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The Crystal Structure of *trans*-Dinitratobis(trimethylenediamine)-cobalt(III) Nitrate

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The crystal structure of *trans*-$[Co(NO_3)_2(tn)_2]NO_3$ (tn: H_2N–CH_2–CH_2–CH_2–NH_2) has been determined from three-dimensional X-ray diffraction data. The dimensions of the monoclinic unit cell are: $a=8.62$ Å, $b=10.04$ Å, $c=9.61$ Å, $\beta=114.0°$, and $Z=2$. The space group is $P2_1/c$. The structure has been refined by the least-squares method to $R=0.114$. The complex ion has a slightly distorted octahedral coordination, with four N atoms of trimethylenediamine molecules at 1.990 ± 0.009 Å and two O atoms of nitrate ions at 1.898 ± 0.007 Å. The two six-membered cobalt-trimethylenediamine rings are identical, as is required by the center of symmetry, and take the chair form. The complex ions and nitrate ions are tightly bound together by N–H···O hydrogen bonds in the layers parallel to the (100) plane, but there exists no evidence for hydrogen bonding between the layers.

Only one investigation[1] has been made into the structure of a complex with trimethylenediamine chelate rings. It is, though, obviously important to obtain more information about the shape and size of the six-membered chelate ring. Several crystals of cobalt complexes of the type $[CoXY(tn)_2]Z$, where X, Y, and Z are Cl, NO_2, NO_3, and NCS, were previously prepared by two of the present authors.[2] We have now initiated a structure investigation of these complexes. This paper will report on the crystal structure of *trans*-$[Co(NO_3)_2(tn)_2]NO_3$.

Another point of interest in this work is how nitrate ions coordinate to the cobalt atom. The crystal structure of the α-form of $Cu(NO_3)_2$ has been studied by Wallwork and Addison,[3] that of $Cu(NO_3)_2\cdot CH_3NO_2$, by Duffin and Wallwork,[4] and that of $Cu(NO_3)_2\cdot 2CH_3CN$, by Duffin.[5] However, the nitrate ion coordinated to the cobalt atom has not yet been reported on. It seemed that it would be of interest to compare the results in our work with those of Cu(II) complexes.[3-5]

Experimental

The *trans*-$[Co(NO_3)_2(tn)_2]NO_3$ was prepared and purified according to the method described in a previous paper.[2] The final pure product appears as thin red-violet needles elongated along the *c*-axis. The unit-cell dimensions were determined from higher-order reflections of Weissenberg photographs (Ni*K*α, $\lambda=1.6591$ Å). The systematic absences were: *h*0*l* for *l* odd and 0*k*0 for *k* 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 *c*-axis (0 to 7th layers), and the *a*- and *b*-axes (0th layer).

Ni*K*α radiation was used throughout. The intensities were estimated visually with a standard film strip and were converted to $|F_0(hkl)|^2$ and $|F_0(hkl)|$ by applying the usual Lorentz, polarization, and spot-shape corrections. No correction was made for absorption and extinction. The range of relative intensities was from 1 to 17000. 916 independent reflections fell within this range, whereas 207 others were too weak to be observed.

Table 1. Crystal data *trans*-$[Co(NO_3)_2(tn)_2]NO_3$
tn: H_2N–CH_2–CH_2–CH_2–NH_2

Monoclinic
$a=8.62\pm0.01$ Å
$b=10.04\pm0.01$
$c=9.61\pm0.01$
$\beta=114.0\pm0.5°$
$Dx=1.72\ g\cdot cm^{-3}$
$Dm=1.72\ g\cdot cm^{-3}$
$Z=2$

Space group C_{2h}^5–$P2_1/c$
Linear absorption coefficient for Ni*K*α, $\mu=33.3\ cm^{-1}$

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[*2] Deceased on Aug. 1, 1968.

1) T. Nomura, F. Marumo and Y. Saito, This Bulletin, **42**, 1016 (1969).

2) H. Kawaguchi, N. Yano and S. Kawaguchi, *ibid.*, **42**, 136 (1969).

3) S. C. Wallwork and W. E. Addison, *J. Chem. Soc.*, **1965**, 2925.

4) B. Duffin and S. C. Wallwork, *Acta Crystallogr*, **20**, 210 (1966).

5) B. Duffin, *ibid.*, **B24**, 396 (1968).

Table 2. Atomic parameters and their e.s.d.'s* ($\times 10^4$) 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	0000	0000	0000	140	65	86	−3	121	−7
O(1)	1536(8)	−391(6)	−906(7)	112	64	45	−11	135	−9
O(2)	2373(10)	1686(7)	−957(9)	175	67	105	27	161	−38
O(3)	3382(10)	76(10)	−1787(10)	167	171	158	7	281	11
O(4)	281(19)	−1072(14)	4267(17)	191	62	87	−7	199	−11
O(5)	880(19)	973(13)	4606(18)	167	48	134	−9	181	−9
O(6)	−661(20)	63(19)	5594(17)	182	159	48	−20	20	−4
N(1)	1013(10)	−1551(7)	1371(9)	118	43	43	−45	72	−47
N(2)	1570(10)	1159(8)	1640(9)	100	49	57	−17	60	−64
N(3)	2469(10)	511(9)	−1245(10)	99	99	47	−19	81	−51
N(4)	−142(46)	−15(35)	4643(31)	82	66	70	8	−377	−26
C(1)	2915(12)	−1705(10)	2034(13)	94	64	96	−55	43	−33
C(2)	3716(13)	−572(12)	3170(12)	112	101	56	−14	58	−23
C(3)	3449(12)	816(11)	2412(13)	79	77	97	−21	69	−54

*e.s.d.'s in parentheses

Structure Analysis

The presence of two formula units in a unit cell of the space group $P2_1/c$ requires the cobalt atoms to occupy one of the sets of two-fold positions. Without loss of generality they can be placed at 000 and $0\frac{1}{2}\frac{1}{2}$. On the other hand, nitrate ions have to take statistical configurations because they do not possess a center of symmetry.

