ACTA CHEMICA SCANDINAVICA 27 (1973) 177–190

The Crystal Structure of $Zr_4(OH)_6(CrO_4)_5H_2O$

WANDA MARK

Department of Inorganic Chemistry, Chalmers University of Technology and the University of Göteborg, P.O. Box, S-402 20 Göteborg 5, Sweden

A re-investigation of the crystal structure of a zirconium chromate phase with the approximate composition $Zr_4(OH)_6(CrO_4)_5(H_2O)_x$ has been performed. In this investigation x was approximately 1, but in an earlier crystal structure determination,[2] x was given as 2.

$Zr_4(OH)_6(CrO_4)_5H_2O$ forms orthorhombic crystals, belonging to the space group *Pnnm* with the cell parameters $a = 11.629$, $b = 13.563$, and $c = 6.882$ Å. X-Ray intensity data were collected with an automatic single crystal diffractometer, and the positions of the atoms were determined by means of three-dimensional Patterson and Fourier syntheses. Using a total of 1679 independent reflexions, least squares full matrix refinements yielded a final R value of 0.038.

The structure consists of infinite chains with the approximate composition $[Zr_4(OH)_6CrO_4]_n^{8n+}$, which are joined in two directions by chromate groups. Zirconium exhibits sevenfold coordination, the coordinated oxygen atoms being situated at the vertices of somewhat distorted pentagonal bipyramids. The Zr–O distances range from 2.069 Å to 2.216 Å.

In connection with an investigation of the $ZrO_2-CrO_3-H_2O$ system, the crystal structures of two different phases in the system have been determined. The OD-structure of $Zr(OH)_2CrO_4$ ($ZrO_2.CrO_3.H_2O$) has been published earlier,[1] while the structure of a zirconium chromate with the approximate composition $4ZrO_2.5CrO_3.4H_2O$ is presented in this paper.

Some years ago, Lundgren[2] reported the crystal structure of $4ZrO_2.5CrO_3.5H_2O$. Due to a lower temperature during its preparation, this product had a higher content of water of crystallization than the product described in the present paper. In spite of this, both products constitute the same phase. A re-investigation of the crystal structure of this phase was undertaken since the rather poor data set, that the earlier determination was based on, yielded some discrepancies between observed and calculated structure factors.

PREPARATION AND ANALYSIS

A solid, amorphous zirconium chromate, "$ZrOCrO_4$", was obtained by adding an aqueous solution of zirconium nitrate to a potassium dichromate solution.[3] After the

amorphous product had been washed and dried, it was dissolved in an aqueous chromium trioxide solution, sealed in Pyrex glass tubes and heated for several days. By varying the Cr : Zr ratio, the acidity and the temperature, products with different chromium and water contents were obtained. Apart from $Zr(OH)_2CrO_4$, which is formed at low acidities in the temperature range 140 – 190°C, the structures of the products prepared in the temperature range 100 – 190°C proved to be nearly identical, according to Guinier powder photographs.

The sample investigated was formed in 10 M CrO_3, after ten days at 167°C. The chromium content was determined by atomic absorption spectroscopy and the water content by Penfield's method.[4] The product was heated to 1200°C in a Mettler thermo-balance in order to obtain the $ZrO_2 + Cr_2O_3$ content, and the density was determined by the flotation method. According to the results obtained (shown below) the product has the approximate formula $4ZrO_2.5CrO_3.4H_2O$, while its actual composition, calculated on the basis of the analysis, is $4ZrO_2.4.9CrO_3.3.7H_2O$.

	% Cr	% ($ZrO_2 + Cr_2O_3$)	% H_2O	Density (g cm^{-3})
Found	24.3	82.5	6.3	3.18
Calculated for $4ZrO_2.5CrO_3.4H_2O$	24.4	82.0	6.8	3.234 (*cf.* below)
Calculated for $4ZrO_2.4.9CrO_3.3.7H_2O$	24.3	82.5	6.4	3.188 (*cf.* below)

UNIT CELL AND SPACE GROUP

Preliminary cell dimensions were obtained from rotation and Weissenberg photographs. To obtain accurate cell dimensions, 43 reflexions were indexed on Guinier powder photographs, which were taken with Cu$K\alpha_1$ radiation using lead nitrate as an internal standard ($a_{Pb(NO_3)_2} = 7.8566$ Å at 21°C). Least squares refinement of the cell parameters yielded the results:

$a = 11.6290 \pm 0.0012$ Å, $b = 13.6534 \pm 0.0014$ Å, $c = 6.8818 \pm 0.0007$ Å, $V = 1092.7$ Å^3.

