ACTA CHEMICA SCANDINAVICA 22 (1968) 2890–2898

The Crystal Structure of Nitropentamminecobalt(III) Chloride, $[CoNO_2(NH_3)_5]Cl_2$

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The crystal structure of nitropentamminecobalt(III) chloride has been determined by two-dimensional Fourier methods and refined with three-dimensional data. The crystals are monoclinic (space group $C2/c$) and there are four formula units in the unit cell, which has the dimensions $a=10.327$ Å, $b=8.661$ Å, $c=10.729$ Å, $\beta=95.04°$ and $V=950.0$ Å^3. The geometrical arrangement of the ligands surrounding the cobalt atom is octahedral, with bond distances Co–N (in NH_3) $1.95_6-1.97_7$ Å, Co–N (in NO_2) 1.91_2 Å, N–O 1.23_9 Å and angle Co–N–O 119.6°. The nitropentamminecobalt(III) ions and the chloride ions are ordered in a somewhat distorted fluorite structure.

Nitropentamminecobalt(III) chloride was first prepared by Jörgensen.[1] The interest of the structure of this material lies in the fact that there is an isomeric form of the cation, nitritopentamminecobalt(III), in which the NO_2^- group is bonded to the cobalt atom through an oxygen atom, whereas it is bonded through the nitrogen atom in the nitro compound. The kinetics of the conversion of the nitritopentammine to the nitropentammine has been studied by Adell [2] based upon changes in absorption spectra.

EXPERIMENTAL

Preparation of the crystals. $[CoNO_2(NH_3)_5]Cl_2$ was prepared according to Brauer [3] by dissolving $[CoCl(NH_3)_5]Cl_2$ in ammonia, neutralizing with hydrochloric acid, adding sodium nitrite and heating. The crystals obtained on cooling the solution were washed in hydrochloric acid and ethanol. $[CoNO_2(NH_3)_5]Cl_2$ was then recrystallized from water in order to get crystals suitable for X-ray work.

X-Ray methods. The structure investigation was based on single crystal X-ray diffraction methods. Multiple-film equi-inclination integrated Weissenberg photographs about the b-axis ($h0l-h7l$) were taken with Zr-filtered Mo$K\alpha$ radiation. The intensities were estimated visually by comparison with standard scales, and were corrected for Lorentz and polarization effects. Since the crystals used were small, μr was less than 0.1, no absorption correction was applied. Extinction corrections were not made. The

three-dimensional intensity data consist of 1116 independent, observed reflections. The cell dimensions were obtained from X-ray powder photographs taken in a Guinier focusing camera with Cu$K\alpha$ radiation, using lead nitrate ($a=7.8566$ Å) [4] as an internal standard.

STRUCTURE DETERMINATION

Unit cell dimensions. The unit cell dimensions were obtained from the measured $\sin^2\theta$-values by a least-squares method using a program written by Lindqvist and Wengelin [5] for the computer SAAB D21. $[CoNO_2(NH_3)_5]Cl_2$ was then found to be monoclinic with $a=10.327\pm0.005$ Å, $b=8.661\pm0.004$ Å, $c=10.729\pm0.009$ Å, and $\beta=95.04°\pm0.04°$. Calculated and observed $\sin^2\theta$-values are given in Table 1.

Space group and cell content. In the photographs only reflections of the following types were observed:

hkl with $h+k=2n$; *h0l* with $l=2n$. Possible space groups are thus No. 15 $C2/c$ and No. 9 Cc.[6] The density of the crystals is 1.804 g/cm^3.[3] The calculated density for a unit cell containing four formula units $[CoNO_2(NH_3)_5]Cl_2$ is 1.813 g/cm^3.

Determination of atomic positions. Assuming the space group to be the centrosymmetric $C2/c$ the only possible positions of four cobalt atoms in the unit cell are 4*e* $(0,0,0;\ \frac{1}{2},\frac{1}{2},0)\pm(0,y,\frac{1}{4})$ [6] since the nitropentamminecobalt(III) ion cannot possibly have a centre of symmetry, although it may have a two-fold axis. The other parameters in the asymmetric unit were determined from a Patterson projection, P(*upw*) shown in Fig. 1. It has besides the peak at (0;0), one large peak at (0.22;0.27) which could be explained as a cobalt-chloride vector, giving the chloride ions the general position 8*f* $(0,0,0;\ \frac{1}{2},\frac{1}{2},0)\pm$

Table 1. X-Ray powder diffraction photograph of $[CoNO_2(NH_3)_5]Cl_2$ taken with Cu$K\alpha$ radiation in a Guinier camera.