At first, a three-dimensional Patterson synthesis was calculated. From the Patterson maps, the approximate positions of the lighter atoms of the complex ions were deduced, but those of the nitrate anion could not be fixed. Attempts were made to deduce the atomic parameters of the nitrate ions from two-dimensional Fourier and difference syntheses of electron density projected along the *b*- and *c*-axes, the signs of which were calculated from the parameter values of the atoms of the complex ion. From these maps, only two oxygens of the nitrate ion could be easily fixed; the others could not be fixed because of the overlapping of the electron density due to its particular statistical arrangement. Finally, the atomic parameters of the other atoms were assigned by assuming the nitrate ions to be triangular. After the inclusion of these parameters in the structure-factor calculation, these was a considerable improvement in the agreement between the observed and calculated structure factors. At this stage, the discrepancy factor, R, became 0.24 for all the observed reflections. The structure thus obtained was refined by three-dimensional Fourier and difference syntheses to $R=0.18$, and later by a block-diagonal least-squares method using a HBLS-4 program written by T. Ashida. In this least-squares method, anisotropic temperature factors were introduced and six cycles of refinement were carried out.

The weighting scheme employed was:

$$w = 0.2 \quad \text{if } F_0 \leqq F_{\text{min.}}\ (=3.0)$$

$$w = 1.0 \quad \text{if } F_{\text{min.}} < F_0 \leqq F_{\text{max.}}\ (=90.0)$$

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

The final discrepancy factor, $R=\sum||F_0|-|F_c||/\sum|F_0|$, was 0.114 for all the reflections. The atomic scattering factors were taken from the International Tables for X-ray Crystallography.⁶⁾ The final atomic parameters and their estimated standard deviations are summarized in Table 2. The observed and calculated structure factors are listed in Table 3.

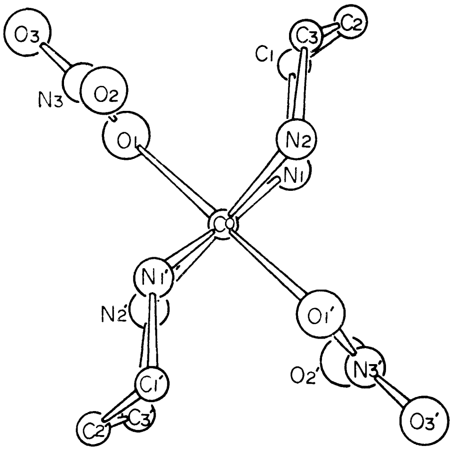

Fig. 1. A perspective drawing of the complex ion, *trans*-[Co$(NO_3)_2$(tn)$_2$]$^+$.