Observed and calculated $\sin^2\theta$ values are listed, together with calculated structure factors, in Table 1.

In accordance with the cell dimensions and the experimental density, the unit cell contains two formula units.

From Weissenberg photographs taken with Cu$K\alpha$ radiation the structure was seen to be orthorhombic, the following reflexions being systematically absent:

$h0l$ with $h+l=2n+1$; $0kl$ with $k+l=2n+1$.

These extinctions are characteristic for space groups Nos. 34, *Pnn*2, and 58, *Pnnm*.[5]

COLLECTION AND PROCESSING OF DATA

The compound $4ZrO_2.5CrO_3.4H_2O$ crystallizes as bright red truncated pyramids, and the crystal chosen for the structure determination had a basal plane with the dimensions 0.13×0.21 mm^2 (y and z directions) and a height of 0.12 mm. It was mounted along the b axis in an automatic single crystal diffractometer (Philips Pailred) and reflexions hkl and $\bar{h}kl$ were registered with Mo$K\alpha$ radiation from the layer lines $h0l - h18l$ with $k = 2n$ and

Table 1. Guinier powder photograph of $\sim 4ZrO_2 . 5CrO_3 . 4H_2O$. $\lambda(CuK\alpha_1) = 1.54050$ Å.

h k l	$10^5 \sin^2\theta$ obs	$10^5 \sin^2\theta$ calc	*F* calc	*I* obs
1 1 0	751	757	37	vvw
1 0 1	1689	1691	182	st
1 2 0	1711	1712	191	st
2 0 0	1755	1755	188	st
2 1 0	2070	2073	51	vvw
1 3 0	3309	3303	59	vvw
0 3 1	4118	4117	116	w
3 1 0	4272	4267	93	vw
2 2 1		4281	54	
1 3 1	4553	4556	88	w
2 3 0	4622	4619	90	vvw
0 0 2	5005	5011	557	vst
0 4 0	5088	5092	–	st
3 0 1	5214	5201	254	vst
3 2 0		5221	327	
3 1 1	5516	5519	72	vvw
1 2 2	6722	6723	138	w
1 4 1	6780	6784	110	w
2 4 0	6847	6847	137	vw
4 0 0	7013	7019	104	vvw
2 1 2	7078	7084	59	vvw
3 1 2	9271	9278	76	vvw
4 2 1	9542	9545	191	m
0 4 2	10102	10103	219	m
3 2 2	10233	10232	128	w
3 4 1	10292	10293	152	w
2 5 1	10969	10964	40	vvw
4 3 1	11130	11136	87	vvw
1 0 3	11711	11713	230	m
1 6 0	11899	11896	165	w
3 5 0		11905	86	
4 0 2	12027	12030	118	vw
4 4 0	12109	12112	120	vw
5 2 0	12246	12241	208	w
3 5 1	13156	13158	85	vvw
2 6 1	14465	14465	96	vvw
5 3 1	15082	15085	83	vvw
3 0 3	15224	15223	227	w
3 6 0	15408	15406	306	w
6 0 0	15801	15794	112	vvw
1 4 3	16798	16805	174	w
1 6 2	16913	16907	124	w
3 5 2		16916	79	
4 4 2	17127	17122	75	vvw
6 2 1	18305	18319	270	m
4 2 3	19562	19567	253	w
4 6 1	19739	19729	225	w
0 0 4	20051	20044	469	vw
3 4 3	20308	20315	153	vw
0 8 0	20358	20369	–	vw
3 6 2	20411	20417	164	vw

from $h0l-h7l$ with $k=2n+1$. It could be seen from the Weissenberg photographs, that those reflexions with $k=2n+1$ were much weaker than those with $k=2n$, and the scanning speed was therefore set to 2.5°/min for layer lines with k even, and to 0.5°/min for layer lines with k odd. The intensities were corrected for Lorentz, polarization and absorption effects, the linear absorption coefficient being 44 cm^{-1}. The preliminary data set thus obtained consisted of 1844 reflexions with k even, and 1485 reflexions with k odd.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

