Acta Cryst. (1964). **17**, 190

Crystal Structure of a Sodium Cobalt Molybdate*

BY JAMES A. IBERS

Chemistry Department, Brookhaven National Laboratory, Upton, Long Island, New York, U.S.A.

AND G. W. SMITH

British Petroleum Company Limited, BP Research Centre, Sunbury-on-Thames, Middlesex, England

(*Received* 16 *April* 1963)

The sodium cobalt molybdate studied here crystallizes in space group *Pnma* (D_{2h}^{16}) of the orthorhombic system in a cell of dimensions $a=5{\cdot}25$, $b=10{\cdot}78$, $c=18{\cdot}02$ Å. There are four formula units in the cell. Complete three-dimensional data out to $\lambda^{-1}\sin\theta_{\text{Mo}}\simeq 1$ were collected with Mo $K\alpha$ radiation by film methods and were estimated visually. The structure was solved by three-dimensional Patterson methods and was refined by both Fourier and least-squares techniques. The least-squares refinement was applied not only to the usual positional and thermal parameters, but also to the site occupancy factors, for only in this way could the details of the composition be established. This analysis of the X-ray data leads to a composition $\text{NaCo}_{2\cdot31}(\text{MoO}_4)_3$, a result consistent with chemical analyses. The structure is formed by a framework of MoO_4 tetrahedra and CoO_6 octahedra, the tetrahedra providing links between sheets and columns formed by the octahedra. In the sheets the octahedra share corners and edges; in the columns they share faces. In both of the octahedral sites cobalt is present to about 75%. A zigzag void left by the MoO_4 links is made up of trigonal prisms sharing edges and is filled by sodium atoms.

Introduction

One of the authors in a previous communication (Smith, 1960, hereafter referred to as I) gave the details of a partial determination of the structure of what was described as orthorhombic cobalt molybdate. The cobalt and molybdenum positions had been derived from a three-dimensional Patterson function based on complete data out to $\lambda^{-1}\sin\theta_{\text{Mo}}\simeq 1$. From the separation of the Mo atoms it was thought that the structure contained free, unlinked MoO_4^{2-} ions, and this, together with the observed density and analyses for Co and Mo, suggested that the composition was probably $\text{Co}_2(\text{MoO}_4)_3$.

The paucity of structural information on complex oxide systems and the interesting properties, both structural and physical, of such systems prompted the present detailed refinement of the structure. The result is more complicated and more interesting than had been anticipated: from the analysis of the X-ray data the compound is found to be $\text{NaCo}_{2\cdot31}(\text{MoO}_4)_3$, and this composition is consistent with chemical analyses. The structure shows several interesting features, including the partial occupancy of cobalt atoms in two independent CoO_6 octahedral sites. In one arrangement of CoO_6 octahedra there is the not too common face sharing to form infinite columns; in the other arrangement a zigzag sheet, as far as we know differing from anything thus far reported, is formed by the sharing of edges and corners.

Review of the previous work on the structure

The crystals were prepared by melting in a sodium chloride flux anhydrous cobaltous chloride and sodium molybdate in the manner described in I. The resultant bright blue material crystallizes in the orthorhombic system, in a cell of dimensions

$$a=5{\cdot}245\pm0{\cdot}003,\ b=10{\cdot}778\pm0{\cdot}005,\ c=18{\cdot}017\pm0{\cdot}006\ \text{Å}\,.$$

The density of 3·79 g.cm^{-3}, reported in I, seems, on the basis of an extensive series of redeterminations, to be a lower limit. Densities between 3·8 and 4·5 g.cm^{-3} have been obtained by flotation of the crystals in thallous malonate–thallous formate solutions. Our best guess of a density (corresponding, perhaps, to an average composition) is 4·2 g.cm^{-3}. Such a density is consistent with four formula units of a compound of composition near to $\text{Co}_2(\text{MoO}_4)_3$ in the unit cell. On the basis of the observed extinctions and an analysis of intensity statistics the space group *Pnma* (D_{2h}^{16}) was adopted in I and leads to the reasonable structure to be described here.

Approximately 2350 independent structure amplitudes, obtained from the visual estimation of intensities recorded with Mo $K\alpha$ radiation by the equi-inclination Weissenberg method, were used in the calculation of a three-dimensional Patterson function. An analysis of this function led to the positional parameters for Co in (8*d*), Mo in (8*d*), and Mo in (4*c*) (hereafter termed Co(8), Mo(8), and Mo(4)) given in parentheses in Table 1. These positional parameters,

---

* Part of this work was performed under the auspices of the U.S. Atomic Energy Commission.

Table 1. *Atomic parameters for* $NaCo_{2\cdot31}(MoO_4)_3$

Atom	Position	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
Mo(8)	8*d*	0·77820 (0·778)*	0·00017	0·48136 (0·483)	0·00008	0·34554 (0·345)	0·00004	0·79 Å^2†	
Co(8)	8*d*	0·25362 (0·250)	0·00031	0·42788 (0·425)	0·00016	0·47365 (0·473)	0·00009	0·67	
Mo(4)	4*c*	0·72154 (0·722)	0·00025	$\frac{1}{4}$		0·55621 (0·556)	0·00007	0·85	
Co(4)	4*c*	0·40023	0·00098	$\frac{1}{4}$		0·75082	0·00020	2·1	
Na	4*c*	0·2532	0·0013	$\frac{1}{4}$		0·3056	0·0004	1·0	0·1
O(1)	8*d*	0·8491	0·0020	0·6179	0·0009	0·2970	0·0005	1·7	0·1
O(2)	8*d*	0·9098	0·0018	0·1194	0·0009	0·5352	0·0005	1·4	0·1
O(3)	8*d*	0·5804	0·0018	0·5158	0·0009	0·4253	0·0005	1·5	0·1
O(4)	8*d*	0·5972	0·0020	0·3853	0·0010	0·2899	0·0006	1·7	0·1
O(5)	8*d*	0·0517	0·0020	0·3997	0·0010	0·3764	0·0006	1·7	0·1
O(6)	4*c*	0·6447	0·0027	$\frac{1}{4}$		0·6513	0·0007	1·4	0·2
O(7)	4*c*	0·4456	0·0032	$\frac{1}{4}$		0·4953	0·0009	2·0	0·2

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	M§	$\sigma(M)$
Mo(8)	0·00855 (40)‡	0·00159 (5)	0·00053 (2)	−0·00035 (10)	0·00045 (5)	−0·00009 (2)	1·0	
Co(8)	0·00384 (54)	0·00204 (11)	0·00049 (3)	0·00004 (18)	0·00001 (9)	0·00020 (5)	0·7719	0·0098
Mo(4)	0·00824 (47)	0·00184 (7)	0·00060 (2)	0	0·00047 (8)	0	1·0	
Co(4)	0·03970 (199)	0·00189 (18)	0·00071 (7)	0	−0·00239 (30)	0	0·7659	0·0140

* Values in parentheses are those derived in I (Smith, 1960). The value of x for Mo(4) was correct in Fig. 1 of I, but incorrect in the text.

† The B's for the four heavy atoms, which were refined anisotropically, are the corresponding effective isotropic values (Hamilton, 1959).

‡ Values in parentheses are estimated standard deviations; *e.g.* β_{11} for Mo(8) is $0\cdot00855 \pm 0\cdot00040$.

§ M is the occupancy factor; thus both the Co(8) and Co(4) sites are approximately 77% filled.

together with the structure amplitudes, were the basis of the present investigation.

Refinement of the structure

From the original data set approximately 2100 structure amplitudes were selected for use in the refinement; very weak intensities and others that were deemed unreliable were eliminated. The refinement proceeded by a combination of least-squares and Fourier techniques. All calculations were carried out on an IBM 7090, local variations of Zalkin's FORDAP Fourier synthesis program and of the Busing-Levy ORFLS least-squares program being employed. The least-squares refinements were carried out on F, with weights taken more or less as suggested by Hughes (1941). The scattering factors used were those for Co, O, Na, and Mo^+ tabulated by Ibers (*International Tables for X-ray Crystallography*, 1962*a*), except that the Mo^+ values were reduced to approximate Mo° values by comparison of the Thomas–Fermi–Dirac values for Mo^+ and Mo°. Dispersion corrections were applied in accordance with the values given by Templeton (*International Tables for X-ray Crystallography*, 1962*b*).

In preparation for a difference Fourier synthesis the calculations were begun with several cycles of least-squares on the Co(8), Mo(8), and Mo(4) positions found in I (Table 1), with separate scale factors for the various layers and separate isotropic thermal parameters for the three atoms. The usual R factor for this refinement was 0·27. On the first difference Fourier synthesis there were two prominent peaks, one of approximate height 90 e.Å^{-3} at 0.40, $\frac{1}{4}$, 0·75, the other of approximate height 40 e.Å^{-3} at 0·25, $\frac{1}{4}$, 0·31. There were also seven smaller peaks whose heights ranged between 20 and 30 e.Å^{-3}. These latter seven were assumed, on the basis of a cork-ball model, to correspond to oxygen atoms, an assumption ultimately justified by the reasonableness of the final structure. The two largest peaks were not understood, but since they were in special positions it was hoped (in vain) that they were spurious and for the time being they were ignored. Several additional cycles of least-squares were run with the three heavy atoms and the seven oxygen atoms, all with individual isotropic thermal parameters. A significant decrease in the R factor to 0·23 occurred. Moreover, the oxygen thermal parameters remained between 1·1 and 1·6 Å^2, and this was convincing evidence that these atoms were properly placed. A second difference Fourier synthesis was then calculated. The only noteworthy features were the two largest peaks, this time with increased heights, that occurred also on the first difference Fourier synthesis.