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

TABLE 3. OBSERVED AND CALCULATED STRUCTURE FACTORS

K	FO	FC
H,L= 0 0		
2	692	804
4	87	125
6	282	278
8	101	93
10	61	53
H,L= 1 0		
0	549	616
1	97	-99
2	274	315
3	146	-125
4	92	111
5	23	16
6	213	199
7	73	74
8	165	175
9	49	40
10	90	87
11	18	-15
H,L= 2 0		
0	92	-58
1	26	-12
2	248	237
3	18	12
4	196	212
5	47	56
6	78	92
7	90	78
8	180	185
9	40	36
10	130	112
11	23	-21
H,L= 3 0		
0	369	342
1	139	136
2	308	321
3	75	81
4	248	248
5	18	7
6	135	140
7	106	100
8	106	83
9	49	40
10	104	91
11	33	-32
H,L= 4 0		
0	37	68
1	125	92
2	42	51
3	35	-32
4	168	156
5	137	-122
6	180	159
7	21	8
8	59	55
9•	14	8
10	71	64
H,L= 5 0		
0	85	90
1	18	-13
2	170	169
3	21	-14
4	146	150
5	59	-60
6	54	47
7	101	-97
8	52	64
9	33	-31
10	61	56
H,L= 6 0		
0	154	144
1	42	-42
2	182	185
3	21	17
4	130	112
5	35	33
6	40	34
7	52	-51
8	87	86
9•	11	-7
H,L= 7 0		
0	59	64
1	21	3
2	56	92
3	21	4
4	61	53
5	30	18
6	73	71
7	26	21
H,L= 8 0		
0	99	102
1	18	19
2	82	76
3	28	25
4	52	48
5	42	35
6	45	33
H,L= 9 0		
0	45	41
1	28	-27
2	40	37
3•	11	-6
H,L= -9 1		
1	38	34
2	42	40
3	44	39
4•	5	-6
H,L= -8 1		
1	87	83
2	30	36
3	36	34
4•	9	12
5	75	68
6	22	-31
H,L= -7 1		
1	128	122
2•	13	-7
3	75	64
4	40	-38
5•	10	12
6	57	-55
7	22	25
8	28	-40
H,L= -6 1		
1	146	147
2	42	-44
3	209	232
4•	11	-20
5	57	32
6•	11	5
7•	10	11
8•	8	6
9	86	84
H,L= -5 1		
1	61	77
2•	9	20
3	216	212
4	78	83
5	178	169
6	81	67
7	95	82
8•	10	8
9	73	76
10•	6	3
H,L= -4 1		
1	172	183
2	81	67
3•	8	21
4	111	99
5	127	123
6	61	51
7	27	26
8•	11	-3
9	20	-27
10•	8	12
H,L= -3 1		
1	210	197
2	47	-52
3	97	130
4	67	65
5	131	131
6•	10	-4
7	103	94
8•	11	-13
9	36	40
10	45	52
11	50	51
H,L= -2 1		
1	212	-143
2	156	-155
3	111	131
4	25	-19
5	134	138
6	126	-122
7	182	198
8	95	-90
9	155	143
10	29	33
11	42	35
H,L= -1 1		
1	221	177
2	112	93
3	178	-116
4	107	-94
5•	8	38
6	46	-48
7	79	94
8•	11	-7
9	23	26
10	27	-32
11	37	31
H,L= 0 1		
2	169	154
3	50	84
4	163	-153
5	286	271
6	50	68
7	158	155
8	128	108
9•	11	-18
10	33	-46
11	22	18
H,L= 1 1		
1	112	147
2	88	-95
3	354	338
4	71	-52
5	323	308
6	38	-30
7	119	118
8•	11	0
9•	11	0
10•	10	-8
11•	7	-5
H,L= 2 1		
1	143	-128
2	22	35
3	232	217
4	165	137
5	90	98
6•	10	2
7•	12	-14
8•	11	-9
9•	11	14
10	25	24
11	33	31
H,L= 3 1		
1	200	-160
2	249	223
3	160	162
4•	9	19
5	154	159
6•	12	26
7	69	73
8	58	63
9	90	83
10•	8	7
11	75	67
H,L= 4 1		
1	30	54
2	155	141
3	145	143
4	21	-27
5	100	90
6	23	-28
7	48	45
8•	10	-14
9	75	66
10•	7	-19
H,L= 5 1		
1	158	135
2	76	-72
3	50	49
4	30	33
5•	11	-12
6	18	-29
7•	10	7
8	71	-67
9	47	43
H,L= 6 1		
1	78	89
2	139	-137
3	44	50
4	18	-27
5	68	65
6	16	-19
7	80	80
8	34	-28
H,L= 7 1		
1	85	80
2•	11	-9
3	83	82
4•	10	-4
5	65	57
6	28	31
7	39	40
H,L= 8 1		
1	64	60
2•	8	9
3	59	50
4	31	29
5	27	21
H,L= -9 2		
0•	12	-25
1•	9	10
2•	9	-4
3•	8	12
4	25	19
5•	6	6
H,L= -8 2		
0	91	86
1•	13	14
2	49	48
3•	12	-3
4	43	47
5•	10	-5
6	65	68
7	19	20
H,L= -7 2		
0	119	128
1	79	-72
2	154	142
3	88	-85
4	94	89
5•	12	-14
6•	12	12
7•	9	2
8	20	17
H,L= -6 2		
0	80	-84
1	170	-146
2	101	91
3	108	-104
4	186	173
5	29	33
6	71	68
7	19	-26
8	62	54
9•	8	-4
H,L= -5 2		
0	153	142
1•	9	-13
2	208	202
3•	10	-3
4	247	254
5	35	37
6	164	164
7•	13	4
8	63	50
9	16	-21
10	40	31
H,L= -4 2		
0	327	329
1	157	139
2	141	165
3	116	116
4	121	131
5	59	56
6	167	156
7	84	88
8	39	30
9•	12	19
10•	15	15
H,L= -3 2		
0	167	178
1	27	-35
2•	7	28
3	82	80
4	21	49
5	77	79
6	186	200
7•	13	-13
8	144	126
9	19	32
10	46	39
11	29	33
H,L= -2 2		
0	547	611
1	167	-158
2	315	333
3	34	-38
4	101	114
5•	9	8
6	170	184
7	103	-102
8	176	172
9•	14	-16
10	103	98
11•	8	9
H,L= -1 2		
1	141	91
2	131	170
3	160	-156
4	43	63
5	126	-136
6	103	114
7	54	[illegible]
8	180	170
9•	13	-20
10	130	119
11	64	-66
H,L= 0 2		
1	199	186
2	250	254
3	166	-113
4	253	250
5	162	-146
6	158	167
7	109	105
8	130	130
9•	13	-11
10	90	86
11	71	-70
H,L= 1 2		
0	843	864
1	37	-42
2	680	685
3	68	28
4	416	402
5	42	34
6	153	160
7•	14	-16
8	42	37
9•	13	-2