h k l	$10^5\cdot\sin^2\theta_{obs}$	$10^5\cdot\sin^2\theta_{calc}$
1 1 0	1352	1354
1 1 $\bar{1}$	1779	1779
1 1 1	1967	1969
0 0 2	2080	2081
2 0 0	2248	2247
1 1 $\bar{2}$	3240	3245
1 1 2	3619	3625
2 0 $\bar{2}$	3945	3948
2 0 2	4702	4707
0 2 2	5247	5250
2 2 0	5404	5415
3 1 0	5870	5847
3 1 $\bar{1}$	6076	6082
2 2 $\bar{2}$	7121	7117
3 1 $\bar{2}$	7356	7359
0 2 3	7855	7852
1 3 $\bar{1}$	8109	8117
1 3 1	8311	8307
4 0 0	8976	8986

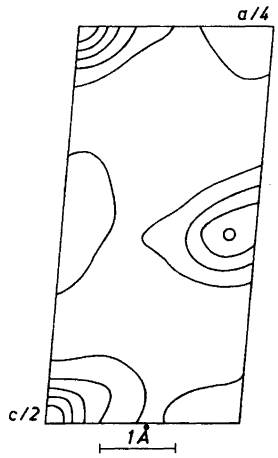

Fig. 1. Patterson projection on (010). Arbitrary units.

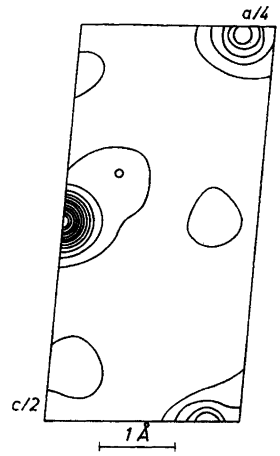

Fig. 2. Electron density projection on (010). Arbitrary units.

$\pm(x,y,z);\pm(x,\bar{y},\frac{1}{2}+z)$ with $x=0.22$ and $z=0.27-0.25=0.02$. Two small peaks at (0.01; 0.21) and (0.20; 0.49) were ascribed to cobalt-nitrogen vectors giving the x- and z-parameters (0.01;0.46) and (0.20;0.24) in the general 8-fold position for four of the ammine groups in the formula unit. The nitrogen atoms of the fifth ammine group and of the nitro group should be situated on the two-fold axis in position 4*e*.

The electron density projection on (010) is shown in Fig. 2. The signs of the structure factors have been determined from the assumed positions from the Patterson projection, P(*upw*). The projection showed the x- and z-coordinates of the oxygen atom to be (0.067; 0.192). A temperature-corrected structure factor calculation for the (*h*0*l*) zone gave a reliability index $R_{h0l}=\sum||F_o|-|F_c||/\sum|F_o|=0.14$. The y-coordinates of the atoms were determined by sterical considerations. To get the large cations as widely separated as possible the y-coordinate of the cobalt atom had to be about 0.25. The ligands attached to the cobalt atom could then be found from geometrical arguments:

Four ammine groups were given the same y-coordinate as the cobalt atom. The fifth ammine group and the nitrogen of the nitro group were assumed to have y-parameters $y_{Co}-0.25$ and $y_{Co}+0.25$, respectively. The oxygen atoms of the nitro group finally were given the value $y_{Co}+0.32$. The chloride ions should then have $y=0$ to be as widely separated from each other and from the cations as possible.

Structure refinement. The structure was refined by a series of structure factor least squares refinement cycles. The program written by Abrahamsson [7] and Aleby [8] for the SAAB D21 computer was used. The reflexions were given weights w according to Rollet's scheme $w=1/\{1+[(|F_o|-a)/b]^2\}$ with $a=88$ and $b=55$.

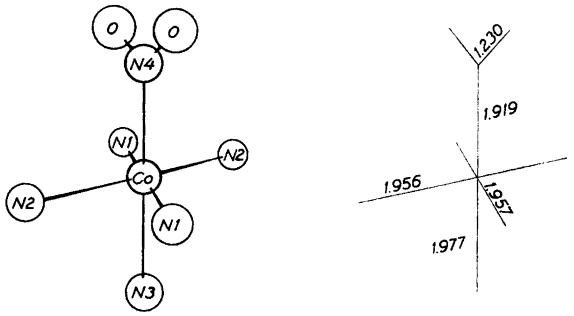

Fig. 3. The ion $[CoNO_2(NH_3)_5]^{2+}$.

The estimated standard deviations have been calculated according to Cruickshank,[9] using the formula $\delta^2(x)=a^{ji}\ (\sum w\Delta^2)/(m-n)$. The atomic scattering factors of Freeman and Watson [10] for Co, of Berghuis *et al.*[11] for Cl^-, and of Hoerni and Ibers [12] for O and N were used as given in Volume III of the *International Tables for X-ray Crystallography*, 1962.[13] The refinement converged after about five cycles to the parameters given in Table 2. All shifts in the parameters dropped to less than one fifth of the estimated standard deviations. The *R*-value for all observed reflexions *hkl* became 0.106. The observed and calculated structure-factors are given in Table 3. The contributions from the hydrogen atoms to the structure factors have not been taken into account.