It was clear at this point that the structure must contain atoms in addition to those already placed. Now that the oxygen atom positions were well established, it was possible to examine in detail the environments of these unknown atoms. The peak at 0·40, $\frac{1}{4}$, 0·75 is in the center of an octahedron of oxygen atoms; this octahedron shares octahedral faces with equivalent octahedra to form infinite columns parallel to a. For the following reasons we felt that this was a reasonable environment for cobalt: (1) there are no molybdates, so far as we are aware,

Table 2. *Observed and calculated structure factors for* NaCo$_{2.31}$(MoO$_4$)$_3$

K	L	OBS	CALC
•••••H= 0•••••			
0	0		1164
0	6	190	200
0	8	55	-47
0	10	274	-293
0	14	48	42
0	16	111	-110
0	18	37	-34
0	20	106	118
0	22	146	-170
0	24	44	-43
0	26	38	29
0	28	49	-51
0	30	59	-55
0	32	87	91
0	34	37	31
0	38	47	50
0	40	43	41
1	3	59	43
1	5	187	209
1	7	22	-20
1	9	23	21
1	11	147	-172
1	13	62	-63
1	15	118	-124
1	21	58	65
1	23	37	37
1	25	48	59
1	27	21	-18
2	0	165	151
2	4	208	-247
2	6	269	288
2	8	61	66
2	10	68	-66
2	12	74	78
2	14	71	76
2	16	233	-274
2	18	42	-47
2	20	34	-33
2	22	83	-98
2	24	33	-26
2	26	123	122
2	36	58	-57
2	38	41	36
3	1	217	-223
3	3	175	-141
3	5	122	-115
3	7	81	-72
3	9	237	-243
3	11	98	96
3	13	13	-11
3	21	79	-90
3	27	45	35
3	29	38	34
3	31	89	99
4	0	275	327
4	2	39	-35
4	4	133	-126
4	6	46	49
4	8	45	-46
4	10	273	-294
4	12	183	194
4	14	80	85
4	18	56	65
4	20	140	166
4	22	64	-74
4	24	39	-43
4	26	36	35
4	28	53	-49
4	30	68	-68
4	32	70	58
5	1	33	-31
5	3	10	-10
5	5	193	191
5	7	146	-155
5	9	85	-83
5	11	118	-120
5	13	98	-96
5	15	173	-172
5	17	39	32
5	19	34	38
5	21	18	19
5	23	58	57
5	25	100	101
5	27	37	-34
6	0	167	-180
6	2	127	-135
6	4	256	-253
6	6	137	119
6	10	23	-23
6	12	140	131
6	14	121	114
6	16	145	-133
6	18	48	41
6	20	44	35
6	26	117	115
6	36	71	-72
7	1	152	-158
7	3	51	-57
7	7	101	-90
7	9	146	-141
7	11	184	201
7	13	15	16
7	17	64	71
7	19	51	48
7	21	124	-133
7	31	71	72
8	0	248	272
8	2	117	-101
8	4	56	-53
8	6	16	-15
8	8	72	-74
8	10	149	-146
8	12	49	44
8	14	73	73
8	16	45	41
8	18	63	65
8	20	149	147
8	22	37	-36
8	28	28	-25
8	30	40	-40
8	32	23	33
9	1	24	-27
9	3	60	60
9	5	258	281
9	9	30	22
9	11	64	66
9	13	16	-3
9	15	122	-126
9	17	78	78
9	19	41	35
9	21	35	-39
9	25	54	53
9	27	79	-88
9	35	41	-32
9	37	39	36
10	0	47	-47
10	2	42	-45
10	4	105	-101
10	6	85	81
10	8	32	31
10	10	33	34
10	12	17	12
10	14	35	37
10	16	83	-95
10	20	35	-28
10	26	68	64
10	36	40	-38
11	1	127	-135
11	3	22	-19
11	5	86	95
11	9	59	-63
11	11	200	212
11	13	63	66
11	17	84	80
11	19	20	22
11	21	117	-131
11	27	57	-52
11	31	58	57
11	29	29	-25
11	33	29	-26
12	0	128	140
12	2	37	42
12	4	34	33
12	10	96	-87
12	12	23	16
12	16	28	28
12	20	30	28
12	22	31	-35
12	32	33	30
13	1	50	-53
13	5	199	191
13	7	32	-31
13	9	32	-28
13	11	33	29
13	13	20	-11
13	15	103	-101
13	17	73	62
13	19	38	33
13	21	27	-25
13	23	28	28
13	25	58	55
13	27	71	-65
14	0	66	-66
14	2	37	36
14	6	58	47
14	8	34	30
14	10	49	48
14	14	36	-23
14	16	65	-67
14	18	47	-39
14	20	68	-72
15	1	97	-102
15	3	48	-47
15	5	24	14
15	7	70	-68
15	9	101	-98
15	11	103	96
15	15	27	-25
15	17	55	48
15	19	28	32
15	21	81	-79
15	31	56	58
16	0	81	67
16	2	36	33
16	4	62	65
16	6	36	-34
16	8	21	-26
16	10	21	-18
16	12	22	-20
16	14	22	-25
16	16	48	35
16	26	47	-39
17	1	21	-28
17	5	82	88
17	7	66	-55
17	9	47	-47
17	13	48	-42
17	15	99	-89
17	17	29	32
17	25	58	57
18	0	79	-82
18	10	69	68
18	20	41	-39
19	1	56	-55
19	3	28	-23
19	7	23	-34
19	9	57	-55
19	11	58	54
19	21	58	-51
20	0	22	-18
20	6	58	-58
20	16	58	68
21	5	58	58
21	15	47	-38
22	0	88	-83
22	10	58	49
23	1	33	-23
23	11	39	38
24	4	39	30
24	6	39	-35
26	0	33	-32
•••••H= 1•••••			
0	2	99	-105
0	3	90	72
0	4	344	405
0	5	12	10
0	6	244	283
0	7	93	-92
0	8	14	3
0	10	138	141
0	11	40	39
0	12	162	166
0	13	37	36
0	14	151	-149
0	15	36	35
0	16	47	-50
0	17	23	24
0	18	144	149
0	19	17	3
0	20	46	-54
0	22	24	-22
0	24	78	84
0	25	20	-21
0	26	39	-35
0	28	112	-111
0	30	32	-17
0	32	27	-27
0	34	76	-72
0	38	47	45
1	2	32	29
1	3	14	-10
1	4	33	30
1	5	93	91
1	6	90	-82
1	7	61	60
1	8	23	21
1	9	153	140
1	10	26	-24
1	11	104	100
1	12	36	-35
1	13	57	-60
1	14	14	-11
1	15	25	-26
1	16	21	-16
1	17	75	-79
1	18	16	12
1	19	91	-95
1	21	37	-39
1	25	21	22
1	27	22	25
2	1	63	-53
2	2	359	-355
2	3	41	38
2	4	147	123
2	5	43	-36
2	6	35	30
2	7	90	-86
2	8	149	-154
2	9	22	20
2	10	166	171
2	11	25	30
2	12	264	259
2	13	23	-16
2	14	17	-11
2	16	22	19
2	18	100	121
2	19	38	-41
2	20	88	-96
2	21	18	-17
2	22	129	-136
2	23	19	14
2	24	41	44
2	26	53	-43
2	28	68	-71
2	29	23	19
2	30	58	53
2	32	24	27
2	34	43	-46
3	1	244	191
3	3	276	224
3	4	9	9
3	6	115	-110
3	7	85	-79
3	9	41	-37
3	11	82	-82
3	13	89	-83
3	14	14	16
3	17	36	38
3	18	29	28
3	19	39	-40
3	21	32	-32
3	23	20	-19
3	25	63	-71
3	27	67	-63
3	35	43	50
4	1	119	108
4	2	115	-95
4	3	69	64
4	4	122	107
4	5	25	-23
4	6	205	195
4	7	22	-19
4	8	206	-200
4	10	12	-10
4	12	39	36
4	13	35	-30
4	14	209	-212
4	15	27	24
4	16	42	-42
4	17	23	25
4	18	85	94
4	19	17	-19
4	22	27	24
4	24	114	112
4	26	22	19
4	28	63	-66
4	34	53	-51
5	1	63	-55
5	2	74	70
5	3	172	146
5	5	91	82
5	6	33	32
5	8	21	20
5	9	181	166
5	10	13	-9
5	11	88	88
5	12	32	-32
5	13	125	-123
5	15	36	-35
5	17	48	-55
5	18	25	-24
5	19	127	-151
5	21	67	-58
5	23	35	34
5	29	58	53
5	33	30	-29
6	1	16	-13
6	2	279	-268
6	4	45	-42
6	5	43	-42
6	6	113	-94
6	7	29	-27
6	8	240	-236
6	9	19	26
6	12	91	85
6	13	22	-26
6	14	68	-63
6	18	63	64
6	19	37	-37
6	20	67	-59
6	21	19	-16
6	22	70	-73
6	24	64	68
6	30	84	85
6	32	53	52
7	1	12	11
7	2	18	18
7	3	205	188
7	4	29	-26
7	5	65	-55
7	6	47	45
7	7	176	-157
7	11	34	-37
7	13	72	-74
7	14	29	28
7	15	45	46
7	16	25	25
7	17	100	109
7	18	26	-26
7	19	19	-22
7	23	52	50
7	25	78	-67
7	27	49	-53
7	29	29	27
8	2	62	-52
8	3	19	16
8	4	97	95
8	6	41	42
8	7	29	-29
8	8	113	-99
8	10	50	-57
8	12	40	-39
8	13	17	15
8	14	156	-154
8	15	21	24
8	16	73	-73
8	17	18	19
8	18	54	57
8	22	37	37
8	24	77	88
8	26	28	26
9	1	187	-195
9	2	25	29
9	3	25	29
9	5	26	-25
9	7	89	-93
9	8	22	23
9	9	146	149
9	10	23	-29
9	11	102	112
9	12	38	-36
9	13	71	-78
9	14	18	14
9	15	52	59
9	17	39	48
9	19	71	-79
9	23	86	90
9	29	49	57
10	1	31	-31
10	2	110	-113
10	6	61	-62
10	7	23	-23
10	8	67	-66
10	10	30	33
10	12	63	69
10	18	25	29
10	20	52	-46
10	22	67	-60
10	30	35	38
11	1	67	-68
11	3	85	91
11	5	77	-81
11	6	42	-40
11	7	157	-160
11	9	25	22
11	13	67	-62
11	14	24	25
11	15	85	92
11	17	136	136
11	21	48	38
11	23	70	72
11	25	34	-41
11	27	35	-46
11	29	30	31
12	1	17	23
12	2	40	43
12	3	18	17
12	4	51	59
12	6	82	90
12	10	19	18
12	14	50	-46
12	22	23	24
12	28	35	-32
13	1	100	-114
13	2	32	39
13	3	53	59
13	7	58	-63
13	8	19	19
13	9	118	114
13	11	71	68
13	13	97	-82
13	15	21	29
13	17	22	29
13	19	80	-84