10	58	58
11•	9	-14
H,L= 2 2		
0	296	306
1	85	-91
2	311	309
3	40	-27
4	241	236
5	21	20
6	103	107
7•	14	-16
8	90	82
9	39	38
10	104	100
11	19	26
H,L= 3 2		
0	45	-18
1	77	50
2	159	178
3•	10	13
4	162	176
5•	12	0
6	59	59
7	45	44
8	154	150
9•	10	21
10	117	116
H,L= 4 2		
0	255	239
1	17	33
2	247	234
3	62	70
4	103	103
5	90	88
6	39	42
7	46	45
8	125	120
9•	9	-4
10	94	88
H,L= 5 2		
0	202	192
1	103	-97
2	57	59
3	85	-76
4•	14	15
5•	13	20
6	108	103
7•	10	-7
8	75	72
9•	6	5
H,L= 6 2		
0	116	106
1	62	-59
2	70	57
3	77	-69
4	73	66
5•	12	-20
6	113	99
7•	9	-22
8	39	38
H,L= 7 2		
0	70	54
1•	12	6
2	98	87
3•	10	13
4	85	77
5•	8	12
6	46	38
H,L= 8 2		
0	43	34
1•	8	4
2	41	34
3•	7	8
H,L=-10 3		
1	65	61
H,L= -9 3		
1•	10	-22
2•	9	7
3•	9	7
4•	8	1
5	18	23
H,L= -8 3		
1	58	61
2•	14	30
3	54	51
4•	12	1
5•	12	23
6	18	28
7	20	21
H,L= -7 3		
1	95	104
2	62	-58
3	102	116
4	20	26
5	105	104
6•	12	-5
7	66	63
8	16	-32
H,L= -6 3		
1	95	110
2	97	-96
3	87	88
4•	13	20
5	98	94
6	83	-83
7	51	55
8	106	-116
9•	8	15
H,L= -5 3		
1	320	320
2	83	84
3	169	186
4•	12	-7
5	75	72
6	39	-39
7	65	64
8	34	-36
9	49	51
10•	7	0
H,L= -4 3		
1	334	327
2	201	195
3	145	163
4•	10	-4
5	129	131
6	19	15
7	154	166
8	55	57
9	111	113
10•	8	9
H,L= -3 3		
1	421	373
2	111	101
3	84	-61
4	99	117
5	54	58
6	36	32
7	111	113
8	39	34
9	30	34
10	28	24
11	37	40
H,L= -2 3		
1	388	397
2	44	-49
3	38	55
4	52	38
5	84	88
6	43	45
7	83	108
8	49	53
9	55	61
10•	10	15
11	63	72
H,L= -1 3		
1	267	-198
2	105	-90
3	287	284
4	266	-244
5	169	175
6	57	-49
7	133	139
8	41	40
9	153	152
10•	10	-29
11	58	55
H,L= 0 3		
1	254	-192
2	179	144
3	263	246
4	50	-63
5	116	115
6	39	-47
7•	12	8
8•	13	-15
9	49	52
10	20	-41
11	32	30
H,L= 1 3		
1	220	245
2	121	119
3	201	196
4	80	65
5	188	205
6	30	-29
7	38	39
8•	14	-17
9•	12	-7
10	16	17
11	43	50
H,L= 2 3		
1	195	188
2•	14	-29
3	192	211
4	17	-13
5	176	180
6	70	-70
7	80	79
8	43	-44
9	37	33
10	36	37
H,L= 3 3		
1	31	23
2	32	34
3	140	135
4	118	111
5•	12	-4
6	20	18
7	25	28
8	40	-48
9	76	77
10•	6	14
H,L= 4 3		
1	27	34
2•	12	0
3•	12	15
4	73	78
5	25	25
6	52	57
7	69	82
8•	9	6
9	69	69
H,L= 5 3		
1	64	72
2•	13	-15
3•	13	-11
4•	13	-13
5	88	91
6•	10	17
7	71	74
8•	7	14
H,L= 6 3		
1	44	44
2•	12	12
3	36	30
4•	10	4
5	42	42
6•	8	-7
7•	13	14
H,L= 7 3		
1•	10	19
2•	10	-26
3	43	46
4	20	-22
5	25	33
H,L=-10 4		
0	102	78
1•	9	-21
2	80	69
H,L= -9 4		
0	68	59
1•	13	-9
2	104	81
3•	12	-13
4	68	55
5•	9	16
H,L= -8 4		
0	65	-69
1•	14	-8
2•	14	2
3•	14	-9
4	61	52
5	33	34
6	34	25
7	44	49
H,L= -7 4		
0	73	62
1	24	-35
2	38	37
3•	14	0
4	135	114
5	37	31
6	143	147
7•	12	-17
8	42	39
H,L= -6 4		
0	267	247
1	38	-37
2	147	125
3	22	-18
4	84	81
5	17	-19
6	106	108
7	59	-65
8•	12	2
9•	9	-21
H,L= -5 4		
0•	13	33
1	18	-19
2	107	103
3	87	-88
4	89	94
5	81	-89
6	79	77
7	17	-17
8	88	91
9•	12	10
10	25	19
H,L= -4 4		
0	200	191
1	61	53
2	243	237
3•	10	-17
4	228	226
5	38	-47
6	181	173
7	34	42
8	139	125
9•	13	15
10	47	35
H,L= -3 4		
0	376	309
1	128	113
2	153	158
3	115	114
4	138	125
5	76	81
6	173	171
7	142	127
8	24	19
9	28	28
10	26	19
11	40	-50
H,L= -2 4		
1•	12	-18
2	32	40
3	32	-32
4	167	167
5	34	32
6	159	149
7	87	95
8	52	49
9	42	43
10	48	44
11•	9	-17
H,L= -1 4		
1	67	-66
2	320	293
3	29	-37
4	397	368
5•	12	-4
6	79	82
7	45	-49
8	110	110
9	16	-22
10	91	96
11•	8	7
H,L= 0 4		
0	85	-64
1	32	31
2	159	150
3	36	37
4	177	183
5•	13	-17
6	36	35
7	63	-60
8	103	93
9	38	-41
10	126	117
11•	6	1
H,L= 1 4		
0	249	236
1	29	26
2	132	124
3	67	-53
4	72	100
5	65	-75
6	118	119
7•	14	-6
8	79	78
9•	13	-8
10	89	82
H,L= 2 4		
0	488	495
1	49	-55
2	345	354
3•	14	-15
4	159	162
5	41	44
6	103	100
7•	14	-15
8	77	78
9	18	-22
10	40	34
H,L= 3 4		
0	231	249
1	136	-133
2	186	196
3	52	-55
4	71	73
5	79	79
6	60	63
7•	14	-15
8	94	99
9•	9	0
H,L= 4 4		
0	83	93
1	45	-52
2	45	55
3	63	-63
4	57	63
5•	14	14
6	107	114
7	42	48
8	71	73
H,L= 5 4		
0	95	95
1	42	56
2	71	69
3	41	44
4	84	83
5	21	26
6	87	88
7	59	63
H,L= 6 4		
0	48	50
1•	13	3
2	49	47
3•	12	-3
4	48	44
5•	10	-17
