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Crystal Structure of the Four-layer Orthorhombic Polytype of Potassium Hexacyanocobaltate(III)

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A four-layer orthorhombic polytype of $K_3Co(CN)_6$ has been identified and the crystal structure determined by three-dimensional X-ray methods using 854 intensities obtained by counter methods with Mo $K\alpha$ radiation at room temperature. The crystal is orthorhombic with space group $Pnc2$ and cell constants of $a=26{\cdot}69$, $b=10{\cdot}353$ and $c=8{\cdot}34$ Å. There are eight formula units per unit cell. The interdependence of parameters associated with the Co and K atoms occupying similar positions in the various layers gave rise to such large correlation coefficients that it was impossible to refine the parameters of all the atoms in the asymmetric unit simultaneously. Two groups of non-interfering parameters were therefore refined separately by full-matrix least squares to a conventional R of 0·09. Bond lengths and bond angles of the different octahedra are given and a possible distortion is discussed in terms thereof.

Introduction

A crystal of Cr-doped $K_3Co(CN)_6$ has been used in a number of nuclear magnetic resonance (n.m.r.) experiments in which, among other things, the second moment (Lourens & Reynhardt, 1971*a*) and the quadrupole interaction (Lourens & Reynhardt, 1971*b*) of the ^{59}Co nuclei were measured. With a view to the interpretation of these results in terms of the atomic environments of the ^{59}Co nuclei, the determination of this structure was undertaken, since a review of the available crystallographic literature on $K_3Co(CN)_6$ shows complete confusion.

This confusion was partially resolved by Kohn & Townes (1961) who first demonstrated the existence of the 1*M*, 2*Or*, 3*M* and 7*M* polytypes. The 4*Or* polytype should now be added to these. The early investigators obviously dealt with several of these and attempted to assign a single space group to explain all their observations.

In this way Barkhatov & Zhdanov (1942) gave cell dimensions very similar to those for the 4*Or* polytype, but by analogy with the results of Gottfried & Nagelschmidt (1930) for $K_3Fe(CN)_6$ they assigned the space group $P2_1/c$ and called it pseudo-orthorhombic. Our impression is that these workers actually encountered the 4*Or* type and not only the 1*M* type as suggested by Kohn & Townes (1961). Okaya & Pepinsky (1956), who first described the 2*Or* polytype correctly, also attempted to explain the earlier results (obtained for other polytypes) in terms of their observations.

Barkhatov (1942) proposed the first structure based on the unit cell of the 1*M* polytype. In their neutron-diffraction study Curry & Runciman (1959) accepted the special positions of the cobalt and potassium atoms suggested by Barkhatov (1942) and determined the structure in (001) projection. Values for the z coordinates of the carbon and nitrogen atoms were calculated geometrically by assuming that the $Co(CN)_6^{3-}$ groups form perfect octahedra. It was, however, impossible to calculate the z coordinate of the potassium atom in a general position.

Sample preparation

The crystal used in this investigation was grown by Rennie & Nielsen (1959) from an aqueous solution of $K_3Co(CN)_6$ containing 0·6% potassium chromicyanide and 0·1% potassium sulphate. They used a dropping temperature method. The addition of the potassium sulphate results in the growth of crystals with large *b* faces.

An atomic absorption analysis indicated that the crystal contains 0·079% chromium (per weight).

Experimental

A spherical crystal, 0·4 mm in diameter, was mounted on a goniometer with the *c* axis as rotation axis. Preliminary oscillation and Weissenberg photographs suggested a one-layer monoclinic structure with space group $P2_1/c$ (No. 14 in *International Tables for X-ray Crystallography*, 1965) as described by Curry & Runciman (1959).

The crystal was mounted on a Hilger & Watts single-crystal diffractometer. Intensity data for the sphere with $\sin\theta/\lambda \leq 0{\cdot}482$ were collected using Mo $K\alpha$ radiation. An ω–2θ scan mode was used, counting for a total of 200 sec per reflexion. This was done in 40 steps of 0·02° and counting for 5 sec per step. A total of 1786 reflexions were measured. 701 of these were not significantly above the background. The determination of the cell dimensions by a method of least squares yielded the following results: $a=6{\cdot}99$, $b=10{\cdot}353$, $c=8{\cdot}34$ Å and $\beta=107{\cdot}33°$. The density calculated for two formula units per unit cell is 1·84 g.cm^{-3}. This value compares well with the measured density of 1·81 g.cm^{-3}. Corrections for absorption, Lorentz and polarization effects were applied using a standard computer program. All Fourier syntheses were calculated by using the centrosymmetric Fourier program of P. Gantzel & H. Hope.

A three-dimensional Patterson synthesis was carried out and found to be fully consistent with the one-layer structure proposed by Curry & Runciman (1959). A three-dimensional Fourier synthesis phased on the heavy-atom positions obtained in this way, however, did not fit this structure at all. Despite all efforts to the contrary, a coordination octahedron like that around the Co atom at (000) persistently occurred around the K atom at $(00\frac{1}{2})$. This suggested either a disordered structure or a polytype as described by Kohn & Townes (1961), but with one half of the layers shifted through half a cell translation along **c**.