DESCRIPTION OF THE STRUCTURE

The complex ion $[CoNO_2(NH_3)_5]^{2+}$ is shown in Fig. 3. All bond lengths and bond angles are given in Table 4 together with their standard deviations. The packing of the nitropentamminecobalt(III) and chloride ions is illustrated in Fig. 4, and packing distances less than 4.0 Å between the ions are collected

Table 2. Atomic coordinates (expressed as fractions of the cell edges) and isotropic thermal parameters with their standard deviations for $[CoNO_2(NH_3)_5]Cl_2$.

The temperature factor $\exp(-B\cdot\sin^2\theta/\lambda^2)$. Space group $C2/c$. 4 formula units in the unit cell. All atoms occupy the eightfold position 8*f* except Co, N_3 and N_4, which occupy the position 4*e*.

Atom	*x*	*y*	*z*	*B* Å²	$\sigma(x)$ 10^5	$\sigma(y)$ 10^5	$\sigma(z)$ 10^5	$\sigma(B)$ Å²
Co	0	0.28561	1/4	1.52	—	19	—	0.02
N_1	0.01777	0.28775	0.43300	2.53	68	100	63	0.10
N_2	0.18917	0.28685	0.24669	2.85	74	106	70	0.11
N_3	0	0.05736	1/4	3.59	—	189	—	0.22
N_4	0	0.50641	1/4	2.85	—	156	—	0.18
O	0.07372	0.57659	0.18601	3.73	75	112	70	0.14
Cl	0.20765	0.01587	0.01294	2.71	21	31	20	0.03

Table 3. Observed and calculated structure-factors. Each line contains h, $|F_o|$, and F_c.

h 0 0

4	211	176
6	88	92
8	13	21
10	74	79
14	23	32

h 0 2

-16	20	-21
-12	52	-60
-10	24	-28
-8	71	-74
-6	56	-60
-4	48	-40
-2	173	-157
2	207	-216
4	48	-43
6	75	-70
8	33	-35
10	13	-9
12	38	-42
16	20	-20

h 0 4

-14	20	22
-10	75	73
-6	78	82
-4	63	67
-2	9	-15
0	274	231
2	40	36
4	176	164
6	69	77
8	30	33
10	55	57
14	23	30

h 0 6

-12	35	-43
-10	19	-25
-8	79	-85
-6	62	-66
-4	77	-84
-2	102	-95
0	49	-51
2	175	-140
4	40	-47
6	96	-92
8	36	-37
10	19	-18
12	27	-30

h 0 8

-14	16	17
-10	50	53
-8	12	7
-6	78	77
-4	44	47
-2	14	13
0	87	83
2	11	-13
4	77	74
6	29	29
8	27	28
10	31	31
14	18	17

h 0 10

-12	17	-20
-8	42	-44
-6	23	-24
-4	67	-60
-2	53	-49
0	33	-30
2	75	-65
4	15	-12
6	61	-58
8	23	-24
10	22	-23
12	23	-23

h 0 12

-10	28	33
-6	50	50
-4	33	30
-2	38	33
0	57	53
4	41	40
6	14	11
8	22	19
10	20	16

h 0 14

-8	20	-21
-4	25	-20
-2	17	-16
0	16	-18
2	30	-28
6	22	-25

h 0 16

-6	22	23
-4	18	11
-2	19	19
0	29	25
4	25	23

h 1 0

3	115	-102
5	60	59
7	48	-46
9	13	19
11	13	-16
13	11	-12

h 1 1

-11	18	-37
-9	51	-52
-7	66	-68
-5	155	-128
-3	115	-91
3	32	-36
5	116	-96
7	45	-50
9	31	-32
11	28	-31
13	11	-10
15	12	-13

h 1 2

-15	15	14
-11	11	13
-9	33	32
-7	43	-42
-5	74	63
-3	115	-92
3	23	-19
5	83	76
7	44	-49
9	27	25
15	11	11

h 1 3

-15	14	16
-11	28	29
-9	23	24
-7	36	36
-5	93	78
-3	26	31
-1	81	74
1	46	43
3	14	17
5	67	61
7	37	40
9	31	37
11	29	31
13	13	18
15	13	14

h 1 4

-15	11	7
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-11	9	-8
-7	48	-46
-5	64	57
-3	56	-48
-1	50	46
1	42	-41
3	72	-70
5	14	12
7	49	-51
9	20	22
11	16	-16

h 1 5

-15	12	-14
-13	12	-15
-11	22	-26
-9	31	-33
-7	36	-37
-5	90	-87
-3	95	-78
-1	137	-107
1	139	-113
3	58	-51
5	85	-77
7	45	-46
9	32	-36
11	33	-34
13	13	-15
15	13	-14

h 1 6

-15	12	11
-11	14	15
-9	22	23
-5	76	66
-3	63	-54
-1	15	42
5	58	59
7	19	-18
9	30	29