H,L= 7 4		
0	52	42
1•	9	-16
2	41	33
3•	14	-25
H,L=-10 5		
1	54	86
2•	10	-22
H,L= -9 5		
1	83	97
2	17	-36
3	100	119
4•	13	14
5	42	53
H,L= -8 5		
1	51	-54
2	18	-16
3	17	27
4	17	7
5	54	63
6•	13	6
7	39	57
H,L= -7 5		
1	81	95
2	97	99
3	20	-20
4	35	48
5	57	72
6	17	4
7	56	72
8•	11	-6
H,L= -6 5		
1	258	250
2	47	49
3	49	43
4	18	-13
5	59	68
6	28	-40
7	80	110
8•	15	-2
9	45	59
H,L= -5 5		
1	170	160
2	93	-92
3	81	102
4	76	-91
5	18	13
6	98	-99
7	74	86
8	45	-43
9	80	92
H,L= -4 5		
1	357	310
2	25	28
3	221	214
4	40	-34
5	52	62
6	18	-4
7	47	63
8	17	1
9	74	91
10	22	-37
H,L= -3 5		
1	325	308
2	122	106
3	277	220
4	47	-63
5	195	175
6	61	67
7	107	100
8	102	97
9	81	90
10•	11	-34
H,L= -2 5		
1	148	147
2	45	41
3	219	201
4	68	61
5	144	123
6	52	56
7	42	37
8	45	43
9	17	46
10•	13	16
H,L= -1 5		
1	194	173
2•	11	-21
3	270	237
4	190	177
5	63	71
6	20	17
7	42	38
8	45	-47
9	78	98
10	47	54
H,L= 0 5		
1	54	61
2	66	-73
3	127	118
4	73	-67
5	73	79
6	59	-62
7	119	114
8	28	-32
9	117	140
10	27	34
H,L= 1 5		
1	66	67
2	37	40
3	25	31
4	47	-48
5	49	46
6	18	-7
7	95	86
8	17	-8
9	73	73
10•	15	-21
H,L= 2 5		
1	202	215
2	17	-14
3	56	59
4	57	73
5	59	64
6	20	30
7	69	81
8•	15	-25
9	18	23
H,L= 3 5		
1	175	167
2	93	-109
3	66	65
4	18	-10
5	100	109
6	18	-20
7	78	85
8•	11	-11
H,L= 4 5		
1	28	19
2	35	56
3	45	54
4	17	13
5	74	82
6•	15	9
7	42	41
H,L= 5 5		
1	17	-8
2	80	97
3	35	43
4	17	27
5	25	32
6•	10	9
H,L= 6 5		
1	37	40
2•	11	18
3	18	22
4•	8	-3
H,L=-10 6		
0	76	77
1•	8	3
2	53	51
H,L= -9 6		
0	92	101
1	19	-26
2	129	111
3•	11	5
4	85	95
5•	15	23
H,L= -8 6		
0	115	110
1•	14	24
2	100	90
3•	15	34
4	76	69
5•	11	3
6	63	59
7•	11	-19
H,L= -7 6		
0	52	52
1	99	95
2•	14	-12
3	44	57
4•	14	-20
5•	15	-17
6	46	47
7	44	55
8	52	52
H,L= -6 6		
0	109	113
1•	14	18
2	71	68
3•	14	-13
4	71	70
5•	15	-36
6	116	116
7	19	35
8	90	93
9	28	39
H,L= -5 6		
0	146	139
1	66	-78
2	160	152
3	39	-40
4	136	129
5•	14	-4
6	86	75
7	26	-39
8	39	37
9•	9	-11
H,L= -4 6		
0	32	-63
1	25	-34
2	113	101
3	115	-102
4	181	178
5	63	-67
6	66	52
7•	14	-4
8	34	32
9•	11	-19
H,L= -3 6		
0	25	-32
1	58	62
2	207	201
3	26	-35
4	294	317
5	68	-65
6	126	125
7	22	38
8	61	53
9•	11	-6
10	45	40
H,L= -2 6		
1	44	63
2	167	161
3	166	178
4	205	200
5	125	127
6	110	95
7•	14	-1
8•	15	9
9•	11	-3
10	29	19
H,L= -1 6		
0	109	121
1	38	-64
2	75	57
3	51	58
4	59	50
5	73	90
6	90	82
7	28	-45
8	41	42
9•	12	25
10	35	36
H,L= 0 6		
0	93	98
1	25	-45
2	119	116
3	42	-51
4	90	91
5•	14	-12
6	93	89
7•	14	-22
8	102	105
9•	9	-5
H,L= 1 6		
0	36	26
1•	12	9
2	59	45
3•	12	-1
4	53	34
5•	15	10
6	66	59
7•	12	0
8	96	98
9	29	-43
H,L= 2 6		
0	143	144
1	35	-45
2	42	38
3	39	-59
4	32	26
5•	14	-20
6	89	100
7•	11	-4
8	32	29
H,L= 3 6		
0	196	195
1•	14	-7
2	110	120
3•	14	-17
4	100	110
5•	12	-17
6	105	108
7•	9	7
H,L= 4 6		
0	42	41
1•	15	31
2	85	89
3•	14	19
4	79	93
5•	9	-20
6	31	31
H,L= 5 6		
0	25	13
1•	11	7
2	58	50
3•	9	-7
4	36	44
H,L= -9 7		
1	63	97
2•	11	-7
3	27	56
4	20	27
5	18	66
H,L= -8 7		
1	146	167
2	30	36
3	97	106
4•	13	7
5	29	59
6•	10	12
H,L= -7 7		
1	17	-18
2	25	23
3	17	29
4	52	-68
5•	15	24
6•	13	13
7	35	60
H,L= -6 7		
1	42	27
2	42	37
3•	15	33
4	41	34
5	58	66
6	37	47
7	42	61
8	25	41
H,L= -5 7		
1	283	151
2	27	-35
3	97	109
4	35	37
5	182	101
6•	15	15
7	56	59
8•	11	-16
9	27	48
H,L= -4 7		
1	27	62
2	145	-120
3	222	179
4	145	-106
5	58	60
6	63	-64
7	23	23
8	34	-49
9	58	66
H,L= -3 7		
1	152	148
2	17	14
3	254	239
4•	13	3
5	52	73
6	17	-18
7	30	35
8	54	-50
9	82	90
H,L= -2 7		
1	273	292
2	32	29
3	124	107
4	59	64
5	83	93
6	17	22
7	88	97
8•	13	-5
9	83	80
H,L= -1 7		
1	271	269
2	44	-46
3	22	21
4	23	34
5	51	59
6	47	50
7	93	95
8	42	42
9	35	35
H,L= 0 7		
1	155	157
2	35	-39
3	80	89
4	59	60
5	35	47
6	75	68
7	90	96
8•	13	20
H,L= 1 7		
1	54	59
2	66	-61
3	54	59
4	44	-41
5	54	66
6•	15	-5
7	92	98
8•	10	6
H,L= 2 7		
1	44	46
2•	15	21
3	17	17
4	42	-43
5	97	95
6•	11	-8
7	59	59
H,L= 3 7		
1	58	69
2	63	84
3	73	72
4•	15	15
5	73	77
6•	8	-3
H,L= 4 7		
1	92	82
2•	11	-2
3	116	97
4•	10	-19