An ($h1l$) precession photograph, similar to those taken by Kohn & Townes (1961) to identify the different polytypes, was taken. This photograph revealed a four-layer orthorhombic structure not previously reported. The previously measured intensities were examined carefully to confirm that the crystal system was in fact orthorhombic.

The new cell dimensions are: $a=26{\cdot}69$, $b=10{\cdot}353$, $c=8{\cdot}34$ Å.

The length of the *a* axis is twice the length of the corresponding axis of the 20*r* polytype described by Okaya & Pepinski (1956). The *h* indices of the measured intensities were transformed to fit the new cell. This reduced the number of observed intensities to 699.

The same crystal was mounted on the diffractometer to measure some of the extra reflexions. Since these reflexions were almost invisible on Weissenberg photographs, it was decided to double the total counting time per intensity. 299 intensities (144 of these were unobserved) for the sphere with $\sin\theta/\lambda \leq 0{\cdot}245$ were collected and put on the same scale as the other set. The same corrections as before were made. Altogether 854 observed intensities were collected.

Determination of the structure

The reflexions which define the 40*r* rather than the 1*M* lattice occur only in limited and special regions and so give rise to the occurrence of a large number of accidental absences. Because of this no decision could be reached as to whether the *hk*0 reflexions were systematically or accidentally absent for *h* odd. It was therefore necessary to consider both of the space groups *Pnca* (No. 60) and *Pncm* (No. 53) or the non-centrosymmetric *Pnc*2 (No. 30 in *International Tables for X-ray Crystallography*, 1965). *Pnca*, however, leads to exactly the same problem encountered with $P2_1/c$. It cannot fully account for the observed electron densities since there are no symmetry elements which can correctly relate the mutually shifted subcells.

Since *Pnca* is the space group of the 20*r* variety (Okaya & Pepinsky, 1956) an attempt was nevertheless made to use this space group in a least-squares refinement, but the calculated structure factors, particularly for 111 which remained very high in comparison with the observed value, showed that the space group assignment was wrong. The minimum *R* was 0·14. The space group *Pncm* fitted neither the structure which was known in outline from our attempts with $P2_1/c$ nor the orientation of the hexacyanocobaltate octahedra as derived from n.m.r. experiments (Lourens & Reynhardt, 1971*a*). According to these there are four magnetically inequivalent cobalt sites in the unit cell. This implies four differently oriented octahedra. These four types are present in two main groups, those in one group being mirror images across the *ac* plane of those in the other group. Each of these two main groups consists of two types of octahedra, the one differing only slightly from the other. The view was taken that the two groups of octahedra described by Kohn & Townes

(1961), represent the two main groups. The only remaining space group and the only one which could be fitted successfully to the trial structure was *Pnc*2.

The program *ORFLS* of Busing, Martin & Levy (1962) was used to do a least squares refinement of atomic parameters of the trial structure on an IBM 360/65 computer. It was impossible to refine the parameters of all 34 atoms in the asymmetric unit simultaneously. This problem relates to the fact that the four subcells in the four-layer structure are very much alike. In the trial structure both Co and K atoms occurred in special positions $a(0,0,z)$ and $b(\frac{1}{2},0,z)$ of the space group with $z(\mathrm{Co})=0$ and $z(\mathrm{K})=\frac{1}{2}$. Furthermore Co and K atoms also occurred in quasi-special positions of the type $\frac{1}{4}$, 0, $\frac{1}{4}$ and $\frac{1}{4},0,\frac{3}{4}$ respectively. Since Co and K atoms have similar scattering powers these atoms appear to be related by non-space group symmetry and, (Stout & Jensen, 1968), large correlation coefficients occurred among their parameters when least squares refinement was attempted. This caused the results of successive cycles to oscillate severely and eventually to diverge. It was therefore necessary to refine the parameters of these atoms separately, one atom at a time. The rest of the parameters could be refined simultaneously.

Table 1. *Fractional coordinates* ($\times 10^4$) *and isotropic temperature factors of the atoms in the asymmetric unit*

Standard deviations are given in parentheses.