h 1 7

-15	13	17
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-11	29	33
-9	25	30
-7	38	37
-5	61	59
-3	49	46
-1	82	72
1	54	60
3	34	34
5	38	37
7	25	22
9	16	18
11	17	18
13	11	11

h 1 8

-13	12	-11
-7	32	-31
-5	14	16
-3	51	-47
-1	36	37
1	15	-14
3	9	-8
5	9	7
7	35	-35
9	12	13
11	15	-14

h 1 9

-15	13	-11
-11	15	-18
-9	16	-21
-7	12	-15
-5	31	-34
-3	24	-23
-1	40	-38
1	53	-50
3	26	-26
5	37	-39
7	22	-23
9	18	-19
11	20	-21
13	12	-12

h 1 10

-5	42	39
-3	15	-19
-1	40	37
1	11	-12
5	19	21
7	9	-7
9	19	22

h 1 11

-11	18	21
-9	17	21
-7	25	26
-5	37	36
-3	33	30
-1	44	41
1	44	41
3	33	33
5	36	32
7	20	22
9	14	15
11	13	14

h 1 12

-3	35	-32
-1	10	12
1	16	-21
7	15	-14

h 1 13

-11	13	-15
-9	15	-18
-7	13	-15
-5	20	-24
-3	13	-15
-1	16	-18
1	19	-22
3	12	-12
5	18	-19
7	12	-11
9	13	-9

h 1 14

-5	11	13
-3	10	-9
-1	20	22
3	10	6

h 1 15

-7	12	12
-5	13	16
-3	13	13
-1	14	15
1	15	17
3	14	14
5	15	16
7	15	13

h 1 16

-3	14	-12
-1	11	4
1	13	-14

h 1 17

-7	12	-11
-5	18	-16
-3	13	-12
-1	15	-14
1	14	-14
3	12	-9

h 2 0

4	38	-34
6	75	-72
8	52	-54
12	33	-36
16	15	-14

h 2 1

-10	16	19
-8	12	15
-6	63	61
-4	35	36
-2	32	31
0	21	24
6	21	25
8	21	25
10	12	12

h 2 2

-14	17	23
-10	55	56
-6	72	67
-4	89	78
-2	89	-69
2	150	-116
4	61	54
6	28	29
10	46	45
14	16	18

h 2 3

-8	11	-9
-6	16	-16
-4	50	-48
0	9	-14
2	25	24
4	12	15
6	26	-28
10	17	-21

h 2 4

-14	14	-1
-12	27	-27
-8	35	-36
-6	18	-20
-4	33	-34
-2	87	-78
0	6	9
2	103	-84
4	10	11
6	59	-58
8	31	-35
10	15	-16
12	30	-36
16	16	-16

h 2 5

-6	28	30
-4	29	28
-2	58	53
0	47	46
2	13	12
4	15	17
6	12	10
8	17	19
10	13	14
12	13	12

h 2 6

-14	16	18
-10	48	51
-6	65	64
-4	55	57
-2	26	23
0	160	130
2	14	-16
4	79	68
6	15	16
8	11	14
10	31	33
14	14	17

h 2 7

-10	12	-13
-4	27	-28
-2	15	-15
0	42	-43
2	11	-14
6	11	-11
10	12	-11

h 2 8

-12	22	-24
-8	30	-34
-4	23	-26
2	63	-57
4	16	15
6	34	-35
12	16	-20

h 2 9

-2	15	15
0	15	19
2	15	18
4	12	14
12	13	8

h 2 10

-14	14	8
-10	29	31
-6	36	38
-4	11	13
-2	15	13
0	63	60
4	56	52
6	12	11
8	19	18
10	17	19

h 2 11

-10	13	-12
-4	15	-14
0	18	-23
2	13	-14
4	12	-14
6	16	-14

h 2 12

-12	16	-16
-8	28	-30
-4	28	-30
-2	15	-17
0	13	-13
2	35	-36
6	24	-28

h 2 14

-10	16	16
-6	17	22
0	15	19
4	19	22
8	13	11

h 2 16

-8	15	-14
-4	18	-19
-2	13	-8
2	17	-17
6	18	-17

h 3 0

3	14	-16
5	135	113
7	13	-10
9	40	43
11	13	14
15	16	15

h 3 1

-15	14	16
-11	37	38
-9	17	22
-7	26	31
-5	52	50
-3	14	20
3	66	64
5	26	40
7	11	9
9	17	19
11	14	13
13	14	15
15	15	9

Table 3. Continued.