Owing to the somewhat different composition of the product, whose structure was investigated by Lundgren, the crystal structure of $4ZrO_2.5CrO_3.4H_2O$ was determined independently of the previous results. In order to facilitate a comparison between the results of the two determinations, the crystal axes of $4ZrO_2.5CrO_3.4H_2O$ were chosen in accordance with those of $4ZrO_2.5CrO_3.5H_2O$.

From a three-dimensional Patterson synthesis the positions of the Zr_1, Zr_2, Cr_1, and Cr_2 atoms were obtained. A third chromium atom, Cr_3, was also located, but it could not on the basis of the heights of the peaks be unambiguously differentiated from an oxygen atom, and therefore it was not taken into consideration at this stage of the investigation. The atomic parameters were refined and a three-dimensional Fourier synthesis, based on the refined parameters, revealed the positions of Cr_3 and two oxygen atoms, O_5 and O_6. The atoms were assumed to occupy the general position 4(*c*) of space group *Pnn*2, and after two more refinements and subsequent Fourier syntheses it was possible to locate all the remaining atoms, *i.e.* O_1-O_4 and O_7-O_{12}.

The special positions 2(*a*) and 2(*b*) in *Pnn*2 are not possible for the two Cr_3 atoms, since the Patterson calculation shows no peaks corresponding to vectors between Zr in 4(*c*) and Cr in 2(*a*) or 2(*b*). Accordingly, the Cr_3 atoms must be statistically distributed between four equivalent positions. The oxygen atoms O_{11} are coordinated to Cr_3 and, consequently, they must also be arranged statistically. The electron density of the oxygen atom O_{12} in the Fourier synthesis is about half that of the other oxygen atoms and the approximately two O_{12} were therefore assumed to be randomly distributed between four equivalent positions. To be more consistent with the structure, in the following the approximate formula will be written $Zr_4(OH)_6(CrO_4)_5H_2O$. This is in agreement with the electron density found for O_{12}, which ought to correspond to water of crystallization.

Preliminary refinements of the scale factors between the layers and the atomic parameters were carried out, assuming the atoms to be situated in the general position 4(*c*) of space group *Pnn*2. The *z* coordinates of all atoms, with the exception of O_1, O_2, and O_{11}, turned out to be very nearly zero, and as the *R* value did not continue to converge after a few cycles of refinement, the space group *Pnn*2 was abandoned in favour of the centro-symmetric *Pnnm*. Atoms with *z* coordinates almost zero were assumed to occupy the special positions 4(*g*) (*xy*0), while the remaining atoms (O_1, O_2, O_{11}) were assumed to be situated in the general position 8(*h*). Refinement of the following parameters was performed with the program LINUS:[6] scale factors, atomic param-

Table 2. Observed and calculated structure factors for $Zr_4(OH)_6(CrO_4)_5H_2O$. (The columns are h, F_o, F_c, and the phase angles, respectively.)