	x	y	z	B (Å^2)
Co(1)	0	0	0	1·31 (35)
Co(2)	$\frac{1}{2}$*	0	40 (20)	1·71 (39)
Co(3)	7506 (3)	8 (7)	2496 (13)	1·68 (38)
K(1)	0	0	4990 (14)	1·93 (37)
K(2)	$\frac{1}{2}$*	0	4965 (12)	1·44 (40)
K(3)	7505 (12)	9 (10)	7515 (20)	1·47 (35)
K(4)	1272 (15)	2913 (20)	53 (26)	1·69 (40)
K(5)	1252 (11)	7264 (18)	2438 (33)	1·60 (12)
K(6)	3715 (14)	2560 (23)	2463 (26)	2·07 (28)
K(7)	3714 (19)	7357 (16)	73 (36)	1·65 (33)
C(1)	470 (23)	502 (51)	1560 (61)	1·49 (44)
C(2)	− 288 (24)	1678 (64)	13 (70)	1·28 (29)
C(3)	476 (21)	515 (52)	−1554 (63)	1·52 (47)
C(4)	5467 (12)	510 (64)	−1550 (74)	1·37 (38)
C(5)	4708 (20)	1677 (52)	−1 (65)	1·54 (42)
C(6)	5481 (31)	524 (70)	1572 (71)	1·95 (50)
C(7)	7981 (54)	486 (61)	4104 (81)	1·58 (38)
C(8)	7021 (21)	− 492 (41)	911 (62)	1·33 (32)
C(9)	7033 (12)	− 522 (42)	4030 (62)	1·05 (31)
C(10)	7971 (22)	512 (52)	967 (74)	1·85 (30)
C(11)	7218 (21)	1671 (63)	2560 (71)	1·46 (21)
C(12)	7779 (23)	−1663 (54)	2446 (73)	1·28 (15)
N(1)	772 (25)	808 (61)	2512 (73)	1·13 (41)
N(2)	− 478 (21)	2706 (51)	21 (71)	2·22 (39)
N(3)	767 (20)	837 (53)	−2505 (84)	2·21 (26)
N(4)	5748 (13)	822 (46)	−2496 (60)	1·05 (33)
N(5)	4524 (13)	2697 (41)	−9 (52)	2·13 (35)
N(6)	5775 (21)	858 (72)	2530 (81)	2·66 (49)
N(7)	8272 (22)	783 (45)	5060 (93)	1·43 (51)
N(8)	6725 (13)	− 777 (54)	−28 (64)	2·65 (40)
N(9)	6756 (21)	− 831 (51)	5003 (80)	1·31 (38)
N(10)	8255 (12)	823 (40)	−80 (81)	1·28 (20)
N(11)	7046 (31)	2677 (61)	2597 (91)	3·41 (51)
N(12)	7959 (21)	−2671 (53)	2417 (72)	1·04 (43)

* Fractional coordinates are not multiplied by 10^4.

Apart from fractional atomic coordinates, isotropic individual temperature factors were refined until the R value ($\sum|\Delta F|/\sum F_0$) reached 0·090. No attempt was made to introduce anisotropic thermal parameters in the refinement. The fractional atomic parameters, together with the individual isotropic temperature factors, are given in Table 1, while the calculated and observed structure factors, on an absolute scale, are shown in Table 2.

Description and discussion of the structure

The structure is shown in projection along two crystallographic axes in Fig. 1.

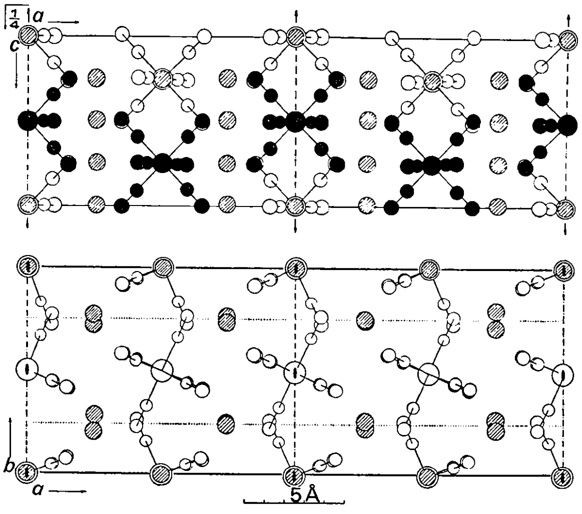

Fig. 1. (001) and (010) projections of the structure. The striped and big circles represent potassium and cobalt atoms, respectively. The bonding sequence is always Co–C–N. Atoms represented by solid circles are associated with molecules lying half a cell translation above the paper.

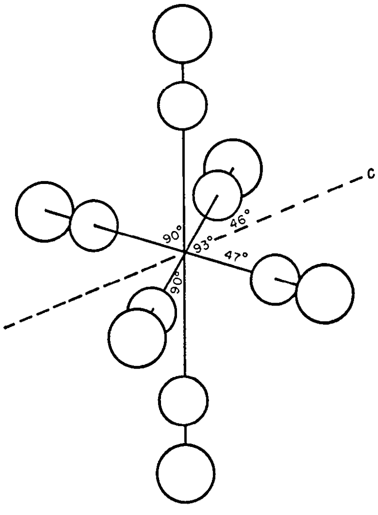

Fig. 2. Distortion of the $K_3Co(CN)_6$ octahedra as averaged over the three crystallographically distinct ions.

There are three crystallographically distinct but chemically similar octahedra in the asymmetric unit. As seen from Tables 3 and 4, which list the important molecular parameters, these three octahedra have very similar geometries. The average Co–C distance is $1{\cdot}89 \pm 0{\cdot}02$ Å while the average C–N is $1{\cdot}16 \pm 0{\cdot}02$ Å.