Table 4. Bond distances and angles and their e.s.d.'s*

Complex ion			
Co-O(1)	1.898(7) Å	N(1)-Co-N(2)	87.7(4)°
N(1)	1.997(9)	O(1)-Co-N(1)	86.7(3)
N(2)	1.983(9)	O(1)-Co-N(2)	96.2(3)
N(1)-C(1)	1.507(15)	Co-N(1)-C(1)	117.9(7)
N(2)-C(3)	1.522(15)	Co-N(2)-C(3)	120.1(7)
C(1)-C(2)	1.533(17)	N(1)-C(1)-C(2)	108.8(9)
C(2)-C(3)	1.546(17)	N(2)-C(3)-C(2)	111.0(9)
N(3)-O(1)	1.336(12)	C(1)-C(2)-C(3)	113.3(10)
O(2)	1.223(13)	Co-O(1)-N(3)	125.0(6)
O(3)	1.190(14)	O(1)-N(3)-O(2)	119.8(9)
	e.s.d. × 10^3	O(1)-N(3)-O(3)	115.3(9)
		O(2)-N(3)-O(3)	124.9(10)
			e.s.d. × 10
Nitrate ion			
N(4)-O(4)	1.22(4) Å	O(4)-N(4)-O(5)	111(3)°
O(5)	1.34(4)	O(4)-N(4)-O(6)	123(4)
O(6)	1.14(4)	O(5)-N(4)-O(6)	115(3)
	e.s.d. × 10^2		e.s.d. × 1

*e.s.d.'s in parentheses

Table 5. The other important interatomic distances in the complex ion and their e.s.d.'s*

O(1)-N(1)	2.674(11) Å	O(1)-C(1)	2.899(14) Å
N(1′)	2.834(11)	C(3)	3.174(14)
N(2)	2.890(11)	O(2)-N(1′)	2.784(12)
N(2′)	2.592(11)	N(2)	2.898(12)
N(1)-N(2)	2.757(12)	C(3)	3.109(15)
N(2′)	2.871(12)	O(1)-O(2)	2.214(11)
C(1)-C(3)	2.572(17)	O(3)	2.136(13)
		O(2)-O(3)	2.139(13)

The atom with an apostrophe indicates the atom related to the one without it by a center of symmetry at the cobalt atom.

*e.s.d.'s × 10^3 in parentheses

Description of the Structure and Discussion

A perspective drawing of the complex ion, *trans*-[$Co(NO_3)_2(tn_2)$]$^+$, is illustrated in Fig. 1. The bond lengths and angles, with their e.s.d.'s as calculated on the basis of the atomic parameters in