13	23	73	71
14	10	58	52
14	12	53	57
14	14	66	61
14	16	39	38
14	22	34	-37
15	3	146	122
15	7	86	-91
15	13	68	-73
15	15	23	23
15	17	58	56
15	19	42	-42
15	23	30	33
15	25	43	-47
16	2	54	54
16	4	27	30
16	6	38	36
16	8	64	53
16	12	23	-27
16	22	25	32
17	1	39	-36
17	3	69	69
17	7	23	-24
17	9	82	76
17	11	33	37
17	13	73	-66
17	19	87	-81
18	4	33	-43
18	6	51	-50
18	14	43	42
19	3	60	68
19	7	42	-47
19	13	39	-39
20	2	53	45
20	4	25	-18
20	10	43	-33
20	12	50	-56
21	1	25	-33
•••••H= 2•••••			
0	0	357	-398
0	2	72	-73
0	3	51	44
0	4	54	48
0	5	144	-145
0	6	218	-231
0	7	115	113
0	8	117	104
0	10	221	220
0	11	45	-44
0	12	23	-12
0	13	54	-48
0	14	37	-36
0	15	55	58
0	16	139	144
0	17	55	-62
0	18	17	-14
0	20	91	-83
0	21	60	55
0	22	115	111
0	23	41	41
0	24	101	93
0	25	30	-30
0	26	31	-30
0	27	41	38
0	28	82	74
0	30	34	35
0	31	32	-22
0	32	58	-66
0	34	39	-38
0	38	66	-54
1	0	13	-20
1	3	83	-89
1	4	77	70
1	5	63	-53
1	6	21	-22
1	7	19	13
1	8	92	85
1	9	61	52
1	10	36	-34
1	11	69	65
1	12	72	74
1	13	131	121
1	14	48	-57
1	15	65	67
1	17	31	29
1	18	43	-45
1	19	48	-51
1	21	36	-34
1	23	61	-60
1	25	43	-47
1	28	22	26
2	0	156	-144
2	1	69	62
2	2	79	73
2	3	128	-106
2	4	79	63
2	5	69	-62
2	6	237	-255
2	7	34	-34
2	8	134	-167
2	9	89	88
2	10	105	105
2	11	46	-50
2	12	116	-126
2	13	60	64
2	14	14	-9
2	15	20	22
2	16	184	208
2	18	52	59
2	19	48	-49
2	20	17	-24
2	21	36	37
2	22	103	102
2	23	33	-34
2	26	82	-84
2	30	23	27
2	31	23	-22
2	32	51	-52
3	0	16	-14
3	1	55	41
3	2	165	132
3	3	217	197
3	4	85	-71
3	5	120	122
3	7	211	196
3	8	77	-71
3	9	147	142
3	10	67	-69
3	11	40	-42
3	14	20	19
3	15	45	54
3	16	44	-44
3	17	45	-47
3	18	33	33
3	21	45	48
3	24	35	-38
3	25	36	-39
3	26	21	19
3	28	27	-20
3	29	48	-46
3	31	58	-62
4	0	252	-268
4	1	45	38
4	2	42	31
4	3	110	96
4	4	179	157
4	5	91	-79
4	6	123	-114
4	7	119	102
4	8	94	87
4	9	54	52
4	10	201	183
4	12	19	-7
4	13	57	-56
4	14	84	-78
4	15	43	43
4	16	47	49
4	17	73	-74
4	18	83	-83
4	20	126	-114
4	21	18	22
4	22	51	48
4	23	24	23
4	24	43	40
4	25	25	-23
4	26	53	-40
4	27	27	29
4	28	68	64
4	29	23	-9
4	30	40	41
4	32	59	-46
5	0	67	69
5	1	125	109
5	2	120	-93
5	3	54	-48
5	4	29	27
5	5	123	-110
5	7	59	55
5	8	55	55
5	9	103	97
5	11	39	33
5	12	64	56
5	13	104	112
5	15	112	127
5	18	39	-38
5	19	51	-56
5	20	18	21
5	22	34	-38
5	23	70	-77
5	25	74	-73
6	0	42	37
6	1	61	59
6	2	208	182
6	3	70	-67
6	4	169	159
6	5	38	-41
6	6	112	-96
6	7	44	-43
6	8	118	-113
6	9	66	67
6	10	52	49
6	11	25	-28
6	12	133	-121
6	13	43	43
6	14	63	-62
6	16	71	74
6	18	17	-22
6	19	26	-34
6	20	73	-68
6	21	19	21
6	22	20	23
6	23	35	-33
6	24	51	-43
6	26	81	-83
7	0	81	81
7	1	131	115
7	3	119	117
7	4	81	-83
7	5	67	-55
7	6	46	45
7	7	77	76
7	8	62	-62
7	9	64	57
7	11	135	-125
7	12	31	-31
7	13	64	-72
7	14	73	74
7	15	41	46
7	16	34	-32
7	17	62	-69
7	18	36	36
7	19	18	14
7	21	89	95
7	22	20	-13
7	23	21	19
7	24	21	-22
7	25	22	-15
7	26	22	15
7	27	32	39
7	28	23	-27
7	31	51	-53
8	0	81	-72
8	2	66	62
8	3	41	40
8	4	132	117
8	5	63	-64
8	6	24	-21
8	7	50	53
8	8	94	97
8	9	15	-15
8	10	98	102
8	11	15	-19
8	12	23	-25
8	13	41	-43
8	14	76	-79
8	15	24	23
8	17	37	-36
8	18	104	-94
8	20	109	-110
8	21	20	29
8	23	30	32
8	24	22	18
8	26	22	-25
8	27	23	27
8	28	50	47
9	0	56	56
9	1	82	90
9	2	35	-40
9	3	59	-60
9	5	213	-201
9	7	38	-35
9	8	49	52
9	9	16	15
9	10	40	-39
9	11	91	-98
9	12	61	55
9	13	24	23
9	15	82	79
9	17	33	-37
9	18	27	-29
9	19	49	-53
9	21	36	46
9	22	30	-29
9	23	38	-40
9	25	39	-36
9	26	23	22
9	27	57	68
9	29	51	44
10	0	42	40
10	1	15	15
10	2	66	70
10	3	58	-54
10	4	35	32
10	6	51	-56
10	7	32	-30
10	8	57	-66
10	9	24	23
10	11	24	-22
10	12	56	-68
10	13	40	41
10	16	67	64
10	18	20	19
10	19	20	-25
10	26	40	-42
11	0	31	32
11	1	70	75
11	2	47	47
11	3	67	69
11	4	58	-59
11	5	83	-86
11	6	38	39
11	7	38	40
11	8	39	-36
11	10	51	-56
11	11	175	-172
11	13	66	-71
11	14	27	30
11	15	19	29
11	16	28	-37
11	17	79	-86
11	18	21	25
11	21	77	92
11	23	32	29
11	24	33	-28
11	27	59	61
12	0	98	-100
12	2	75	-59
12	3	43	40
12	6	18	-18
12	7	44	42
12	8	52	54
12	10	53	51
12	12	27	33
12	13	28	-26
12	17	21	-28
13	0	35	35
13	1	58	70
13	2	41	-40
13	3	37	-36
13	5	147	-134
13	8	27	26
13	9	27	30
13	10	19	-25
13	11	70	-72
13	12	43	47
13	13	29	32
13	15	74	80
13	17	22	-36
13	19	39	-48
13	20	23	21
13	21	40	39
13	22	23	-27
13	23	33	-39
13	25	42	-42
13	27	42	45
14	3	34	-28
14	4	34	-32
14	6	34	-30
14	7	35	-26
14	8	61	-59
14	10	20	-27
14	13	30	25
14	14	30	37
14	16	47	44
14	18	48	51
14	20	50	49
15	0	39	39
15	1	79	73
15	3	62	65
15	4	29	-36
15	5	29	-29
15	6	29	27
15	7	73	71
15	8	30	-30
15	9	56	53
15	10	21	-16
15	11	85	-72
15	13	22	-21
15	14	32	39
15	15	56	47
15	17	40	-49
15	21	64	59
16	0	35	-31
16	2	45	-45
16	4	21	-24
16	6	21	18
16	8	31	34
16	12	22	34
16	13	23	-21
17	0	33	30
17	1	55	53
17	2	22	-22
17	5	60	-60
17	7	32	31
17	9	56	58
17	13	41	48
17	15	63	67
18	0	68	63
18	10	41	-44
19	0	23	16
19	1	41	38
19	3	41	46
19	7	48	47
19	9	34	39
19	10	24	-18
19	11	24	-34
20	0	34	29
20	8	42	33
22	0	63	57
24	0	21	14
•••••H= 3•••••			
0	2	43	51
0	3	99	-108
0	4	201	-209
0	5	52	51
0	6	249	-273
0	7	74	79
0	8	97	103
0	10	57	-51
0	11	16	14
0	12	98	-110
0	13	75	79
0	14	101	116
0	15	35	-33
0	16	18	-16
0	17	73	-70
0	18	101	-106
0	19	24	24
0	20	20	18
0	22	22	21
0	23	39	-43
0	24	61	-62
0	25	53	46
0	26	38	36
0	27	28	31
0	28	94	97
0	34	75	68
1	1	28	33
1	2	29	-29
1	4	48	-52
1	5	76	-86
1	6	10	-8
1	7	31	-27
1	8	53	-49
1	9	67	-70
1	10	35	32
1	11	40	-36
1	12	51	47
1	13	49	48
1	15	59	53
1	17	90	87
1	19	68	74
1	20	29	-23
1	21	30	30
1	22	31	-28
1	27	25	-24
2	1	79	94
2	2	153	174
2	3	78	-85
2	4	93	-106
2	6	53	-45
2	7	46	42
2	8	104	109
2	9	109	-117
2	10	103	-101
2	11	58	-55
2	12	144	-167
2	13	63	62
2	16	44	-40
2	17	18	-27
2	18	86	-97
2	19	80	80
2	20	71	74
2	22	108	102
2	23	48	-44
2	24	28	-23
2	26	34	38
2	28	54	53
2	29	52	-46
2	30	57	-50
3	1	133	-144
3	2	51	39
3	3	201	-230
3	4	56	48
3	5	66	-67
3	6	62	60
3	7	65	62
3	9	28	20
3	11	66	62
3	13	76	72
3	14	67	-61
3	15	35	24
3	19	28	26
3	20	20	17
3	21	30	32
3	24	23	28
3	25	59	65
3	27	44	41
4	2	58	46
4	3	76	-77
4	4	185	-189
4	6	98	-102
4	7	93	104
4	8	97	104
4	10	14	18
4	12	27	-28
4	13	67	71
4	14	120	160
4	15	40	-40
4	16	52	47
4	17	47	-43
4	18	109	-99
4	20	30	29
4	23	32	-30
4	24	82	-77
4	25	34	34
4	27	31	30
4	28	37	41
5	1	67	64
5	2	69	-85
5	3	68	-64
5	5	70	-55
5	6	19	-14
5	8	58	-57
5	9	100	-114
5	10	27	24
5	11	60	-57
5	12	67	61
5	13	81	94
5	15	41	33
5	17	48	46
5	18	45	43
5	19	115	117
5	20	37	-34
5	21	38	37
5	22	39	-37
5	29	32	-35
5	30	27	22
6	1	73	82
6	2	136	150
6	3	55	-48
6	6	92	95
6	7	42	33
6	8	138	165
6	9	74	-80
6	11	53	-48
6	12	49	-44
6	13	40	35
6	14	45	45
6	18	72	-65
6	19	60	54
6	20	62	51
6	22	57	57
6	23	33	-31
6	24	49	-47
6	29	46	-38
6	30	82	-74
7	1	14	13
7	2	46	-40
7	3	125	-125
7	4	80	84
7	5	61	51
7	6	49	39