Table 2. *Observed and calculated structure factors on absolute scale*

h	Fo	Fc
	K=0,	L=0
4	195	177
7	22	16
8	254	243
12	32	24
14	13	21
16	358	358
20	42	43
24	255	255
28	47	49
32	91	96
36	14	14
	K=1,	L=0
2	33	13
8	123	112
12	65	64
16	65	57
24	6	4
28	8	6
32	25	23
	K=2,	L=0
0	183	163
8	9	3
12	446	444
16	80	85
20	246	251
24	64	61
28	173	171
36	71	83
	K=3,	L=0
4	324	317
8	33	34
12	116	106
16	31	26
24	8	8
28	49	48
32	7	8
36	29	25
	K=4,	L=0
0	420	439
4	135	121
8	376	373
11	6	8
12	10	12
16	272	271
20	123	122
24	188	194
28	7	17
32	88	97
36	27	28
	K=5,	L=0
4	111	103
8	40	33
11	6	3
13	7	10
14	9	6
16	10	8
20	31	23
24	19	16
28	7	12
	K=6,	L=0
3	6	17
4	313	321
8	206	202
12	222	224
16	35	38
20	154	161
24	34	34
28	104	107
32	65	72
	K=7,	L=0
4	15	14
7	7	6
8	37	32
12	24	21
16	58	59
20	9	10
24	50	47
28	28	27
	K=8,	L=0
0	140	146
4	101	98
8	200	211
12	104	102
16	151	157
20	73	78
24	80	84
28	38	41
	K=9,	L=0
4	38	38
8	21	11
12	25	23
24	9	7
28	9	4
	K=10,	L=0
0	59	61
4	92	103
8	77	108
12	147	156
16	86	90
20	51	57
24	40	43
	K=11,	L=0
8	17	18
	K=12,	L=0
0	93	105
4	81	85
8	67	77
12	80	85
16	54	59
20	33	35
	K=13,	L=0
4	17	20
8	24	30
16	22	17
	K=14,	L=0
0	51	56
4	42	49
8	56	68
	K=1,	L=1
0	90	99
1	7	11
2	103	111
4	104	112
5	8	16
6	48	48
8	9	9
10	6	6
11	6	9
12	19	19
14	8	7
16	9	7
18	31	29
19	13	7
21	10	5
23	12	5
27	15	12
35	10	3
	K=2,	L=1
2	37	46
4	8	10
5	6	13
6	38	47
8	12	13
9	7	11
10	43	54
11	11	7
12	24	27
16	26	28
17	13	17
18	26	38
21	11	12
37	13	8
	K=3,	L=1
0	85	99
1	7	23
2	34	34
4	23	36
6	15	14
8	63	70
9	8	19
10	13	13
12	12	19
14	47	47
15	18	17
16	81	89
17	19	8
23	21	18
31	13	7
33	9	14
	K=4,	L=1
1	9	23
2	76	93
3	8	18
4	26	31
6	14	21
8	39	43
9	12	27
10	70	89
11	10	18
12	10	15
13	7	15
15	6	17
16	7	8
17	8	10
27	13	13
33	13	9
	K=5,	L=1
0	26	42
2	35	37
3	14	21
4	100	112
5	22	26
6	34	36
8	7	21
10	39	49
11	14	17
12	78	90
13	11	17
14	34	21
15	9	15
25	12	9
27	12	6
31	13	8
35	15	13
	K=6,	L=1
2	30	44
4	28	32
5	8	21
6	80	105
7	13	17
8	18	20
10	40	56
11	7	16
15	7	19
17	11	18
19	7	13
23	8	11
25	9	13
29	9	10
31	12	12
33	12	3
	K=7,	L=1
1	14	17
4	13	26
5	7	14
6	33	32
7	9	20
9	10	19
15	10	9
17	10	20
25	13	12
29	9	13
	K=8,	L=1
5	9	12
7	11	12
9	7	6
11	7	12
13	9	13
15	12	10
23	10	18
25	10	9
	K=9,	L=1
3	7	8
11	10	12
13	13	13
15	10	8
17	11	15
25	10	8
	K=10,	L=1
5	11	12
9	9	10
19	12	9
25	11	10
	K=11,	L=1
1	13	13
3	9	13
5	10	15
7	10	6
9	14	5
17	9	7
	K=12,	L=1
1	12	14
7	11	10
9	9	15
11	9	12
	K=13,	L=1
13	15	9
	K=0	L=2
2	313	293
6	451	457
10	236	223
12	27	16
14	108	97
18	174	172
22	167	170
26	65	71
30	93	95
34	91	91
	K=1,	L=2
2	97	93
6	392	386
10	220	196
14	133	127
18	128	124
22	77	73
26	77	75
30	63	66
34	50	51
	K=2,	L=2
2	129	115
6	354	344
10	348	336
14	204	200
18	170	169
22	112	114
26	95	96
30	85	88
34	84	86
	K=3,	L=2
2	292	281
6	163	154
10	62	60
14	97	96
18	150	153
22	114	110
26	42	44
30	24	24
34	37	38
	K=4,	L=2
2	306	293
6	175	165
10	177	168
14	217	212
18	163	159
22	124	127
26	98	103
30	68	76
34	43	45
	K=5,	L=2
2	52	55
6	166	164
10	153	151