h 3 2

-13	13	-17
-11	17	-21
-7	57	-61
-5	10	10
-3	80	-75
1	21	-19
3	46	+43
5	15	18
7	54	-54
9	11	10
11	19	-21

h 3 3

-15	14	-9
-13	14	-15
-11	18	+18
-9	29	-32
-7	11	-9
-5	16	-20
-3	8	5
-1	8	-8
1	81	+84
3	21	-23
5	56	-56
7	20	+18
9	12	-8
11	22	-23

h 3 4

-15	16	15
-11	13	15
-9	18	24
-7	17	-17
-5	88	83
-3	37	-35
-1	84	76
1	39	37
5	83	77
7	11	+11
9	41	43
11	13	10

h 3 5

-9	19	21
-7	38	39
-5	41	43
-1	59	54
1	47	46
3	71	68
5	55	57
7	36	35
9	21	23
11	17	14
13	14	13

h 3 6

-13	16	-18
-11	13	-13
-9	12	-13
-7	45	-47
-3	82	-77
-1	8	-11
1	57	-55
3	40	-37
7	49	-46
11	19	-23

h 3 7

-11	15	-16
-9	32	-34
-7	26	-26
-5	49	-49
-3	18	-22
-1	10	-12
1	38	-38
5	41	-43
7	17	-19
9	12	-11
11	19	-14

h 3 8

-11	17	19
-9	14	14
-5	52	51
-3	27	+25
-1	51	50
5	34	35
7	13	-11
9	22	25

h 3 9

-11	16	14
-7	23	23
-5	27	26
-3	14	17
-1	23	23
3	19	21
5	19	20
7	22	24
9	16	17
11	14	13

h 3 10

-7	19	-20
-3	46	-41
1	42	+39
3	16	-16
5	12	-10
7	25	-29
11	17	-18

h 3 11

-9	16	-18
-7	13	-13
-5	35	-35
-3	28	-25
-1	25	+25
1	31	-30
3	14	+8
5	25	+26
7	13	-14
9	14	-13
11	15	-13

h 3 12

-11	17	16
-7	13	7
-5	31	31
-1	38	35
3	14	13
5	17	18
9	15	14

h 3 13

-7	15	13
-5	16	14
-3	17	16
-1	17	18
3	14	11

h 3 14

-3	16	-18
1	19	-19

h 3 15

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-5	14	-13
-1	14	-13
1	16	+16
5	15	-13

h 3 16

-5	15	13
-1	21	17
3	15	11

h 3 17

-1	17	10
1	16	10
3	16	9

h 4 0

4	99	89
6	56	57
8	10	13
10	49	47
14	16	18

h 4 1

-14	13	-19
-12	20	+24
-10	28	-33
-8	36	+41
-6	26	-32
-4	72	-79
4	43	+41
6	61	-57
10	27	-28
12	12	-16
14	11	-9

h 4 2

-12	27	-31
-8	43	+46
-6	37	+40
-4	30	-35
-2	86	-87
2	92	+81
6	42	+42
8	28	-32
12	25	+27

h 4 3

-12	15	20
-10	34	32
-8	10	13
-6	47	47
-4	10	2
-2	33	35
0	68	68
2	52	49
4	69	70
6	25	27
8	24	28
10	13	16
12	16	17
14	12	14

h 4 4

-14	13	14
-10	38	39
-6	52	48
-4	58	53
-2	8	7
0	121	113
2	13	-15
4	77	69
6	27	28
8	15	19
10	37	38
14	16	18

h 4 5

-14	12	-13
-12	13	-13
-10	25	-30
-8	35	-38
-6	30	-34
-4	61	+61
-2	17	-18
0	81	-80
2	70	+65
4	59	+56
6	72	+68
8	14	-16
10	28	+29
12	14	-13
14	12	+10

h 4 6

-12	21	-26
-8	45	+44
-6	23	+22
-4	50	+45
-2	74	+68
0	22	-22
2	93	+78
6	44	+42
8	16	-18
10	11	-9
12	20	-22

h 4 7

-12	14	19
-10	25	27
-8	19	25
+6	56	55
-4	25	27
-2	39	38
0	30	29
2	28	27
4	43	40
6	24	25
8	20	25
10	10	10
12	12	11

h 4 8

-10	30	33
-6	40	37
-4	21	19
-2	10	9
0	69	61
2	10	-9
4	52	45
8	14	12
10	16	18
14	13	12

h 4 9

-10	13	-16
-8	16	-17
-6	17	-21
-4	42	+40
-2	8	-8
0	34	-35
2	14	-15
4	21	-20
6	34	-35
8	12	-12
10	18	-22

h 4 10

-12	15	-14
-8	25	+28
-4	26	+28
-2	25	-26
0	13	-13
2	54	-47
6	36	-33
8	11	-9
10	11	-10
12	14	-14

h 4 11

-10	12	13
-8	13	15
-6	32	31
-4	24	24
-2	42	36
0	25	25
2	28	23
4	23	21
6	19	18
8	20	19
10	12	11
12	12	11

h 4 12

-10	19	22
-6	29	29
-4	9	10
-2	15	14
0	33	30
4	30	29
8	14	11
10	12	8

h 4 13

-10	14	-13
-8	11	-9
-6	11	-13
-4	22	-23
-2	12	-9
0	22	-24
2	10	-8
4	11	-9
6	13	-13