Table 2 (*cont.*)

K	L	OBS	CALC
7	7	78	82
7	8	23	-19
7	9	29	-24
7	13	70	66
7	14	47	-48
7	15	52	-56
7	16	28	-27
7	17	125	-107
7	18	30	32
7	23	45	-40
7	24	53	46
7	25	62	56
7	27	64	50
8	2	39	35
8	3	39	-46
8	4	39	-40
8	5	33	28
8	6	53	-47
8	7	41	45
8	8	101	136
8	10	72	70
8	12	46	41
8	13	39	32
8	14	109	136
8	15	20	-23
8	16	21	31
8	17	43	-42
8	18	44	-43
8	22	24	-28
8	23	24	-22
8	24	72	-73
8	25	31	28
8	26	26	-25
8	27	26	16
9	1	113	152
9	2	68	-79
9	5	24	21
9	6	17	10
9	7	51	53
9	8	73	-76
9	9	102	-113
9	10	19	18
9	11	55	-61
9	12	63	61
9	13	70	72
9	15	42	-34
9	17	38	-37
9	18	39	40
9	19	57	56
9	20	33	-32
9	22	35	-35
9	23	80	-71
9	28	27	-23
10	1	40	38
10	2	77	79
10	4	26	19
10	6	32	28
10	8	67	65
10	9	48	-51
10	11	20	-22
10	12	36	-41
10	19	34	36
10	20	24	31
10	22	44	39
11	1	51	58
11	2	19	-21
11	3	87	-84
11	4	48	50
11	5	44	42
11	6	44	48
11	7	99	119
11	8	45	-43
11	9	20	-24
11	13	70	58
11	14	71	-64
11	15	73	-64
11	17	95	-103
11	18	24	27
11	21	44	-36
11	23	79	-70
11	24	46	39
11	25	33	37
11	27	27	30
12	1	29	-25
12	2	29	-27
12	4	77	-77
12	6	79	-74
12	7	21	22
12	8	30	-30
12	9	21	21
12	14	28	30
13	1	97	107
13	2	61	-58
13	3	37	-34
13	7	55	46
13	8	68	-56
13	9	85	-86
13	10	23	19
13	11	47	-49
13	12	47	48
13	13	63	63
13	17	25	-18
13	18	36	39
13	19	64	56
13	20	26	-26
13	22	27	-31
13	23	54	-51
14	8	41	-36
14	9	23	-19
14	10	51	-50
14	12	52	-47
14	14	62	-55
14	16	25	-25
15	2	24	-24
15	3	96	-96
15	4	59	48
15	7	65	59
15	13	77	61
15	14	45	-36
15	15	26	-22
15	17	65	-49
16	1	25	-21
16	2	43	-43
16	6	25	-28
16	8	25	-29
16	9	25	28
17	1	26	25
17	2	31	-38
17	3	52	-52
17	8	26	-32
17	9	65	-61
17	12	33	31
17	13	54	61
18	4	38	44
18	6	33	36
19	3	67	-61
19	7	27	32