14	34	40
18	77	78
22	64	61
26	15	14
30	55	58
34	40	39
	K=6,	L=2
2	250	249
4	6	20
6	150	142
10	170	172
14	172	177
18	74	79
22	69	68
26	102	108
30	81	84
	K=7,	L=2
2	37	45
6	54	57
10	90	97
14	29	33
18	17	21
22	40	40
26	23	21
30	24	29
	K=8,	L=2
2	183	176
6	107	109
10	103	109
14	116	123
18	115	115
22	92	99
26	78	82
30	35	38
	K=9,	L=2
2	36	43
6	27	30
10	8	7
18	36	40
22	30	32
	K=10,	L=2
2	90	94
6	110	116
10	93	98
14	82	85
18	75	83
22	80	87
26	45	54
	K=11,	L=2
2	13	12
6	19	31
10	9	4
18	10	10
22	10	8
	K=12,	L=2
2	88	98
6	83	93
10	56	61
14	26	39
14	37	39
18	57	68
	K=13,	L=2
2	10	10
6	10	8
10	14	4
	K=14,	L=2
2	46	52
6	53	60
	K=1,	L=3
0	26	33
2	8	8
4	36	37
5	10	5
6	54	52
7	11	10
8	53	53
9	18	7
10	89	93
11	35	20
12	86	87
13	25	19
14	59	58
15	12	5
16	16	6
19	8	7
21	8	7
27	14	4
33	12	11
35	26	8
	K=2,	L=3
1	6	14
2	54	63
3	10	7
4	34	40
6	19	20
7	10	18
8	58	55
9	15	16
10	64	67
11	20	17
12	11	12
13	6	6
14	26	35
15	7	8
17	12	13
23	10	5
	K=3,	L=3
0	18	27
2	7	8
3	8	17
4	37	51
5	6	14
6	40	31
7	11	18
8	80	88
9	13	15
10	57	59
11	6	8
12	25	23
14	64	64
15	17	19
17	12	14
21	9	9
25	17	7
27	13	6
33	11	12
35	13	4
	K=4,	L=3
2	33	38
4	36	36
5	7	16
6	81	94
7	7	17
8	19	19
10	38	49
12	19	26
17	14	12
21	13	8
23	11	5
29	18	20
	K=5,	L=3
3	9	20
4	80	99
5	12	21
6	42	44
7	9	9
10	40	40
11	10	19
13	8	16
19	11	16
23	12	12
	K=6,	L=3
4	19	20
5	7	16
6	25	34
9	10	17
13	11	13
25	15	11
	K=7,	L=3
1	18	15
13	8	14
	K=8,	L=3
5	8	12
7	12	12
19	10	8
27	13	6
	K=9,	L=3
3	10	13
5	15	12
13	13	11
17	12	13
19	16	10
21	12	3
25	9	13
	K=10,	L=3
1	12	11
13	16	9
19	10	10
21	10	10
	K=11,	L=3
1	10	13
3	11	13
17	13	12
19	9	13
	K=12,	L=3
3	10	9
	K=13,	L=3
3	15	7
7	13	11
11	15	14
	K=14,	L=3
3	10	15
	K=0,	L=4
0	565	579
3	6	4
4	76	57
8	309	300
12	97	95
16	279	276
20	24	22
24	173	171
28	49	53
32	116	117
	K=1,	L=4
4	45	46
8	99	91
12	33	30
16	68	63
20	11	14
24	11	13
28	10	6
32	22	19
	K=2,	L=4
0	63	52
4	338	319
8	84	77
12	388	394
16	70	71
20	167	162
24	26	24
28	152	155
32	29	31
	K=3,	L=4
2	6	9
4	120	92
5	7	6
8	49	44
12	51	47
16	41	40
20	18	17
24	27	32
28	15	8
	K=4,	L=4
0	299	291
4	91	83
8	296	294
10	7	15
12	43	37
16	222	218
20	88	86
24	151	154
28	18	19
32	84	92
	K=5,	L=4
4	27	23
8	32	33
12	24	24
16	65	65
20	7	3
24	42	41
28	17	23
	K=6,	L=4
0	54	50
4	248	260
8	137	132
12	157	156
16	30	30
20	143	150
24	41	43
28	87	91
	K=7,	L=4
4	36	35
8	14	12
12	13	4
16	11	12
24	24	23
	K=8,	L=4
0	168	173
4	104	100
8	133	138
12	50	45
16	124	128
20	92	96
24	90	95
28	29	30
	K=9,	L=4
4	38	36
12	25	22
16	20	15
20	11	2
24	10	6
	K=10,	L=4
0	94	96
4	97	103
8	65	63
12	88	96
16	72	75
20	70	76
24	53	58
	K=11,	L=4
4	13	14
8	26	28
12	8	2
16	12	12
20	8	7
	K=12,	L=4
0	106	112
4	78	82
8	47	52
12	51	55
16	48	51
	K=13,	L=4
8	10	8
	K=1,	L=5
3	13	9
5	15	15
7	7	9
8	29	29
9	10	5
10	18	12
13	11	8
19	10	9
23	12	7
27	8	10
33	13	5
	K=2,	L=5
5	8	12
6	11	16
8	9	5
13	9	2
15	9	4
17	9	15
27	10	7
29	12	7
	K=3,	L=5
1	9	15
3	7	14
6	16	11
9	9	10
15	18	11
17	15	12
23	9	14
25	11	9
	K=4,	L=5
15	10	14
21	10	9
	K=5,	L=5
1	7	11
3	12	19