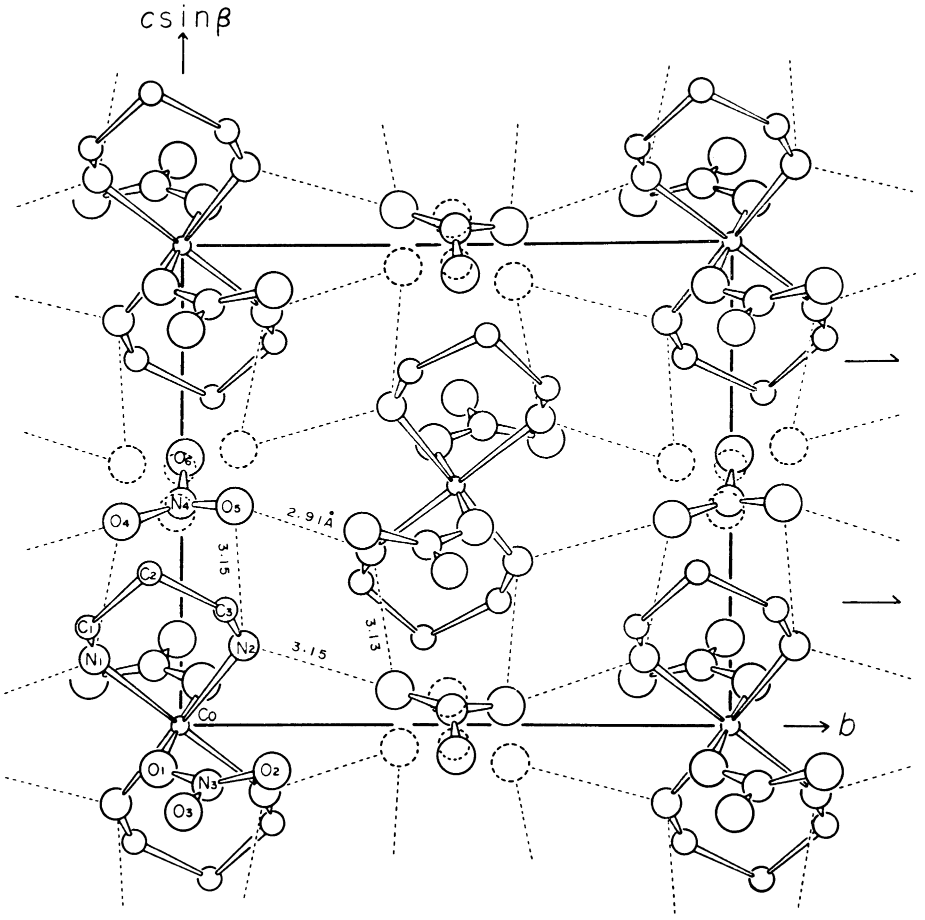

Fig. 2. The structure projected upon a plane normal to the *a*-axis.

TABLE 6. INTERMOLECULAR CONTACTS NOT EXCEEDING 3.5 Å

O(1)-O(4)(2)	3.306(18) Å	O(3)-C(3)(2′)	3.156(16) Å
O(5)(2)	3.361(19)	O(4)-N(1)(1)	3.131(19)
N(4)(2)	3.32 (4)	N(1)(3′)	3.024(19)
O(2)-O(4)(2)	3.132(18)	N(2)(4′)	3.147(19)
O(5)(3″)	2.836(20)	N(3)(2)	2.962(19)
N(2)(3″)	3.032(12)	O(5)-N(1)(4)	2.911(20)
C(3)(3″)	3.284(15)	N(2)(1)	3.145(20)
O(3)-O(3)(2′)	3.436(20)	N(2)(3)	3.394(20)
O(4)(2)	3.245(19)	O(6)-N(1)(2″)	3.418(20)
O(6)(2)	3.464(21)	N(2)(2″)	3.323(20)
N(4)(2)	3.02 (4)	C(2)(2″)	3.380(20)
C(2)(2′)	3.314(15)	N(3)-N(4)(2)	3.10 (4)

1) $x, \quad y, \quad z$
2) $-x, \quad -y, \quad -z$ 2′) $1-x, \quad -y, \quad -z,$ 2″) $-x, \quad -y, \quad 1-z$
3) $x, \quad 1/2-y, \quad 1/2+z$ 3′) $x, \quad -1/2-y, \quad 1/2+z$ 3″) $x, \quad 1/2-y, \quad -1/2+z$
4) $-x, \quad 1/2+y, \quad 1/2-z$ 4′) $-x, \quad -1/2+y, \quad 1/2-z$
e.s.d.'s $\times 10^3$ in parentheses

Table 2, are listed in Table 4, while the other important interatomic distances in the complex ion are listed in Table 5. The structure projected upon a plane normal to the *a*-axis is shown in Fig. 2. The important intermolecular contacts (*i.e.*, those less than 3.5 Å) are listed in Table 6. The interatomic distances and bond angles were calculated using a DAPH program written by T. Ashida.

The cobalt atoms are surrounded by two oxygen atoms of nitrate ions and four nitrogen atoms of trimethylenediamine molecules, which form a slightly distorted octahedron. Two nitrate ions are coordinated to a cobalt atom in *trans*-positions. The distortion of the coordinated octahedron is more marked than those in the nitroamminecobalt(III) complexes studied recently.[7,8] For example, the N(1)-Co-N(2), O(1)-Co-N(1), and O(1)-Co-N(2) angles are 87.7, 86.7, and 96.2° respectively. The N(1)-Co-N(2) angle of 87.7° in the Co-tn ring is less than those found in $[Co(tn)_3]Br_3 \cdot H_2O$[1] (96, 92, and 95°). Short contacts were found between O(2) and N(1′), and between O(2) and N(2), the distances being 2.898 and 2.784 Å respectively. A check on the angles (Co-N-O) at N(1′) and N(2) indicates that such short distances are not a intramolecular hydrogen bond: the angles are 75.4 and 78.0° respectively.

The Co-O (NO_3) distance of 1.897 Å agrees well with the corresponding values of 1.900 Å in ammonium ethylenediaminetetraacetatocobaltate(III) dihydrate.[9] The Co-N (tn) distances of 1.997 and 1.983 Å agree well with the values, 1.954—2.006 Å, in $[Co(tn)_3]Br_3 \cdot H_2O$ and nitroamminecobalt(III) complexes.[1,7,8]

The N-O (coordinated to the Co atom) distance in the nitrate ions of 1.336 Å is significantly longer than the other N-O distances of 1.223 and 1.190 Å. These values generally agree well with those found in the related compounds,[3,5] but the Co-O-N angle of 125.0° is larger than those of 110 and 113° in $Cu(NO_3)_2$,[3] and of 110 and 114° in $Cu(NO_3)_2 \cdot 2CH_3CN$.[5] This seems to be partly due to the short contacts described above. The plane of the nitrate ion coordinated to the cobalt atom is listed in Table 7. This plane makes an angle of 91.6° with the coordination plane and is approximately parallel to the direction of the N(1)—N(2) vector.