*****H= 4*****

K	L	OBS	CALC
0	0	231	218
0	1	173	-175
0	2	123	105
0	3	81	-82
0	4	36	-40
0	5	22	17
0	6	135	143
0	7	85	-75
0	8	37	-32
0	9	82	-73
0	10	137	-126
0	11	115	96
0	13	48	45
0	14	27	13
0	15	39	-35
0	16	86	-86
0	17	44	40
0	18	20	17
0	19	29	30
0	20	30	23
0	21	76	-81
0	22	70	-71
0	24	70	-70
0	25	27	23
0	26	31	21
0	27	32	-25
0	28	64	-60
0	31	57	52
0	32	57	52
0	38	45	44
1	0	56	65
1	2	38	46
1	3	43	48
1	5	33	30
1	6	42	-36
1	7	16	-11
1	8	42	-37
1	9	57	-55
1	10	47	-46
1	11	49	-49
1	13	83	-82
1	15	42	-41
1	16	40	40
1	17	26	-29
1	18	19	21
1	19	39	45
1	20	35	32
1	23	47	50
1	25	23	31
2	0	99	107
2	1	49	-59
2	2	75	-49
2	3	15	-15
2	4	46	-42
2	6	125	140
2	7	23	-24
2	8	112	110
2	9	45	-39
2	10	96	-89
2	11	35	35
2	12	86	82
2	13	32	-28
2	15	120	-114
2	16	161	-141
2	17	26	28
2	18	47	-50
2	19	20	22
2	22	85	-81
2	23	39	36
2	25	63	58
2	26	60	52
2	27	43	-37
3	0	119	-119
3	1	32	-29
3	2	15	-13
3	3	141	-134
3	4	15	12
3	5	79	-71
3	7	136	-128
3	9	103	-86
3	10	81	74
3	11	15	-13
3	14	17	-19
3	15	30	-33
3	17	23	26
3	18	27	-32
3	20	46	-43
3	25	34	34
3	29	45	48
3	31	32	44
4	0	156	156
4	1	98	-79
4	2	24	-19
4	3	64	-57
4	4	74	-62
4	5	30	26
4	6	95	78
4	7	49	-42
4	8	98	-87
4	9	50	-45
4	10	85	-78
4	11	164	142
4	13	16	18
4	14	67	66
4	15	25	-24
4	16	37	-38
4	17	27	35
4	18	63	62
4	19	20	18
4	20	85	80
4	21	87	-78
4	22	31	-33
4	28	54	-46
4	31	42	46
5	1	85	-76
5	2	48	40
5	3	31	28
5	4	60	51
5	5	62	59
5	6	95	-80
5	7	40	-36
5	8	32	-30
5	9	96	-87
5	11	16	-15
5	12	16	-17
5	13	95	-90
5	15	91	-86
5	16	74	75
5	18	28	26
5	19	36	40
5	23	62	57
5	25	42	49
5	26	43	-44
6	0	33	-29
6	1	19	-14
6	2	173	-143
6	4	118	-97
6	5	129	105
6	6	51	48
6	8	69	58.
6	10	43	-46
6	11	41	38
6	12	99	92
6	13	25	-29
6	14	45	42
6	15	86	-86
6	16	52	-51
6	17	20	23
6	19	21	17
6	20	66	65
6	24	42	37
6	25	52	43
6	26	62	55
6	27	25	-29
7	0	116	-111
7	1	41	-39
7	3	79	-70
7	5	38	30
7	6	44	-39
7	7	60	-52
7	8	16	19
7	9	24	-20
7	10	104	99
7	11	94	86
7	12	25	-23
7	13	42	44
7	14	19	-18
7	15	34	-36
7	16	20	21
7	17	59	56
7	20	71	-71
7	21	69	-57
7	22	29	23
8	0	22	15
8	1	87	-81
8	2	22	-25
8	3	42	-37
8	4	98	-92
8	7	42	-38
8	8	55	-59
8	9	31	-26
8	10	63	-60
8	11	70	62
8	12	27	27
8	13	34	34
8	14	49	58
8	16	21	24
8	17	21	24
8	18	86	82
8	19	22	16
8	20	61	69
8	21	58	-50
8	28	26	-36
9	0	16	8
9	1	76	-67
9	2	59	55
9	3	49	54
9	4	70	63
9	5	150	129
9	6	80	-78
9	7	25	25
9	8	26	-27
9	10	19	17
9	11	76	79
9	12	34	-37
9	14	20	-28
9	15	47	-48
9	16	75	73
9	17	22	25
9	19	40	44
9	21	34	-41
9	23	25	26
9	26	37	-45
9	27	46	-51
10	0	23	-18
10	2	48	-53
10	4	37	-36
10	5	53	60
10	6	33	31
10	8	51	57
10	12	46	50
10	15	44	-44
10	16	39	-38
11	0	93	-93
11	1	47	-45
11	2	19	15
11	3	43	-46
11	4	39	39
11	5	56	66
11	6	28	-35
11	7	20	-23
11	10	73	82
11	11	91	109
11	12	21	-23
11	13	49	60
11	14	22	-32
11	17	58	62
11	18	24	-31
11	20	50	-60
11	21	50	-59
12	0	85	80
12	2	41	47
12	3	20	-24
12	8	30	-42
12	11	27	36
12	12	27	-35
13	0	24	-18
13	1	48	-56
13	2	30	38
13	3	21	26
13	4	58	54
13	5	85	94
13	6	58	-65
13	11	46	55
13	15	42	-47
13	16	49	57
14	8	33	39
14	14	25	-30
14	16	25	-41
15	0	67	-73
15	1	33	-40
15	3	41	-49
15	4	24	18
15	7	38	-51
15	9	24	-34
15	10	49	62
15	11	35	44
16	2	24	41
16	6	25	-6
18	0	54	-43
19	0	45	-36
20	0	22	-22
22	0	53	-37
23	0	21	-18
24	0	20	-13

*****H= 5*****

K	L	OBS	CALC
0	1	9	-1
0	3	123	146
0	4	115	117
0	5	9	-13
0	6	143	137
0	7	99	-98
0	9	13	15
0	10	88	84
0	12	104	100
0	13	109	-107
0	14	78	-77
0	15	21	24
0	17	81	82
0	18	62	62
0	19	38	-38
0	20	25	-17
0	22	22	-20
0	23	42	43
0	24	30	30
0	25	49	-46
0	26	26	-30
0	27	49	-45
0	28	73	-64
0	34	47	-43
0	35	33	34
1	4	31	40
1	5	28	32
1	6	48	49
1	7	40	47
1	8	28	24
1	9	46	50
1	10	14	-9
1	11	25	22
1	12	41	-45
1	14	34	-32
1	15	25	-27
1	17	33	-33
1	19	54	-52
1	20	21	22
1	22	22	27
2	2	73	-89
2	3	71	73
2	4	39	40
2	6	16	15
2	7	30	-28
2	8	36	-35
2	9	116	113
2	10	82	89
2	11	56	57
2	12	84	98
2	13	81	-79
2	18	53	47
2	19	80	-82
2	20	56	-53
2	22	55	-53
2	23	57	54
2	26	24	-25
2	28	44	-39
2	29	45	47
3	1	74	78
3	3	112	114
3	4	86	-79
3	6	49	-44
3	7	12	-13
3	8	13	12
3	9	14	-12
3	10	15	12
3	11	35	-39
3	12	16	10
3	13	51	-51
3	14	50	51
3	16	26	27
3	18	28	-35
3	19	36	-40
3	21	38	-42
3	24	29	-34
3	25	49	-50
4	1	22	-22
4	2	73	-65
4	3	95	84
4	4	77	68
4	6	56	51
4	7	123	-109
4	8	70	-67
4	9	26	29
4	10	15	-17
4	12	16	17
4	13	78	-74
4	14	88	-87
4	15	41	48
4	16	23	-23
4	17	69	76
4	18	50	48
4	23	50	39
4	24	64	65
4	25	52	-44
4	27	51	-48
5	1	12	10
5	2	68	66
5	3	59	49
5	5	62	55
5	8	61	56
5	9	74	69
5	10	32	-30
5	11	33	26
5	12	78	-73
5	13	47	-50
5	15	19	-21
5	16	19	-17
5	17	41	-41
5	18	36	-31
5	19	75	-76
5	20	27	33
5	21	22	-23
5	22	57	51
6	1	98	-92
6	2	127	-108
6	3	35	32
6	4	32	-27
6	6	68	-57
6	7	22	-20
6	8	102	-99
6	9	88	89
6	10	17	-15
6	11	46	47
6	13	45	-47
6	14	27	-26
6	18	21	21
6	19	54	-54
6	20	39	-34
6	23	42	43
6	24	43	38
7	2	21	21
7	3	79	73
7	4	89	-86
7	5	16	-17
7	6	93	-79
7	7	95	-80
7	8	54	46
7	13	47	-38
7	14	69	71
7	15	29	32
7	16	29	27
7	17	37	36
7	18	38	-38
7	23	24	21
7	24	43	-44
7	25	31	-38
8	2	23	-24
8	3	71	68
8	4	17	18
8	6	24	18
8	7	61	-59
8	8	72	-74
8	10	26	-36
8	13	45	-50
8	14	113	-96
8	17	59	54
9	1	94	-88
9	2	87	83
9	5	18	-17
9	7	37	-36
9	8	94	80
9	9	61	59
9	11	53	45
9	12	71	-66
9	15	22	31
9	17	22	30
9	18	46	-48
9	19	23	-26
9	20	29	31
9	21	24	27
9	22	43	45
9	23	31	41
10	1	46	-48
10	2	42	-37
10	6	39	-29
10	8	28	-33
10	9	45	46
10	10	25	22
10	11	30	28
10	12	21	22
10	13	22	-19
10	19	30	-36
10	20	24	-25
11	1	45	-47
11	2	40	41
11	3	35	34
11	4	70	-74
11	5	58	-61
11	6	46	-41
11	7	72	-71
11	8	63	56
11	14	69	66
11	15	40	52
11	16	23	27
11	17	77	75
11	18	52	-53
11	24	37	-47
11	25	46	-23
12	1	21	19
12	4	43	44
12	6	37	41
12	7	27	-30
12	8	22	17
12	9	22	-15
13	1	44	-46
13	2	59	64
13	8	61	61
13	9	57	53
13	12	59	-56
13	13	30	-32
13	14	24	16
13	18	36	-39
13	19	26	-36
13	20	26	29
13	22	26	40
14	7	24	22
14	8	24	27
14	9	24	22
14	10	34	36
14	12	25	31
14	14	36	44
15	3	48	60
15	4	49	-56
15	6	42	-48
15	7	43	-45
15	8	30	35
15	13	36	-42
15	14	36	47
16	1	25	31
16	2	25	22
17	2	36	40
17	3	36	40