h 4 14

-8	15	-15
-4	15	-17
2	18	-18
6	17	-17

h 4 15

-4	12	9
-2	16	15
0	12	12
2	15	14
6	12	10
8	12	9

h 4 16

-6	17	15
-2	14	11
0	15	13
4	17	14

h 4 17

-4	15	-12
-2	12	-7
0	16	+14
2	12	-8
4	14	-9

h 5 0

3	95	-95
5	41	+45
7	83	+82
9	17	+20
11	31	-31
13	14	+16

h 5 1

-13	10	-12
-9	23	+28
-7	21	-22
-5	37	+41
-3	44	+49
5	42	+40
7	24	-27
11	16	-20

h 5 2

-15	18	21
-11	24	27
-9	40	43
-7	13	14
-5	119	110
-3	7	11
5	83	82
9	42	43
11	18	17
13	11	9
15	15	14

h 5 3

-11	16	18
-7	21	24
-5	33	33
-3	15	16
-1	50	51
1	5	+8
3	27	26
5	11	12
7	19	17
9	19	22
13	12	12

h 5 4

-17	14	-12
-13	14	+16
-11	16	+17
-9	10	+10
-7	48	+49
-5	21	+21
-3	91	+85
-1	36	+41
1	58	-61
3	50	-50
5	23	-23
7	66	-63
9	14	+15
11	37	+36
13	13	-16
15	12	-10

h 5 5

-13	12	-10
-9	16	+20
-5	27	+33
-3	40	+40
-1	23	+24
1	53	-55
5	35	+31
7	14	+15
9	11	+11
11	14	-19

h 5 6

-15	19	20
+11	26	29
-9	28	32
-7	12	15
-5	90	86
-3	23	21
-1	111	95
1	59	57
3	29	26
5	66	61
9	40	37
11	12	13
13	12	12
15	12	11

h 5 7

-11	17	18
-7	17	20
-5	16	15
-3	15	17
-1	44	41
1	9	10
3	30	28
7	10	10
9	10	9

h 5 8

-13	16	-19
-11	12	-15
-9	15	-17
-7	25	+29
-5	8	-8
-3	56	+51
-1	12	-14
1	51	+49
3	24	+25
5	13	-12
7	32	-32
11	20	-22

h 5 9

-9	14	-15
-5	12	-16
-3	9	-10
-1	10	-10
1	30	-32
5	22	-22
11	11	-10

h 5 10

-15	15	12
-11	20	21
-9	12	16
-7	10	10
-5	41	42
-1	54	52
1	29	27
3	33	28
5	41	38
7	12	9
9	27	25
11	12	10

h 5 11

-11	12	12
-7	16	16
-3	11	11
-1	19	18
1	10	9
3	21	22
7	13	11

h 5 12

-13	13	-14
-11	13	-11
-9	20	-20
-7	20	-22
-5	13	-15
-3	37	-33
-1	10	+8
1	38	-35
3	16	-16
5	16	+16
7	20	-20
11	13	+13

Table 3. Continued.

h 5 13

-9	12	-11
-5	13	-13
1	12	-13
5	13	-13

h 5 14

-11	13	13
-9	12	8
-7	11	9
-5	17	20
-1	21	22
3	14	14
5	15	15
9	14	12

h 5 15

-7	12	8
3	13	9
5	12	4
7	12	7

h 5 16

-9	12	-11
-7	12	-10
-5	16	-11
-3	20	-17
1	22	-19
3	13	-8
5	15	-12

h 5 18

-1	15	12

h 6 0

4	9	11
6	8	1
8	9	-11
10	11	10
12	16	-16

h 6 1

-16	16	15
-12	17	20
-10	33	35
-8	9	16
-6	67	70
-4	25	30
-2	53	58
0	20	19
2	28	31
4	14	15
6	14	12
8	11	-11
10	14	13
12	13	-8

h 6 2

-10	22	23
-8	11	-12
-6	21	-26
-2	11	-16
4	26	32
8	11	-11
10	14	13
12	13	-8

h 6 3

-12	13	-11
-10	14	-17
-8	21	-24
-6	11	-12
-4	46	-51
0	38	-47
2	21	-24
4	9	-10
6	46	-49
10	27	-29
12	14	-14

h 6 4

-12	15	-14
-8	22	-22
-4	11	10
-2	16	-17
0	22	24
2	46	-48
6	18	-17
10	11	8
12	14	-11

h 6 5

-12	16	16
-10	21	22
-6	48	51
-4	19	23
-2	54	56
0	45	51
2	37	35
4	46	50
6	25	24
8	33	34
10	18	17
12	18	18

h 6 6

-10	20	20
-6	22	21
-2	17	-18
0	30	28
2	21	-21
4	37	33
10	12	8

h 6 7

-14	14	-16
-12	13	-12
-10	22	-24
-8	24	-24
-6	14	-19
-4	47	-48
-2	10	-10
0	51	-49
2	21	-21
4	18	-13
6	33	-32
10	20	-20
12	14	-7