	H 0 0			2	57	53	0.04	20	30	34	-3.09	13	29	26	0.07		H 2 5		
2	186	188	0.02	4	30	31	-3.05	21	22	19	0.10	15	36	33	0.08	2	41	45	0.06
4	117	104	-3.11	10	66	66	-3.07	22	36	39	-3.07	20	15	19	-3.07	4	115	114	-3.08
6	117	112	3.13	12	77	77	-3.06	23	20	22	-3.04					6	169	170	-3.10
8	65	59	3.14					24	15	16	-3.04		H 1 9			8	52	52	-3.11
10	155	153	-3.11		H 0 9							3	20	17	-3.06	12	19	20	0.02
12	130	129	-3.08	1	59	58	0.02		H 1 3			6	30	24	-3.08	16	76	79	0.07
16	35	32	0.10	3	83	84	0.07	0	26	24	3.14	7	30	29	0.07	18	31	36	0.08
20	30	34	0.04	5	34	35	0.10	1	23	24	3.13	8	22	20	-3.07				
22	40	41	0.07	7	93	94	-3.07	3	44	45	-3.10	10	17	17	0.11		H 2 6		
9	58	58	-3.06	5	22	21	0.01	13	20	17	0.07	1	86	86	-3.10				
	H 0 1			13	37	35	-3.07	6	65	64	-3.11	16	36	34	0.08	3	152	151	-3.09
1	184	182	0.01	15	37	39	-3.07	7	80	75	0.04	18	18	17	0.10	5	90	88	-3.13
3	255	254	0.03	19	33	33	0.10	8	51	48	-3.10	19	36	33	-3.04	7	59	58	-3.12
5	42	47	0.10					9	16	13	0.02					9	111	111	-3.08
7	256	251	-3.11		H 0 10			10	44	42	0.06		H 1 10			11	24	27	0.03
9	97	93	-3.08	0	177	174	0.05	11	33	31	0.02	3	24	22	-3.07	13	82	81	0.07
13	68	68	-3.09	2	63	62	0.03	12	26	24	0.01	9	17	14	-3.06	15	50	51	0.04
15	77	75	-3.10	4	20	19	-3.00	13	29	28	0.05	10	35	32	0.07				
19	48	52	0.08	6	22	22	3.11	14	17	18	0.00	12	29	27	0.08		H 2 7		
21	33	35	0.05	8	30	27	3.13	15	20	19	0.08	13	30	27	0.06	4	145	147	-3.10
				10	68	69	-3.08	16	65	61	0.05	14	18	11	-3.02	6	161	161	-3.10
	H 0 2			12	67	64	-3.05	17	22	22	-3.10	15	31	31	0.08	8	49	47	-3.11
0	552	557	0.02	16	23	24	0.10	18	18	19	0.11					10	31	30	0.09
2	70	77	0.04					19	55	56	-3.07		H 1 11			12	35	34	0.01
4	125	118	-3.11		H 0 11			21	22	23	-3.12	6	26	19	-3.07	16	65	67	0.08
6	21	15	3.07	1	41	38	0.03	22	24	28	-3.06	7	23	21	0.09	18	26	27	0.10
10	106	107	-3.09	3	61	63	0.08					8	18	15	-3.06				
12	121	118	-3.08	5	23	26	0.11		H 1 4			16	27	25	0.09		H 2 8		
14	27	24	3.10	7	64	68	-3.06	1	23	23	0.03					1	60	51	-3.08
20	34	33	0.04	9	43	46	-3.06	2	34	32	0.04		H 1 12			3	87	86	-3.06
22	38	40	0.07	13	26	26	-3.06	3	61	59	-3.10	3	17	14	-3.04	5	48	45	-3.13