*****H= 6*****

K	L	OBS	CALC
0	0	150	-176
0	1	89	91
0	2	50	-58
0	3	48	54
0	4	23	-26
0	5	21	-22
0	6	42	-51
0	7	83	79
0	9	59	63
0	10	57	67
0	11	85	-99
0	13	27	-22
0	14	22	12
0	15	41	38
0	16	49	51
0	17	50	-54
0	18	24	21
0	19	27	-20
0	21	79	80
0	22	59	65
0	32	47	-40
1	0	24	-28
1	1	8	15
1	2	22	-37
1	3	11	-17
1	5	25	-27
1	6	38	45
1	7	17	22
1	8	31	34
1	10	35	39
1	11	48	49
1	12	27	23
1	15	36	37
1	16	37	-42
1	18	28	-30
2	0	46	-57
2	1	37	53
2	4	20	25
2	8	26	-26
2	9	52	56
2	10	29	30
2	11	44	-43
2	12	32	-27
2	13	33	37
2	15	82	102
2	16	80	87
2	17	39	-38
2	19	41	-37
2	22	32	42
2	23	32	-35
2	25	59	-55
3	0	66	79
3	1	35	36
3	3	34	35
3	5	41	50
3	7	42	50
3	8	44	-43
3	9	50	57
3	10	57	-64
3	11	22	15
3	20	43	39
4	0	61	-66
4	1	61	86
4	2	23	24
4	3	48	52
4	4	30	33
4	5	32	-33
4	7	49	51
4	8	29	33
4	9	48	47
4	10	50	43
4	11	74	-85
4	12	42	-39
4	13	35	-33
4	14	36	-32
4	17	28	-38
4	20	44	-44
4	21	64	74
5	0	17	11
5	1	22	16
5	2	37	-33
5	4	39	-42
5	5	34	-26
5	6	65	74
5	7	52	51
5	8	49	44
5	9	55	52
5	11	34	37
5	12	43	40
5	13	52	49
5	15	48	48
5	16	63	-65
5	18	30	-25
6	0	47	42
6	1	40	36
6	2	58	61
6	3	25	-15
6	4	67	75
6	5	118	-115
6	9	34	33
6	11	25	-29
6	12	45	-49
6	14	39	-41
6	15	69	69
7	0	93	96
7	3	22	26
7	4	45	-41
7	6	23	20
7	9	43	35
7	10	82	-92
7	11	59	-51
7	18	31	29
7	20	46	45
8	0	42	-30
8	1	53	47
8	2	34	31
8	3	42	34
8	4	45	35
8	7	44	35
8	8	37	30
8	9	26	23
8	10	38	36
8	11	68	-62
8	13	29	-27
8	16	31	-24
8	17	31	-30
8	18	32	-39
8	20	47	-46
8	21	48	47
9	0	32	29
9	2	57	-50
9	3	41	-33
9	4	58	-60
9	5	83	-86
9	6	80	74
9	8	43	36
9	11	35	-33
9	12	51	42
9	14	43	32
9	16	71	-62
9	17	32	-28
10	3	27	-23
10	4	27	28
10	5	68	-57
10	15	56	45
10	16	32	30
11	0	87	85
11	1	40	29
11	4	41	-36
11	5	51	-40
11	6	36	27
11	10	98	-75
11	11	89	-67
11	13	45	-36
11	14	46	34
11	20	61	55
11	21	50	44
12	0	64	-51
13	0	26	23
15	0	76	64
16	0	28	-26
17	0	22	20
18	0	22	24
19	0	54	40
22	0	40	29

*****H= 7*****

K	L	OBS	CALC
0	3	89	-103
0	4	50	-59
0	6	59	-70
0	7	101	113
0	8	29	-26
0	9	23	-24
0	10	48	-45
0	12	54	-50
0	13	72	68
0	15	54	-46
0	17	67	-64
0	19	28	29
0	20	25	21
0	24	33	6
0	26	29	33
1	2	21	-33
1	3	10	-10
1	4	25	-29
1	5	18	-17
1	6	24	-25
1	7	15	-14
1	10	17	18
1	12	44	39
1	14	42	31
1	17	23	24
1	19	25	25
1	20	26	-20
1	22	27	-28
2	2	26	32
2	3	49	-55
2	4	28	-29
2	6	20	-16
2	7	41	37
2	9	88	-83
2	10	48	-47
2	11	50	-49
2	12	44	-47
2	13	51	55
2	19	76	75
2	21	26	23
2	23	39	-43
3	1	43	-44
3	3	60	-66
3	4	63	66
3	5	14	-15
3	6	62	56
3	14	49	-40
3	15	22	21
3	16	33	-27
3	19	25	31
3	21	26	24
3	24	28	29
3	25	28	28
4	2	14	12
4	3	90	-95
4	5	28	25
4	7	92	85
4	8	40	40
4	13	65	59
4	14	45	42
4	15	40	-34
4	17	70	-71
4	19	26	27
4	23	28	-35
5	1	23	-20
5	2	57	-60
5	3	33	-29
5	4	17	-14
5	5	32	-31
5	8	47	-43
5	9	34	-22
5	10	29	25
5	12	65	63
5	13	45	35
5	17	35	35
5	18	36	25
5	19	45	40
5	20	27	-26
5	21	27	19
5	22	39	-35
6	1	71	64
6	2	44	41
6	3	25	-26
6	4	18	18
6	6	47	42
6	7	19	19
6	8	53	54
6	9	66	-65
6	11	44	-38
6	13	33	35
6	14	23	29
6	19	60	53
6	23	28	-37
6	24	29	-30
7	2	27	-28
7	3	19	-22
7	4	69	60
7	6	50	47
7	7	21	21
7	8	48	-42
7	14	65	-66
7	16	31	-27
7	18	38	40
8	2	20	15
8	3	47	-45
8	7	66	69
8	8	45	39
8	10	33	30
8	12	24	21
8	13	30	30
8	14	44	44
8	15	36	-36
8	17	54	-47
9	1	49	46
9	2	70	-70
9	5	22	20
9	8	58	-57
9	11	53	-17
10	1	47	41
10	2	23	24
10	9	35	-37
11	1	24	36
11	2	35	-40
11	4	56	60
11	5	35	35
11	6	44	43
11	7	25	28
11	8	45	-42
11	14	55	-58
11	15	28	-32
11	16	28	-30
11	17	28	-41
11	18	28	36
13	2	38	-61
13	8	39	-50
13	12	40	50

*****H= 8*****

K	L	OBS	CALC
0	0	55	55
0	1	54	-54
0	2	25	25
0	3	49	-49
0	4	29	29
0	5	44	37
0	6	38	32
0	7	50	-49
0	9	54	-47
0	11	62	70
0	13	32	17
0	15	32	-23
0	16	40	-34
0	17	37	39
0	21	58	-56
1	6	25	-26
1	7	19	-20
1	8	35	-31
1	16	29	28
1	18	31	31
2	0	18	20
2	2	20	20
2	3	15	16
2	4	20	17
2	5	66	94
2	6	23	28
2	8	21	14
2	9	50	-51
2	11	34	30
2	13	32	-35
2	15	70	-68
2	16	29	-33
2	17	30	26
2	19	32	29
3	0	51	-66
3	2	33	-32
3	3	24	-24
3	5	33	-34
3	7	42	-36
3	8	31	26
3	9	40	-38
3	10	48	45
3	13	27	-29
3	15	29	-24
4	1	46	-60
4	3	33	-33
4	7	55	-54
4	9	29	-27
4	11	52	52
4	13	39	30
4	17	44	42
5	0	20	-10
5	2	36	35
5	4	31	28
5	6	46	-44
5	7	24	-29
5	8	35	-33
5	9	25	-21
5	11	33	-29
5	12	34	-33
5	16	43	46
6	0	31	-34
6	1	32	-28
6	2	36	-32
6	3	23	24
6	4	33	-31
6	5	69	76
7	0	63	-63
7	4	25	26
8	2	38	-36
8	3	38	-28
9	0	25	-21
9	2	49	40
9	4	40	39
10	6	43	4
11	0	77	-65
13	0	22	-22
14	0	22	20
15	0	55	-48
20	0	27	-10

*****H= 9*****

K	L	OBS	CALC
0	3	65	61
0	7	65	-63
0	12	47	21

*****H=10*****

K	L	OBS	CALC
3	0	39	37
6	0	22	31
7	0	39	40
8	0	22	26

in which the sharing of octahedral faces occurs; (2) although such an arrangement apparently has not been reported previously for cobalt it has been reported for Ni^{4+} (which is isoelectronic with Co^{3+}) in BaNiO$_3$ (Lander, 1951); (3) neither the density nor the chemical analyses are consistent with additional molybdenum in the structure. The other peak at 0·25, $\frac{1}{4}$, 0·31 is at the center of a trigonal prism of oxygen atoms which is an extremely unlikely environment for either cobalt or molybdenum. On the other hand it is a common one for sodium, and because of the method of preparation sodium is a very likely 'impurity' in the structure. A series of least-squares calculations was therefore run with additional cobalt and sodium atoms in the positions indicated. Marked improvement of the R factor from 0·23 to 0·15 occurred. However, the thermal parameter not only for this Co (hereafter termed Co(4)), but also for Co(8), was very large, even in comparison with the oxygen thermal parameters. It seemed likely that neither cobalt site was fully occupied, a conclusion that also follows from our estimate of a reasonable density and from the demands of charge balance. Since there was absolutely no evidence on any of the X-ray photographs to support the existence of a super-cell it must be assumed that if partial occupancy occurs it is a random, or nearly random, process. From Fourier techniques it is both difficult and laborious to determine simultaneously the degree of occupancy of a site and the thermal parameter of the atom in that site, for a given peak height and shape can be simulated by any number of combinations of occupancy and thermal motion. If randomness is assumed it is not difficult to carry out such a determination by least-squares methods and if the data extend to reasonable angles the resultant values of occupancy factor and thermal parameter need not be strongly correlated. In the present case a series of least-squares calculations was run with the occupancy factors on the four heavy atoms and the sodium as additional parameters.* The R factor decreased significantly from 0·15 to 0·11. Moreover, whereas in accordance with our expectations the cobalt sites were not fully occupied, it was particularly encouraging that the occupancies of the Mo(8), Mo(4), and Na sites refined to 1·02 ± 0·03, 1·02 ± 0·03, and 0·98 ± 0·05, respectively. In further refinements only the occupancy factors for Co(8) and Co(4) were varied.