h 6 8

-10	12	8
-8	21	-19
-4	11	-9
-2	10	-9
0	20	20
2	22	-21
4	14	13
6	17	-17

h 6 9

-12	15	13
-10	17	12
-6	26	25
-2	27	28
0	17	19
2	20	22
4	22	24
6	16	14
8	19	20
10	14	10
12	14	14

h 6 10

-10	13	10
-8	12	-9
-6	19	17
0	15	15
2	17	-16
4	19	16

h 6 11

-14	15	-10
-10	17	-18
-8	17	-15
-6	17	-16
-4	37	-32
-2	12	-10
0	44	-37
2	19	-18
4	20	-19
6	25	-24
8	13	-7
10	17	-15

h 6 12

-6	13	4
-4	14	-11
-2	11	-6
0	24	-18
2	14	9
6	14	-5

h 6 13

-10	16	10
-8	15	11
-6	17	17
-4	13	8
-2	16	17
0	13	9
2	15	14
8	14	9

h 6 14

-4	13	-2

h 6 15

-4	17	-14
0	18	-17
4	16	-11
6	18	-12

h 6 16

4	15	2
6	15	-5

h 6 17

-6	15	10
-4	15	9
-2	15	12
2	15	10

h 7 0

3	12	15
5	59	64
9	27	30
11	19	19
15	15	14

h 7 1

-11	12	8
-9	12	-11
-3	14	-16
3	11	16
5	8	-7
11	12	-9

h 7 2

-13	15	-17
-11	22	-24
-9	13	-13
-7	32	-36
-3	28	-36
3	37	-38
7	32	-29
11	18	-17
13	13	-9

h 7 3

-13	13	-5
-11	14	10
-9	11	-11
-3	13	-14
-1	16	21
1	17	-22
3	19	21
5	8	-8
11	12	-8

h 7 4

-15	15	12
-11	20	17
-9	21	22
-5	43	47
-3	15	-14
-1	37	43
1	35	38
3	16	20
5	58	58
9	27	28
11	15	13

h 7 5

-9	13	-12
-7	10	8
-5	8	-4
-3	8	-6
-1	15	17
1	21	-23
3	14	15
5	11	-13

h 7 6

-13	15	-14
-11	15	-17
-9	20	-20
-7	37	-39
-5	16	-18
-3	40	-44
-1	11	-14
1	40	-40
3	33	-33
5	18	-22
7	37	-35
11	20	-17

h 7 7

-11	12	7
-9	11	-9
-7	11	11
-1	9	11
1	15	-17
3	13	15
5	10	-9
11	13	-4

h 7 8

-11	16	16
-9	15	16
-7	12	8
-5	39	39
-3	9	-6
-1	28	28
1	9	8
3	10	7
5	27	29
9	19	19

h 7 9

-9	12	-8
-7	11	8
-1	11	6
1	12	-11
3	12	13
5	10	-9

h 7 10

-9	15	-11
-7	18	-18
-5	16	-13
-3	37	-31
1	27	-28
3	16	-14
5	18	-16
7	23	-24
9	14	-8
11	17	-16

h 7 11

-7	12	7
1	13	-8
3	12	9
5	14	-7

h 7 12

-11	15	14
-7	13	11
-5	29	27
-1	31	28
1	12	10
3	12	11
5	16	15
9	15	12

h 7 13

-5	13	-5
1	12	-5

h 7 14

-7	14	-7
-3	14	-14
1	17	-16

h 7 16

-5	14	12
-1	19	15
3	14	10
5	15	9

Table 4. Bond distances and angles in the nitropentamminecobalt(III) ion.

	Distance (Å)	e.s.d. (Å)		Angle (°)	e.s.d. (°)
Co—2N_1	1.956	0.007	N_1—Co—N_1	178.9	0.5
Co—2N_2	1.957	0.008	N_1—Co—N_2	90.7	0.3
Co— N_3	1.977	0.016	N_1—Co—N_3	90.5	0.3
Co— N_4	1.912	0.014	N_1—Co—N_4	89.5	0.3
N_4—O	1.230	0.011	N_2—Co—N_2	179.4	0.6
			N_2—Co—N_3	90.3	0.3
			N_2—Co—N_4	89.7	0.3
			N_3—Co—N_4	180	—
			O —N_4—O	120.8	1.4
			O —N_4—Co	119.6	0.7

Table 5. Packing distances less than 4.0 Å in $[CoNO_2(NH_3)_5]Cl_2$.

	Distance Å		Distance Å
$Cl-N_1$	3.35	$Cl-N_3$	3.45
$Cl-N_1$	3.79	$Cl-N_4$	3.77
$Cl-N_1$	3.40	$Cl-O$	3.34
$Cl-N_1$	3.46	$Cl-O$	3.81
$Cl-N_2$	3.45	N_1-N_1	3.98
$Cl-N_2$	3.87	N_1-N_4	3.86
$Cl-N_2$	3.51	N_2-N_3	3.97
$Cl-N_2$	3.35	$O-N_1$	2.97
$Cl-N_3$	3.49	$O-N_2$	3.09

Table 6. Interatomic distances in the nitropentamminecobalt(III) ion other than bond distances.