				15	30	29	-3.06	4	23	20	-3.11	10	21	19	0.10	7	37	34	-3.11
	H 0 3							5	12	12	3.12	12	23	19	0.10	9	89	91	-3.07
1	231	230	0.01		H 0 12			8	15	15	-0.00					13	56	57	0.09
3	221	227	0.03	0	99	98	0.08	9	36	34	-3.10		H 1 13			15	33	34	0.05
5	38	40	0.11	2	26	27	0.07	10	59	56	0.05	6	19	15	-3.07				
7	273	267	-3.11	10	36	38	-3.05	12	46	43	0.07	7	19	19	0.08		H 2 9		
9	117	114	-3.09	12	49	49	-3.04	13	47	47	0.05					4	92	91	-3.08
11	23	24	3.09					15	56	53	0.06		H 2 0			6	109	108	-3.08
13	56	55	-3.08		H 0 13			20	27	31	-3.09	1	184	191	-3.12	8	39	36	-3.11
15	61	60	-3.09	3	52	53	0.08	22	32	34	-3.06	3	331	327	-3.12	16	53	55	0.08
17	23	23	0.03	7	60	62	-3.06	23	21	23	-3.05	5	220	208	-3.14	18	24	26	0.10
19	49	53	0.08	9	42	44	-3.06					6	15	17	0.03				
21	32	31	0.05						H 1 5			7	101	100	-3.13		H 2 10		
					H 0 14			2	15	13	-3.11	9	167	165	-3.10	1	54	55	-3.08
	H 0 4			0	80	80	0.09	3	42	39	-3.10	11	57	58	0.02	3	102	101	-3.08
0	469	469	0.03	2	28	27	0.06	4	13	14	0.02	13	120	121	0.05	5	58	57	-3.13
2	112	114	0.02					5	17	15	0.02	15	72	73	0.03	7	40	39	-3.12
4	70	70	-3.09		H 1 0			6	45	43	-3.10	17	19	17	0.02	9	60	62	-3.05
6	47	45	3.12	1	26	37	0.02	7	44	41	0.06	21	27	25	0.11	11	22	21	0.02
8	33	30	3.14	2	44	51	0.03	8	35	34	-3.09					13	58	60	0.07
10	118	117	-3.10	3	87	93	-3.12	10	26	25	0.09		H 2 1			15	30	33	0.06
12	107	109	-3.07	4	15	19	-3.10	11	20	20	0.03	2	56	54	0.06				
16	26	27	0.12	5	41	37	3.13	13	28	26	0.05	4	185	191	-3.10		H 2 11		
20	22	29	0.04	8	40	38	-0.00	15	31	30	0.05	6	271	270	-3.11	4	66	65	-3.07
22	33	36	0.08	9	50	49	-3.11	16	50	49	0.06	8	77	75	-3.12	6	81	81	-3.07
				10	71	68	3.06	18	22	25	-3.08	10	20	20	0.15	8	24	22	-3.09
	H 0 5			12	52	51	0.06	19	40	43	-3.05	12	39	40	0.01	16	41	41	0.10
1	76	73	0.02	13	61	60	0.04	21	22	22	-3.12	16	95	95	0.06				
3	142	140	0.05	14	14	12	-3.00	22	21	18	-3.03	18	34	39	0.08		H 2 12		
5	54	53	0.08	15	67	65	0.05									1	36	32	-3.05
7	141	142	-3.09	20	33	36	-3.10		H 1 6				H 2 2			3	52	52	-3.04
9	68	70	-3.07	22	35	35	-3.06	1	12	12	0.06	1	126	138	-3.11	5	19	17	-3.11