The shape and size of the trimethylenediamine chelate ring is illustrated in Fig. 3. Some least-squares and other important planes are listed in

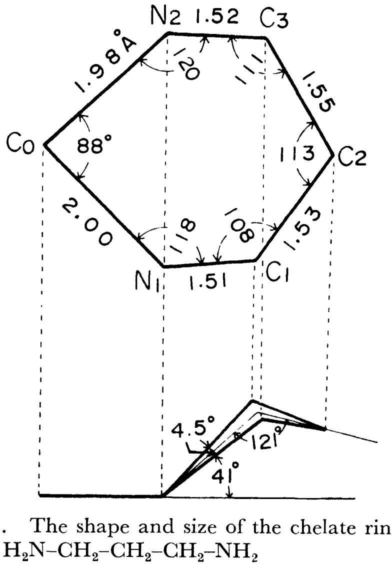

Fig. 3. The shape and size of the chelate ring.
tn: $H_2N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$

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

[8] I. Oonishi, H. Fujimaki, F. Muto and Y. Komiyama, *ibid.*, **43**, 733 (1970).

[9] H.A. Weakliem and J. L. Hoard, *J. Amer. Chem. Soc.*, **81**, 549 (1959).

Table 7. Least-squares and other planes in the complex ion and the nitrate ion

Coefficients of (least-squares) plane $AX+BY+CZ+D=0$

		A	B	C	D	($\times 10^3$)
Coordination plane	(α)	-921	94	379	0	
N(1), N(2), C(1), C(3)	(β)	427	41	-904	981	
C(1), C(2), C(3)	(γ)	-987	106	123	1656	
Nitrate ion coordinated to Co atom	(δ)	393	-120	912	18	
Nitrate ion	(η)	-541	219	-812	2506	

X (Å) $=ax+cz\cos\beta$ $Y=by$ $Z=cz\sin\beta$

Angles between the (least-squares) planes

	β	γ	δ (degree)
α	43.0	15.2	88.4
β		58.1	48.6
γ			73.2

Distances from the planes

	α	β	γ ($\times 10^3$)	δ ($\times 10^3$)		η ($\times 10^2$)	
Co	0	(981)	(1656)	Co	(18)	O(4)	0
N(1)	0	-26	(1307)	O(1)	0	O(5)	0
N(2)	0	32	(1254)	O(2)	0	O(6)	0
C(1)	(-1065)	30	0	O(3)	0	N(4)	(24)
C(2)	(-806)	(-719)	0	N(3)	(-12)		
C(3)	(-989)	-32	0				

( ) not included in the least-squares calculations

Table 7. The two six-membered Co-tn rings are identical, as is required by centrosymmetry, and take the chair form. They are nearly identical to those in $[Co(tn)_3]Br_3\cdot H_2O$[1)] except for the bond lengths of N–C. The N–C distances of 1.522 and 1.507 Å are longer than the mean values of 1.47 Å in $[Co(tn)_3]Br_3\cdot H_2O$,[1)] but not significantly so. The angle between the coordination plane (α) and the plane of N(1), N(2), C(3), and C(1) (β) is 43°, significantly larger than the values of 31°, 34°, and 38° in $[Co(tn)_3]Br_3\cdot H_2O$.[1)] From these values it appears that the chelate rings in $[Co(tn)_3]Br_3\cdot H_2O$ are, as a result of non-bonded hydrogen interactions, rather more flattened out than those in *trans*-$[Co(NO_3)_2(tn)_2]NO_3$, where there exists no such repulsion, as the two chelate rings are in *trans*-positions. The angle between the β plane and the plane of C(1), C(2), and C(3) is 122°, which value agrees well with those in $[Co(tn)_3]Br_3\cdot H_2O$ (122°, 118°, and 122°). The Co–N–C bond angles of 117.9° and 120.1° are larger than the normal tetrahedral angle, but the mean value of the N–C–C and C–C–C angles is 111.0°, which is closer to the normal tetrahedral angle. The distortions of the chelate ring and of the octahedral coordination described above appear to make the complex less stable than that with five-membered chelate rings,[10)] as in the case of $[Co(tn)_3]Br\cdot H_2O$.[1)] The bond lengths and angles in the nitrate ion are different from those in *trans*-$[Co(NO_2)_2(NH_3)_4]NO_3\cdot H_2O$[7)] and *cis*-$[Co(NO_2)_2(NH_3)_4]NO_3$.[8)] The difference seems to be due to the presence of disorder in the arrangement of nitrate ions; at any rate, it is insignificant. The structure is built up of complex cations $[Co(NO_3)_2(tn)_2]^+$ and nitrate ions; thus, it is essentially ionic. A complex ion is surrounded by four nitrate ions in the layers parallel to the (100) plane. In these layers there are hydrogen bonds between complex ions and nitrate ions. They are indicated by dotted lines in Fig. 2. There exists no hydrogen bond between the layers.

The numerical calculations were carried out on the FACOM231 computer at this University and the HITAC5020E computer at the Computer Center, The Tokyo University.

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10) J. C. Bailar, Jr., and J. B. Work, *ibid.*, **68**, 232 (1946).