	Distance Å		Distance Å
$Co-O$	2.74	N_1-O	3.73
N_1-N_1	3.91	N_2-N_2	3.91
N_1-N_2	2.78	N_2-N_3	2.79
N_1-N_2	2.75	N_2-N_4	2.73
N_1-N_3	2.79	N_2-O	2.83
N_1-N_4	2.72	N_2-O	3.81
N_1-O	2.93	N_3-N_4	3.89

in Table 5. Distances between the atoms within the complex ion other than bond distances are given in Table 6.

The geometrical arrangement of the ligands in the complex ion is octahedral. The nitrogen atoms of four ammine groups and the cobalt atom lie in the same

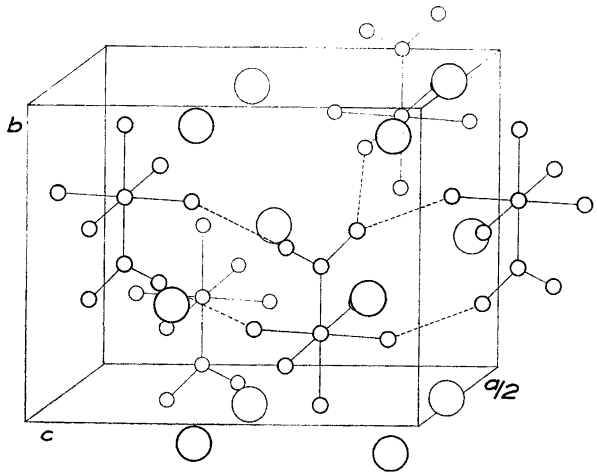

Fig. 4. The packing of ions in $[CoNO_2(NH_3)_5]Cl_2$. The dashed lines indicate possible hydrogen bonds.

plane within the limits of error with bond distances 1.95_7 Å. The bond distance between the nitrogen atom of the fifth ammine group and the cobalt atom is somewhat longer (1.97_7 Å) and the bond distance to the nitrogen atom of the nitro group somewhat shorter (1.91_2 Å). The differences are not quite large enough to be significant, since σ is 0.007—0.016 Å. The bond distance between oxygen and nitrogen in the nitro group is 1.23_0 Å and the angle Co—N—O is 119.6°. The nitropentamminecobalt(III) ions are packed in a cubic close-packed manner. The ions seem to be linked together with hydrogen bonds between the oxygen atoms of the nitro group and the ammine groups.

The chloride ions occupy tetrahedral positions between the complex ions so that the structure may be considered as a somewhat distorted fluorite structure. The shortest distance between a chloride ion and a different atom (oxygen) is 3.34 Å, and between two chloride ions is 4.16 Å.

Acknowledgements. I wish to thank Professor Cyrill Brosset for all facilities put at my disposal. My thanks are also due to Professor Georg Lundgren for valuable discussions and to Andrew Jelen, Ph.D., for correction of the English text.

This work has been supported by "Ograduerade forskares fond" and by Chalmers University of Technology, which has supplied a grant to cover the costs of the computer work, which was performed at the Göteborg Universities' Computing Centre.

REFERENCES

1. Jörgensen, S. M. *Z. anorg. Chem.* **5** (1893) 147; **19** (1899) 109.
2. Adell, B. *Svensk Kem. Tidskr.* **56** (1944) 318; **57** (1945) 260; *Z. anorg. Chem.* **252** (1944) 272.
3. Brauer, G. *Handbuch der präparativen anorganischen Chemie* II. Bd, 2. Aufl. Ferdinand Enke, Stuttgart 1962, p. 1336.
4. *International Tables for X-ray Crystallography*. Kynoch Press, Birmingham 1962, Vol. III, p. 122.
5. Lindqvist, O. and Wengelin, F. *Arkiv Kemi* **28** (1967) 179.
6. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. I, p. 101.
7. Abrahamsson, S. *Arkiv Kemi* **24** (1964) 389.
8. Aleby, S. *Arkiv Kemi* **24** (1964) 395.
9. Cruickshank, D. W. J., Pilling, D. E., Bujosa, A., Lovell, F. M. and Truter, M. R. *Computing Methods and the Phase Problem*, Pergamon, Oxford 1961, p. 32.
10. Freeman, A. J. and Watson, R. E. *Acta Cryst.* **14** (1961) 231.
11. Berghuis, J., Haanappel, I. J. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. and Veenendaal, A. L. *Acta Cryst.* **8** (1955) 478.
12. Hoerni, J. A. and Ibers, J. A. *Acta Cryst.* **7** (1954) 744.
13. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III, p. 202.

Received April 16, 1968.