13	56	59	-3.09	23	27	27	-3.06	2	20	18	0.06	3	121	128	-3.08	9	52	54	-3.05
15	64	64	-3.09					3	41	39	-3.09	5	102	94	-3.13	13	33	34	0.12
19	39	43	0.09		H 1 1			4	15	11	-3.08	7	46	49	-3.12				
21	26	29	0.05	2	23	20	-3.11	8	15	16	-0.00	9	176	175	-3.10		H 2 13		
				3	73	72	-3.12	9	30	28	-3.09	11	32	16	0.05	4	63	62	-3.07
	H 0 6			4	31	28	0.01	10	46	45	0.06	13	92	91	0.06	6	67	69	-3.06
0	331	323	0.04	5	37	36	0.01	12	42	39	0.07	15	53	56	0.04				
2	87	87	0.03	6	74	74	-3.12	13	38	39	0.05	17	24	23	0.02		H 2 14		
4	38	38	-3.06	7	73	69	0.04	15	48	46	0.06	21	28	33	0.09	1	30	29	-3.05
6	34	32	3.11	8	53	52	-3.10	20	25	26	-3.09					3	48	48	-3.05
8	31	29	3.14	10	44	41	0.06	22	23	29	-3.05		H 2 3						
10	95	98	-3.09	11	31	30	0.03					2	17	11	2.86		H 3 0		
12	100	98	-3.07	13	31	31	0.04		H 1 7			4	250	253	-3.11	1	55	59	0.03
16	23	24	0.13	15	33	31	0.05	3	27	26	-3.08	6	264	261	-3.11	2	87	90	-3.12
20	25	23	0.04	16	65	62	0.05	6	39	37	-3.10	8	83	81	-3.12	3	26	22	-3.12
22	27	32	0.08	17	20	18	-3.08	7	47	43	0.05	10	42	45	0.07	5	11	10	-0.18
				18	26	25	0.08	8	33	29	-3.09	12	53	51	0.01	6	73	74	0.04
	H 0 7			19	54	53	-3.06	10	28	27	0.08	14	24	24	-0.04	7	77	78	0.04
1	110	111	0.01	21	23	27	-3.12	11	22	22	0.03	16	87	90	0.06	9	47	46	0.05
3	125	124	0.05	22	23	24	-3.05	13	21	18	0.07	18	35	34	0.09	10	30	31	0.00
5	32	31	0.12					15	20	15	0.09					11	68	65	-3.10
7	148	147	-3.09		H 1 2			16	42	43	0.07		H 2 4			12	89	86	0.05
9	90	90	-3.09	1	34	36	0.02	18	17	17	0.11	1	121	125	-3.11	13	49	49	-3.10
11	21	18	3.08	2	59	59	0.02	19	42	42	-3.05	3	183	184	-3.10	15	42	43	-3.11
13	40	40	-3.07	3	76	76	-3.11					5	122	119	-3.13	16	43	42	-3.09
15	44	41	-3.07	4	29	30	-3.12		H 1 8			7	67	66	-3.12	18	31	31	-3.10
19	41	41	0.09	9	42	42	-3.11	2	15	14	0.07	9	135	136	-3.09	19	20	19	-3.04
21	26	23	0.06	10	60	58	0.05	3	29	27	-3.07	11	32	33	0.03	22	18	22	-3.05
				12	44	42	0.07	9	21	20	-3.08	13	98	97	0.06	23	33	33	0.10
	H 0 8			13	49	46	0.05	10	36	34	0.07	15	53	57	0.04	24	20	22	-3.03
0	192	188	0.06	15	52	53	0.06	12	32	30	0.08	21	22	26	0.10				