A third difference Fourier synthesis, based on these structure factors, showed as the highest peak one in the vicinity of Co(4); its height of 13 e.Å^{-3} was approximately half that of an oxygen peak. Careful analysis of this difference Fourier synthesis revealed that the vibrations of Co(4) were anisotropic, with the principal direction of vibration along a, whereas the vibrations of the other heavy atoms were nearly isotropic (Table 5). In a final series of least-squares calculations the four heavy atoms were allowed to vibrate anisotropically, but the light atoms (including sodium) were constrained to vibrate isotropically. This refinement of 72 parameters (11 scale factors, 2 occupancy factors, 31 positional parameters, 20 anisotropic thermal parameters, 8 isotropic thermal parameters) on the 2089 data converged rapidly to the final set of parameters given in Table 1. In Table 2 we compare the calculated structure factors with the observed (brought to a common, absolute scale). The over-all R factor is 0·095, and an analysis of R as a function of h, k, l, and $\lambda^{-1} \sin \theta$ shows no unexpected trends. None of the calculated structure amplitudes for the unobserved reflections accessible on the photographs exceeds our estimates of $F_{\min}$, and for this reason they are not listed in Table 2. Examination of the correlation matrix reveals no unexpected correlations between parameters, and, in fact, the highest correlations, those between occupancies and thermal parameters for both types of Co atom, do not exceed 0·6. A fourth, and final, difference Fourier synthesis, based on the data of Table 2, shows no peak higher than about 3 e.Å^{-3}, approximately 10% of the height of an oxygen atom in this structure. It is clear that no other atoms remain to be found.

Composition

The formula NaCo$_{2\cdot31\pm0\cdot02}$(MoO$_4$)$_3$ follows from the data of Table 1 and in Table 3 we compare the X-ray and chemical percentage compositions. The agreement is as good as can be expected, as is the agreement between calculated (4·17 g.cm^{-3}) and measured densities, both because of a possible range of compositions in the samples and also because some of the analyses were done on microgram quantities of material. In particular the high sodium analysis is not surprising because contamination of the samples by sodium-containing salts is likely. Therefore it is probably better to compare the Co/Mo ratios in Table 3. Here the agreement is satisfactory. It should be pointed out that in problems of this type, where the actual composition can vary from crystal to crystal, the refinement of the X-ray data with variable occupancy factors provides a powerful means of establishing the composition of the particular crystal studied.

Table 3. *X-ray and chemical compositions*

	X-ray	Chemical range	Chemical 'average'
wt.% Mo	45·0	43 to 51%	45 ± 2%
wt.% Co	21·3 ± 0·2	18·1 to 21·1%	20 ± 2%
wt.% Na	3·6	—	7 ± 2%
moles Co/ moles Mo	0·770 ± 0·008	0·64 to 0·75	0·72 ± 0·07

---

* Because the B's of the seven oxygen atoms are essentially equal it is assumed that all oxygen sites are fully occupied.

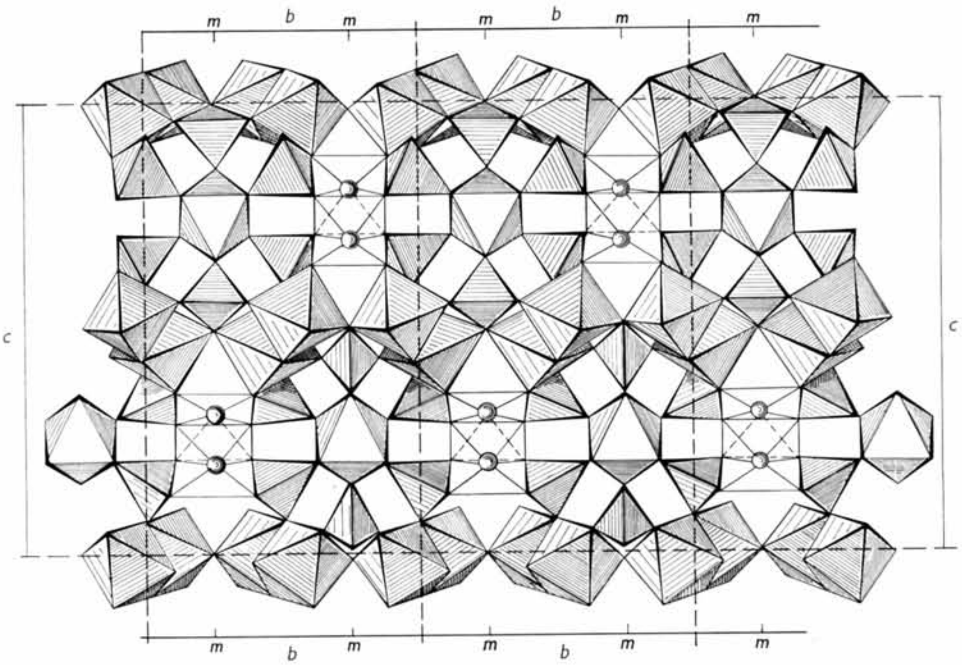

Fig. 1. Tilted plan view of *bc* plane, of two unit cells, through one thickness of *a* showing hexagonal motif formed by MoO_4 tetrahedra around the Co(4) octahedra which share faces. The Co(8) octahedra share edges and form zigzag chains parallel to *a*. The chains are also linked to each other by corners to make up a double zigzag sheet in the *ab* plane (see Fig. 2). Na sites are shown at the centers of trigonal prisms.

Description of the structure

As we note above, the unit cell contains two crystallographically non-equivalent sets of heavy cations. Co(8) and Mo(8) lie in eightfold general positions while Mo(4) lies on the mirror plane and Co(4) lies on the screw diad parallel to *a*. From the parameters of Table 1 it follows that the structure is formed from a framework of MoO_4 tetrahedra and CoO_6 octahedra in such a way that the tetrahedra provide links between sheets and columns formed by the octahedra. In the sheets the octahedra share corners and edges; in the columns they share faces. The zigzag void parallel to *a* that is left by the MoO_4 linkages consists of trigonal prisms sharing edges and is filled with sodium atoms. A slightly tilted plan view of the structure is shown in Fig. 1.

The oxygen octahedra around the Co(8) atoms make up double zigzag sheets parallel to the *ab* plane at $z=0$ and $z=\frac{1}{2}$. These would correspond to Co_2O_7 if all the Co(8) sites were filled. One of these sheets is sketched in Fig. 2. The sheet is composed of zigzag chains of octahedra, sharing edges, which extend vertically up the *a* axis, two octahedra being equivalent to the *a* interval. Each of the chains is joined to its neighbors on either side by sharing of corners at the oxygen sites on the mirror planes, at intervals of *a* also. A sheet so formed has in it triangular holes which provide a three-point linkage for some of the tetrahedra, as described below. As far as we are aware, such a double zigzag sheet has not been described previously.

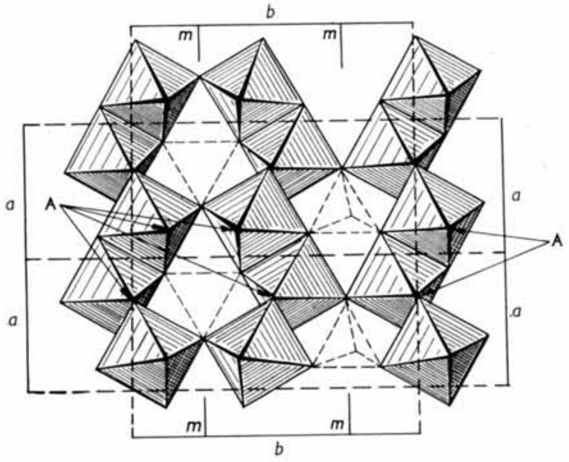

Fig. 2. Co(8) zigzag octahedral sheet in the *ab* plane. Tetrahedra about the Mo(4) which have three point linkages with the sheet in the triangular holes are shown dotted. Tetrahedra about the Mo(8) atoms are not shown, but the two point linkages are at *A*. Outline of two unit cells is shown dotted.

Between the sheets are sited hexagonal motifs composed of MoO_4 tetrahedra that surround the Co(4) atoms on the screw diad, and these therefore lie in octahedral holes (Fig. 1). The octahedra so formed share faces to make up an infinite column parallel to *a* (Fig. 3). Taken together with the tetrahedra the motif has approximate symmetry 6_3. The columns and tetrahedra pack in an approximate hexagonal manner on the *bc* plane, which itself is nearly orthohexagonal.

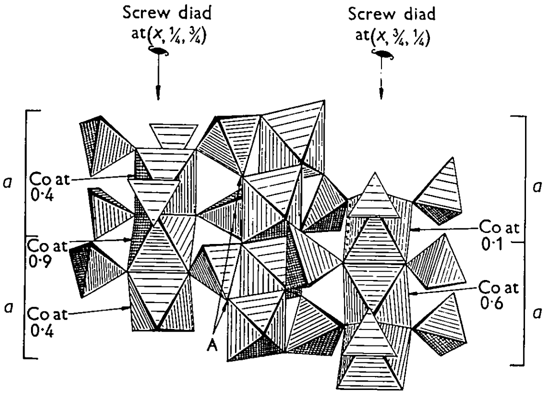

Fig. 3. Sketch to illustrate how the hexagonal motifs of MoO_4 tetrahedra around the screw diads parallel to *a* are linked to each other by the Co(8) octahedra. Only one chain of these octahedra is shown. The other chain is linked to this one by corners at points such as *A* at intervals of *a*. Plane of paper is (011). Na sites are omitted.

The sharing of octahedral faces, though not too common, has been reported in a number of compounds, but this appears to be the first example involving cobalt*. In most of the reported structures, for example $BaTiO_3$ (Burbank & Evans, 1948), there exist discrete dimeric M_2X_9 groups formed by the sharing of one face between two octahedra. However, in the $BaNiO_3$ structure (Lander, 1951) there is a continuous sharing of faces to form an infinite column. The Ni–Ni distance is 2·42 Å, which is slightly shorter than the bond in the metal (2·49 Å). Owing to the partial occupancy of the Co(4) site, the present case is somewhere in between these two examples: only three out of the four possible sites need be occupied by Co.