7	7	13
11	9	14
19	16	12
23	11	7
25	15	5
27	17	12
29	15	6
	K=6,	L=5
15	12	12
29	10	10
	K=7,	L=5
1	10	14
3	9	15
5	9	12
13	9	10
15	9	9
17	14	13
19	9	9
23	9	9
25	17	12
	K=8,	L=5
1	8	12
5	13	10
17	11	10
19	13	14
	K=9,	L=5
3	11	9
9	10	15
11	10	4
13	19	9
17	10	12
	K=10,	L=5
3	11	5
9	11	8
	K=11,	L=5
15	14	12
	K=12,	L=5
1	14	9
7	10	13
	K=0,	L=6
2	247	228
6	229	213
10	80	76
14	53	47
18	144	134
22	155	149
26	60	59
30	48	50
	K=1,	L=6
2	89	87
6	165	158
10	123	109
14	103	97
18	70	70
22	51	51
26	66	66
30	42	42
	K=2,	L=6
2	158	143
6	184	172
10	148	141
14	108	104
18	137	132
22	115	109
26	78	76
30	47	48
	K=3,	L=6
2	109	106
6	145	143
10	41	46
14	25	31
18	128	125
22	83	80
26	11	12
30	32	35
	K=4,	L=6
2	183	175
6	112	107
10	108	98
14	137	130
18	120	114
22	97	98
26	73	74
30	45	51
	K=5,	L=6
2	74	77
6	33	38
10	103	101
14	68	65
18	20	22
22	40	42
26	39	38
	K=6,	L=6
2	138	138
6	109	103
10	133	129
14	125	123
18	49	50
22	40	39
26	73	77
	K=7,	L=6
2	17	16
6	66	66
10	56	58
18	33	37
22	34	34
	K=8,	L=6
2	86	88
6	86	83
10	110	108
14	101	104
18	72	72
22	44	51
	K=9,	L=6
2	26	31
6	13	15
14	14	9
18	19	24
22	15	21
	K=10,	L=6
2	30	43
6	87	88
10	96	97
14	77	77
18	46	50
	K=11,	L=6
6	13	10
10	7	3
	K=12,	L=6
2	55	60
6	67	72
	K=1,	L=7
1	13	6
5	11	9
11	10	15
13	9	12
27	15	11
	K=2,	L=7
3	8	10
5	12	11
13	11	8
21	10	6
23	14	4
27	19	5
	K=3,	L=7
1	12	16
5	9	1
7	8	11
9	9	11
15	10	10
17	15	5
	K=4,	L=7
9	9	16
15	8	6
25	11	4
	K=5,	L=7
3	13	16
11	15	10
13	11	9
17	11	5
	K=6,	L=7
9	13	15
19	9	9
	K=7,	L=7
5	11	7
9	10	7
15	13	10
17	13	9
	K=8,	L=7
1	13	8
3	13	9
11	13	10
17	9	10
	K=9,	L=7
11	12	7
	K=10,	L=7
7	10	5
	K=0,	L=8
0	298	266
4	52	44
8	178	159
12	41	43
16	162	149
20	8	5
24	119	112
	K=1,	L=8
4	14	19
8	36	32
12	20	15
16	28	25
24	15	10
	K=2,	L=8
0	41	41
4	192	172
8	41	37
12	213	193
16	37	38
20	116	110
24	25	27
	K=3,	L=8
4	59	44
8	15	11
12	20	22
16	19	14
20	12	5
	K=4,	L=8
0	167	156
4	54	46
8	169	156
12	27	28
16	137	130
20	52	52
24	95	98
	K=5,	L=8
4	16	12
12	13	11
16	28	24
20	14	7
24	21	23
	K=6,	L=8
0	42	35
4	152	143
8	75	76
12	100	98
16	21	20
20	91	88
	K=7,	L=8
4	13	14
12	7	6
20	8	3
	K=8,	L=8
0	95	94
4	60	54
8	89	88
12	42	40
16	82	83
	K=9,	L=8
4	22	22
12	14	14
	K=10,	L=8
0	55	53
4	59	61
8	48	45
	K=1,	L=9
9	13	8
11	11	8
21	10	10
	K=2,	L=9
1	12	10
5	14	3
11	9	5
21	11	8
23	12	9
	K=3,	L=9
15	19	14
	K=4,	L=9
7	9	16
11	13	7
13	9	7
17	18	12
19	12	6
	K=5,	L=9
1	10	7
5	14	11
9	10	7
	K=6,	L=9
1	11	7
3	14	9
7	11	6
9	11	11
11	14	9
13	9	5
	K=7,	L=9
7	13	12
9	13	16
11	14	5
	K=8,	L=9
11	10	10
	K=9,	L=9
1	16	10
	K=0, L=10	
2	77	73
6	118	102
10	92	76
14	61	52
18	56	54
	K=1, L=10	
2	41	42
6	91	86
10	56	48
14	46	44
18	56	49
	K=2, L=10	
2	54	46
6	97	84
10	106	96
14	78	71
18	62	58
	K=3, L=10	
2	74	66
6	35	38
10	34	41
14	44	45
18	40	41
	K=4, L=10	
2	82	75
6	65	58
10	71	61
14	79	73
	K=5, L=10	
2	25	25
6	52	51
10	45	44
	K=6, L=10	
2	91	83
6	59	56
10	60	55
	K=7, L=10	
2	21	25
6	15	11
	K=1, L=11	
5	9	5
	K=2, L=11	
3	10	6
5	13	10
9	10	6
	K=3, L=11	
1	10	10
	K=4, L=11	
5	9	5

