N–O distances and the O–N–O angles of nitro groups in various complex ions are listed. The N–O distances range from 1.16 to 1.27 Å, and the O–N–O angles, from 114 to 127°.

The nitrate ion has an approximate threefold axis, and the N atom is 0.02 Å apart from the plane composed of three O atoms. The mean value of N–O distances (1.24 Å) agrees with that found in *trans*-$[Co(NO_2)_2(NH_3)_4]NO_3 \cdot H_2O$ (1.25Å).

Table 6. The intratomic 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
$[Co(NO_2)(NH_3)_5]Br_2$[6]	1.976 (19) Å	NO_2	1.921 (21) Å	NH_3
	1.985 (15)	NH_3		
	1.972 (16)	NH_3		
$[Co(NO_2)_2(NH_3)_5]Cl_2$[7]	1.977 (16)	NO_2	1.912 (14)	NH_3
	1.957 (8)	NH_3		
	1.956 (7)	NH_3		
cis-$[Co(NO_2)_2(NH_3)_4]NO_3$	1.999 (12)	NO_2	1.948 (14)	NH_3
	2.006 (14)	NO_2	1.900 (15)	NH_3
	2.003 (14)	NH_3		
	1.981 (14)	NH_3		
trans-$[Co(NO_2)_2(NH_3)_4]NO_3$ H_2O[1]	1.954 (11)	NH_3	1.933 (11)	NO_2
	1.986 (12)	NH_3	1.937 (11)	NO_2
	1.963 (12)	NH_3		
	1.973 (12)	NH_3		
$[Co(NO_2)_3(NH_3)_3]$[2]	1.97	NO_2	1.97	NO_2
	1.98	NH_3	1.97	NO_2
	1.99	NH_3	1.96	NH_3
$NH_4[CO(NO_2)_4(NH_3)_2]$[3]	2.01	NH_3	1.96	NO_2
	2.01	NH_3	1.96	NO_2
			1.96	NO_2
			1.96	NO_2
$K[Co(NO_2)_4(NH_3)_2]$[8]	2.00	NH_3	1.96	NO_2
	2.00	NH_3	1.96	NO_2
			1.96	NO_2
			1.96	NO_2

e.s.d.'s $\times 10^3$ in parentheses

Table 7. The shape and size of nitro groups in nitroamminecobalt (III) complexes

	N–O		O–N–O
$[Co(NO_2)(NH_3)_5]Br_2$[6]	1.161 (22) Å	1.161 (22) Å	113.9 (19)°
$[Co(NO_2)(NH_3)_5]Cl_2$[7]	1.230 (11)	1.230 (11)	120.8 (14)
cis-$[Co(NO_2)_2(NH_3)_4]NO_3$	1.218 (19)	1.246 (17)	114.7 (14)
	1.211 (20)	1.224 (19)	119.2 (14)
trans-$[Co(NO_2)_2(NH_3)_4]NO_3 \cdot H_2O$[1]	1.215 (16)	1.262 (16)	118.7 (10)
	1.235 (17)	1.260 (17)	119.8 (10)
$[Co(NO_2)_3NH_3)_3]$[2]	1.24	1.25	127
	1.25	1.27	119
	1.25	1.27	121
$NH_4[(Co(NO_2)_4(NH_3)_2]^3$	1.23	1.23	116
	1.24	1.26	118
	1.20	1.22	119
	1.20	1.23	118
$K[Co(No_2)_4(NH_3)_2]$[8]	1.23	1.24	115
	1.21	1.26	116
	1.20	1.22	118
	1.20	1.23	124

e.s.d.'s $\times 10^3$ in parentheses

The structure is built up of complex cations $[Co(NO_2)_2(NH_3)_4]^+$ and nitrate ions; thus, it is essentially ionic. The closest approach between the complex ion and the nitrate ion occurs between the oxygen atom of the nitrate ion and the nitrogen atom of the coordinated ammonia. The binding

6) F. A. Cotton and W. T. Edwards, *Acta Crystallogr.*, **B24**, 474 (1968).
7) O. Bortin, *Acta Chem. Scand.*, **22**, 2890 (1968).
8) Y. Komiyama, This Bulletin, **29**, 300 (1956).

force between the complex ions is mainly due to the N–H···O interactions between NH_3 and NO_2 groups. By means of these N–H···O interactions the complex ions and the nitrate ions are bound tightly together, forming a three-dimensional network. It is interesting to note here that no special networks consisting of the complex ions are found in this structure such as those found in *trans*-$[Co(NO_2)_2(NH_3)_4]NO_3 \cdot H_2O$,[1] $[Co(NO_2)_3(NH_3)_3]$,[2] and $NH_4[Co(NO_2)_4(NH_3)_2]$,[3] in which all the complex ions (or molecules) possess at least a pair of nitro groups coordinated in *trans*- positions and in which the arrangement of the cobalt atoms themselves have a higher symmetry than that required by the corresponding space group:

	Space group	Pseudo-symmetry
trans-$[Co(NO_2)_2(NH_3)_4]NO_3 \cdot H_2O$	D_2^4-$P2_12_12_1$	D_{2h}^{25}-*Immm*
$[Co(NO_2)_3(NH_3)_3]$	D_2^4-$P2_12_12_1$	D_{2h}^{17}-*Bbmm*
$NH_4[Co(NO_2)_4(NH_3)_2]$	D_2^4-$P2_12_12_1$	D_{2h}^{16}-*Pbnm*

$[Co(NO_2)(NH_3)_5]Br_2$[6] and $[Co(NO_2)(NH_3)_5]Cl_2$[7] also do not possess such a particular type of network nor any such array of cobalt atoms with a higher symmetry.

It may be concluded that the binding force between the complex ions in the crystals of nitroamminecobalt(III) complexes are mainly the N–H···O interactions between NH_3 and NO_2 groups. In particular, if the two nitro groups and the two ammonia groups are both coordinated in *trans*-positions, the two-dimensional network formed by the complex ions possesses a particularly high symmetry and the arrangement of the cobalt atoms exhibits pseudo-symmetry.

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