Both types of MoO_4 tetrahedra share one oxygen with the Co(4) octahedral columns. However, the other three oxygen atoms are shared differently. In the Mo(4) tetrahedra all three remaining oxygen atoms are linked directly to the Co(8) octahedral sheet in the triangular holes mentioned above, whereas the Mo(8) tetrahedra share only two of the remaining oxygen atoms with the sheet (points *A*, Fig. 2). The fourth oxygen atom is joined to a sodium atom, and as such each sodium atom lies on the mirror plane at the center of a trigonal prism of oxygen atoms.

The observed needle- and plate-like habits of the crystals (refer to I) can perhaps be explained in terms of the polyhedral packing that exists in this structure. Thus the very long needles, needle axis *a*, could arise from extended growth of the face-sharing Co(4) octahedra. On the other hand, the platelets, whose normal is *c*, could arise from the two-dimensional growth of the Co(8) octahedral sheet. It is even possible that these habits could arise from differing occupancies of the Co(8) and Co(4) sites.

Table 4. *Selected interatomic distances in* $NaCo_{2\cdot31}(MoO_4)_3$

Mo(8) tetrahedron

Mo(8), 0–4, 0	1·726(10)	
–1, 0	1·751(10)	
–5, 0	1·773(10)	
–3, 0	1·811(09)	
3, 0–4, 0	2·818(14)	
1, 0–4, 0	2·837(15)	
4, 0–5, 1	2·853(15)	
3, 0–5, 1	2·908(14)	
1, 0–3, 0	2·922(14)	
1, 0–5, 1	2·951(15)	

Co(4) octahedron

Co(4), 0–1, 6	2·109(11)	(2)
–1, 3	2·117(11)	(2)
–6, 0	2·204(14)	
–6, 7	2·215(14)	
1, 3–1, 8	2·848(20)	(2)
6, 0–1, 6	2·987(15)	(4)
6, 0–1, 8	3·099(16)	(2)
1, 3–1, 5	3·123(11)	(2)
6, 7–1, 6	3·153(16)	(2)

Na trigonal prism

Na, 0–5, 0	2·312(11)	(2)
–4, 0	2·337(12)	(2)
–4, 9	2·399(11)	(2)

Mo(4) tetrahedron

Mo(4), 0–2, 0	1·760(10)	(2)
–6, 0	1·761(13)	
–7, 0	1·817(16)	
2, 0–2, 2	2·815(19)	
2, 0–6, 0	2·879(15)	(2)
2, 0–7, 0	2·903(17)	(2)
6, 0–7, 0	3·000(21)	

Co(8) octahedron

Co(8), 0–5, 0	2·070(10)
–3, 3	2·107(09)
–3, 0	2·144(10)
–2, 4	2·178(10)
–7, 0	2·200(08)
–2, 5	2·241(10)
3, 0–3, 3	2·841(18)
5, 0–2, 5	2·861(14)
3, 0–2, 5	2·891(14)
7, 0–3, 3	2·905(13)
5, 0–2, 4	2·964(14)
2, 4–3, 3	2·984(14)
2, 5–3, 3	3·006(14)
2, 4–2, 5	3·022(19)
3, 0–5, 0	3·167(14)
3, 0–7, 0	3·209(13)
7, 0–2, 4	3·225(18)
5, 0–7, 0	3·385(18)

Cation–Cation

Co(4), 0–Co(4), 7	2·623(2)	(2)
Co(8), 0–Co(8), 3	3·162(4)	
Co(8), 0–Co(8), 10	3·225(4)	
Na, 0–Na, 9	3·301(8)	(2)
Mo(8), 0–Mo(8), 11	4·328(2)	(2)
Mo(8), 0–Mo(4), 5	4·288(2)	

The first symbol denotes the atom in accordance with Table 1; the second number denotes the following symmetry transformations of the parameters of Table 1:

0: x, y, z
1: $1+x, y, z$
2: $x, \frac{1}{2}-y, z$
3: $1-x, 1-y, 1-z$
4: $x-1, \frac{1}{2}-y, z$
5: $1-x, \frac{1}{2}+y, 1-z$
6: $\frac{3}{2}-x, 1-y, \frac{1}{2}+z$
7: $x-\frac{1}{2}, y, \frac{3}{2}-z$
8: $1-x, y-\frac{1}{2}, 1-z$
9: $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}-z$
10: $\bar{x}, 1-y, 1-z$
11: $\frac{1}{2}+x, y, \frac{1}{2}-z$

Following the distance the first number in parentheses is the estimated standard deviation; the second number, if any, is the number of such distances.

In Table 4 we list the principal interatomic distances; these have been calculated by the Busing–Levy ORFFE program from the final least-squares tape and hence in the estimates of errors on these distances account is taken of correlations between parameters. The distances reported in Table 4 appear to be normal,

---

* *Note added in proof.*— Our attention has been drawn to Gushee, Katz & Ward (1957), in which this same face-sharing was found for $BaCoO_{2\cdot85}$.

for example when compared with the tabulation of Ondik & Smith (*International Tables for X-ray Crystallography*, 1962*c*). Moreover, the Co(4)–O distances, which range from 2·11 to 2·22 Å, do not differ significantly from the Co(8)–O distances (2·07 to 2·24 Å), nor do the Mo(4)–O distances (1·76 to 1·82 Å) differ significantly from the Mo(8)–O distances (1·73 to 1·81 Å).

Table 5. *Root-mean-square amplitudes of vibration*

Atom	Max. (Å)	Int. (Å)	Min. (Å)
Mo(8)	0·1158 ± 0·0021	0·0949 ± 0·0017	0·0870 ± 0·0017
Co(8)	0·1134 ± 0·0029	0·0849 ± 0·0033	0·0731 ± 0·0052
Mo(4)	0·1144 ± 0·0025	0·1039 ± 0·0019	0·0910 ± 0·0025
Co(4)	0·2411 ± 0·0060	0·1054 ± 0·0049	0·0944 ± 0·0057

The directions of the principal axes for Co(4) are discussed in the text.

Oxidation states and their distribution

Discussion of the oxidation states of cobalt and molybdenum and their distribution in this compound is necessarily speculative*, but a few remarks seem worthwhile. Since molybdenum is very probably at most hexavalent, it is necessary, in order to preserve charge balance, that some of the cobalt be in an oxidation state greater than two, presumably three. The ratio of Co^{3+} to Co^{2+} depends upon the average oxidation state of the molybdenum. It seems probable that electron exchange is not taking place between Co^{2+} and Co^{3+}, or else the color of the crystals would be black, rather than bright blue. Thus we guess that the two oxidation states of cobalt are well separated and we offer the following suggestions about their distribution. The Co(8) sites are probably Co^{2+} sites, for the Co(8) positions are well separated from one another (>3·1 Å), as is usual in Co^{2+} compounds. Thus we suggest that both states of cobalt occur in the Co(4) sites and that separation is achieved simply by letting entire columns consist of either divalent or trivalent cobalt. (If the molybdenum is all hexavalent, then 50% of the cobalt in the Co(4) positions is trivalent.) By analogy with the isoelectronic Ni^{4+} in $BaNiO_3$ it seems probable that a column of Co^{3+} would have all Co(4) sites occupied (Co–Co = 2·623 ± 0·003 Å) whereas in order to avoid metal–metal bonds a column of Co^{2+} would have only half of the sites occupied. The marked anisotropy of the Co(4) atoms (Table 5), in which the direction of the major axis of the vibration ellipsoid makes angles with *a*, *b*, and *c* of 14°, 90°, and 76° respectively, and hence is essentially along *a*, could be a manifestation of different Co(4) *x* parameters for Co^{3+} occupancy and for occupancy by the slightly larger Co^{2+}. Up to a point then the occupancy of the Co(8) sites depends upon the demands of charge balance imposed by the distribution of Co^{2+} and Co^{3+} in the Co(4) positions. However depletion of Co^{2+} in the Co(8) sheets is certainly limited by the eventual collapse of the entire structure.

We are grateful to J. K. Rowley for performing the micro-analyses. We have enjoyed many useful conversations with W. C. Hamilton. We have profited greatly from several conversations with A. D. Wadsley and we are indebted to him for his helpful criticisms of our initial sketches. We wish to thank the Chairman and Directors of the British Petroleum Company for permission to publish this paper.

References

Burbank, R. D. & Evans, H. T. (1948). *Acta Cryst.* **1**, 330.

Gushee, B. E., Katz, L. & Ward, R. (1957). *J. Amer. Chem. Soc.* **79**, 5601.

Hamilton, W. C. (1959). *Acta Cryst.* **12**, 609.

Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.

International Tables for X-ray Crystallography (1962*a*). Vol. 3, Table 3.3.1A. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1962*b*). Vol. 3, Table 3.3.2C. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1962*c*). Vol. 3, Table 4.1.1. Birmingham: Kynoch Press.

Lander, J. J. (1951). *Acta Cryst.* **4**, 148.

Smith, G. W. (1960). *Nature, Lond.* **188**, 306.

---

* *Note added in proof.*— The molar magnetic susceptibility of $NaCo_{2.31}(MoO_4)_3$, at room temperature is 32 800.10^{-6}. No unambiguous assignment of oxidation states is possible from this value. We are indebted to N. Elliott for making the measurement.