These distances agree well with other values which have been quoted in the literature. The average Co–C bond length calculated by Curry & Runciman (1959) is 1·89 Å. Pauling, Springall & Palmer, (1939) found a C–N distance of 1·16 ± 0·02 Å in methyl cyanide and Monfort (1942) found a similar value in potassium sodium platinocyanide.

Table 3. *Observed molecular bond lengths in* Å

Standard deviations are given in parentheses.

		Average
Co(1)–C(1)	1·881 (11)	
Co(1)–C(2)	1·900 (11)	1·89 (1)
Co(1)–C(3)	1·892 (11)	
Co(2)–C(4)	1·872 (11)	
Co(2)–C(5)	1·903 (11)	1·90 (1)
Co(2)–C(6)	1·913 (12)	
Co(3)–C(7)	1·921 (12)	
Co(3)–C(8)	1·911 (11)	
Co(3)–C(9)	1·864 (11)	1·89 (1)
Co(3)–C(10)	1·870 (11)	
Co(3)–C(11)	1·887 (11)	
Co(3)–C(12)	1·876 (11)	
C(1)—N(1)	1·175 (12)	
C(2)—N(2)	1·179 (12)	1·17 (1)
C(3)—N(3)	1·158 (12)	
C(4)—N(4)	1·136 (12)	
C(5)—N(5)	1·165 (12)	1·16 (1)
C(6)—N(6)	1·172 (13)	
C(7)—N(7)	1·155 (13)	
C(8)—N(8)	1·150 (12)	
C(9)—N(9)	1·144 (12)	
C(10)–N(10)	1·200 (12)	1·16 (1)
C(11)–N(11)	1·139 (13)	
C(12)–N(12)	1·148 (12)	

The Co–C–N bonds are almost collinear, the maximum deviation being 2°. As can be seen from Table 4, there is for each of the octahedra, one C–Co–C bond angle which differs appreciably (~3°) from a right angle. It can be described as a digonal distortion with the crystallographic *c* axis as the digonal axis. The average distortion for the three distinct octahedra is indicated in Fig. 2. Although it is known from n.m.r. results (Sugawara, 1959) that at the Co nuclei there are asymmetric electric field gradients which have their origin in the asymmetry of the $Co(CN)_6$ groups, the fact that the refinement of this structure was done in two different cycles could make this result somewhat contentious.

The stacking mechanism can only formally be described in terms of the rotations suggested by Kohn & Townes (1961). The most useful description to our minds is in terms of four monoclinic subcells with two adjacent ones, as shown in Fig. 3, shifted through *c*/2 along **c**. This is fully consistent with a step-growth mechanism (Frank, 1952) which leads to the occurrence of various polytypes depending on the height of an exposed screw-dislocation ledge and it seems likely that all the other polytypes of $K_3Co(CN)_6$ have structures of this same type.

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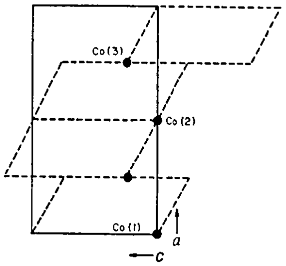

Fig. 3. Diagram to illustrate the relationship between the 1*M* and 40*r* unit cells.

Table 4. *Observed bond angles in degrees*

Standard deviations are given in parentheses.

C(1)—Co(1)–C(2)	91·0 (7)	C(4)—Co(2)–C(5)	90·8 (7)
C(1)—Co(1)–C(3)	87·0 (7)	C(4)—Co(2)–C(6)	86·9 (7)
C(2)—Co(1)–C(3)	90·8 (7)	C(5)—Co(2)–C(6)	90·9 (7)
C(1)—Co(1)–C(1′)*	92·4 (7)	C(4)—Co(2)–C(4′)	92·6 (7)
C(2)—Co(1)–C(1′)	88·8 (7)	C(5)—Co(2)–C(4′)	89·1 (7)
C(2)—Co(1)–C(3′)	89·4 (7)	C(5)—Co(2)–C(6′)	89·1 (7)
C(3)—Co(1)–C(3′)	93·5 (6)	C(6)—Co(2)–C(6′)	93·5 (6)
C(7)—Co(3)–C(11)	90·4 (7)	Co(1)–C(1)—N(1)	178·6 (1·2)
C(9)—Co(3)–C(7)	93·4 (7)	Co(1)–C(2)—N(2)	178·5 (1·2)
C(9)—Co(3)–C(11)	89·0 (7)	Co(1)–C(3)—N(3)	179·7 (1·2)
C(7)—Co(3)–C(10)	87·3 (7)	Co(2)–C(4)—N(4)	179·6 (1·2)
C(7)—Co(3)–C(12)	89·5 (7)	Co(2)–C(5)—N(5)	179·1 (1·2)
C(8)—Co(3)–C(9)	87·1 (7)	Co(2)–C(6)—N(6)	178·5 (1·2)
C(8)—Co(3)–C(10)	92·9 (7)	Co(3)–C(7)—N(7)	179·5 (1·2)
C(8)—Co(3)–C(11)	89·8 (7)	Co(3)–C(8)—N(8)	178·7 (1·2)
C(8)—Co(3)–C(12)	90·2 (7)	Co(3)–C(9)—N(9)	178·0 (1·2)
C(9)—Co(3)–C(12)	90·9 (7)	Co(3)–C(10)–N(10)	178·0 (1·2)
C(10)–Co(3)–C(11)	91·5 (7)	Co(3)–C(11)–N(11)	179·7 (1·2)
C(10)–Co(3)–C(12)	88·9 (7)	Co(3)–C(12)–N(12)	178·7 (1·2)

* Atoms (1) and (1′) have fractional coordinates (x,y,z) and $(\bar{x},\bar{y},z)$ respectively.

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Die Kristallstrukturen von Hexamminchrom(III)-Hexafluoromanganat(III) und Hexamminchrom(III)-Hexafluoroferrat(III)

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The crystal structures of $[Cr(NH_3)_6]MnF_6$ and of $[Cr(NH_3)_6]FeF_6$ have been determined from three-dimensional X-ray data collected by counter methods. The structures have been refined by full-matrix least-squares techniques to final conventional *R*-values of 3·0% for 294 independent reflexions for $[Cr(NH_3)_6]MnF_6$ and of 3·4% for 648 independent reflexions for $[Cr(NH_3)_6]FeF_6$. The compounds crystallize in the cubic space group *Pa*3 (T_h^6), with four formula units in a cell ($a = 10·059(3)$ Å for $[Cr(NH_3)_6]MnF_6$ and 10·079(3) Å for $[Cr(NH_3)_6]FeF_6$). A dynamical Jahn-Teller effect for the MnF_6^{3-} ion is discussed. Evidence for hydrogen bonding in complex hexafluorides containing the $[Cr(NH_3)_6]^{3+}$ ion is given.

Einleitung

Röntgenographische und infrarot-spektroskopische Untersuchungen an den Verbindungen K_3MnF_6, K_2NaMnF_6 und Cs_2KMnF_6 ergaben D_{4h}-Symmetrie der MnF_6^{3-}-Anionen. Sechs Fluoratome umgeben Mn^{3+} in Form eines gestreckten Oktaeders (Peacock, 1957; Knox, 1963; Wieghardt & Siebert, 1971; Schneider & Hoppe, 1970). Diese statische Verzerrung des Komplexoktaeders wird als eine Folge des Jahn–Teller Theorems (Jahn & Teller, 1937) gedeutet.

Die kürzlich dargestellten Salze $[M(NH_3)_6]MnF_6$ (M = Cr, Co, Rh) kristallisieren in der kubischen Raumgruppe T_h^6-*Pa*3. Die Lagesymmetrie der MnF_6^{3-}-Anionen ist C_{3i} (S_6). Das bedeutet aber, dass die Symmetrie der MnF_6^{3-}-Ionen in diesen Salzen nicht D_{4h} sein kann (Wieghardt & Siebert, 1971*a*). Da sich auch die Infrarot-Spektren wesentlich von denen der K_3MnF_6- und K_2NaMnF_6-Salze unterscheiden (s.unten), wurde die Kristallstruktur von $[Cr(NH_3)_6]MnF_6$ bestimmt.

Eine zweite Kristallstrukturanalyse wurde von dem isotypen Salz $[Cr(NH_3)_6]FeF_6$ durchgeführt, da das Fe^{3+}-Ion keinen Jahn–Teller Effekt zeigt. Es eignet sich daher gut zu einem Vergleich mit $[Cr(NH_3)_6]MnF_6$.

Experimentelles

$[Cr(NH_3)_6]MnF_6$ und $[Cr(NH_3)_6]FeF_6$ wurden nach einer von Wieghardt & Siebert (1971*a*,*b*) beschriebenen Methode dargestellt. Die Salze kristallisieren in kleinen, gut ausgebildeten Würfeln, die optisch isotrop sind. Drehkristall- und Weissenberg-Aufnahmen ergaben kubische Symmetrie. Aufgrund der systematischen Auslöschungen $0kl$ für $k = 2n+1$, $h0l$ für $l = 2n+1$, $hk0$ für $h = 2n+1$ und der gleichen Intensität aller Reflexe mit cyclisch vertauschbaren Indizes kommt nur die Raumgruppe T_h^6-*Pa*3 in Frage.

Die Gitterkonstanten wurden aus diffraktometrisch bestimmten Winkeln θ von jeweils 2 Reflexen $h00$, $0k0$, $00l$ berechnet. In Tabelle 1 sind die Kristalldaten zu-