Table 2. Continued.

	H 3 1		
0	113	116	-3.11
1	88	88	0.03
2	40	37	0.03
3	13	13	0.03
4	86	87	0.04
5	85	83	-3.11
6	16	18	0.03
7	30	29	0.04
9	66	66	0.05
11	56	56	0.03
14	37	38	-3.09
15	20	17	0.07
16	69	68	-3.07
19	49	47	-3.05
21	26	28	-3.07
	H 3 2		
1	43	45	0.03
2	63	64	-3.11
3	26	22	-3.12
5	28	26	-3.07
6	68	66	0.05
7	79	76	0.04
8	22	21	-3.09
9	44	41	0.05
10	21	23	0.00
11	42	38	-3.07
12	79	75	0.06
13	40	36	-3.08
15	30	32	-3.11
16	33	30	-3.07
18	19	21	-3.08
19	27	28	-3.07
22	22	25	-3.07
23	28	28	0.11
24	24	26	-3.05
	H 3 3		
0	70	72	-3.09
1	51	51	0.05
2	20	19	0.05
3	18	18	0.02
4	96	93	0.03
5	75	70	-3.10
6	20	21	0.03
7	39	39	0.03
9	71	69	0.04
10	17	16	-3.09
11	55	54	0.03
14	40	40	-3.10
16	70	67	-3.08
19	50	50	-3.06
21	24	25	-3.06
	H 3 4		
1	34	35	0.04
2	52	53	-3.10
6	58	57	0.05
7	67	65	0.05
9	37	35	0.06
10	26	25	0.00
11	48	45	-3.08
12	75	70	0.06
13	41	40	-3.09
15	32	33	-3.11
16	34	32	-3.08
18	26	24	-3.09
19	22	21	-3.05
22	18	21	-3.05
23	25	28	0.11
	H 3 5		
0	66	66	-3.09
1	50	50	0.05
2	22	22	0.04
4	51	49	0.06
5	51	49	-3.09
6	17	14	0.04
7	15	16	0.07
9	47	46	0.06
11	40	39	0.04
12	15	14	0.12
14	29	27	-3.08
15	18	19	0.06
16	57	56	-3.07
19	38	39	-3.04
21	18	25	-3.07
	H 3 6		
1	25	27	0.05
2	38	38	-3.09
6	40	41	0.07
7	50	49	0.06
9	34	31	0.06
10	20	18	0.00
11	41	39	-3.08
12	62	60	0.07
13	34	34	-3.08
15	28	28	-3.11
16	29	27	-3.07
18	19	21	-3.09
19	18	18	-3.04
22	17	18	-3.05
	H 3 7		
0	41	42	-3.07
1	29	28	0.08
2	13	14	0.06
4	51	48	0.06
5	39	36	-3.08
6	20	18	0.03
7	25	22	0.04
9	47	46	0.06
11	36	36	0.04
14	32	31	-3.09
16	48	50	-3.06
19	33	38	-3.05
	H 3 8		
1	17	18	0.08
2	26	26	-3.07
5	14	13	-3.02
6	32	31	0.08
7	41	39	0.07
9	26	24	0.07
10	16	12	0.01
11	20	22	-3.04
12	48	46	0.08
13	25	23	-3.06
15	19	17	-3.09
16	21	18	-3.04
19	21	20	-3.06
	H 3 9		
0	32	30	-3.05
1	22	21	0.10
4	36	33	0.07
5	29	26	-3.06
7	18	13	0.06
9	35	32	0.08
11	25	24	0.05
16	42	41	-3.05
19	28	30	-3.04
	H 3 10		
2	21	22	-3.06
6	26	26	0.09
7	32	32	0.08
9	19	18	0.09
10	20	13	0.01
11	28	27	-3.07
12	39	38	0.08
13	28	26	-3.07
16	17	20	-3.06
	H 3 11		
0	25	25	-3.05
1	16	17	0.10
4	26	24	0.09
5	21	20	-3.05
9	28	24	0.09
16	28	31	-3.04
	H 3 12		
6	17	18	0.11
7	19	22	0.10
11	16	14	-3.02
12	28	28	0.10
	H 3 13		
4	23	21	0.09
9	23	22	0.09
	H 4 0		
2	134	137	-3.12
4	128	120	3.13
6	62	53	-0.01
7	13	16	-3.07
8	111	112	0.02
10	165	166	0.03
11	20	24	0.07
12	136	133	0.05
16	52	52	-3.10
20	19	19	-3.05
22	20	25	-3.05
	H 4 1		
1	106	110	-3.11
3	159	152	-3.11
4	13	16	-3.10
5	136	137	-3.12
7	127	121	0.05
9	139	142	0.03
11	84	83	0.00
12	18	21	-3.07
13	54	55	0.06
15	29	26	0.07
17	22	21	-3.11
19	33	33	-3.05
21	24	23	-3.06
	H 4 2		
0	202	219	-3.09
2	52	56	-3.09
4	86	75	3.12
6	25	21	-3.12
7	17	17	-3.08
8	47	46	0.04
10	121	122	0.04
11	20	24	0.07
12	125	121	0.05
14	24	22	-0.00
16	36	37	-3.08
20	18	19	-3.05
22	28	25	-3.05
	H 4 3		
1	169	174	-3.12
3	153	153	-3.11
5	104	103	-3.11
7	163	159	0.04
9	147	148	0.03
11	93	91	0.00
12	19	19	-3.07
13	45	45	0.07
15	21	17	0.11
17	30	29	-3.12
19	35	35	-3.05
21	22	21	-3.06
	H 4 4		
0	249	260	-3.10
2	93	94	-3.11
4	57	54	3.12
6	17	16	-0.02
7	14	15	-3.07
8	71	70	0.02
10	128	126	0.03
12	109	109	0.05
16	43	41	-3.09
22	21	23	-3.04
	H 4 5		
1	60	60	-3.09
3	101	99	-3.09
5	84	85	-3.11
7	79	78	0.08
9	90	94	0.05
11	51	53	0.01
13	52	51	0.06
15	27	28	0.07
19	31	27	-3.04
21	22	20	-3.06
	H 4 6		
0	203	209	-3.10
2	77	76	-3.11
4	42	36	3.11
6	17	14	-0.02
8	58	57	0.03
10	104	105	0.04
12	97	94	0.06
15	17	17	-3.04
16	28	33	-3.08
19	17	17	0.11
22	21	21	-3.04
	H 4 7		
1	99	101	-3.11
3	100	97	-3.10
5	46	48	-3.08
7	101	103	0.05
9	101	101	0.04
11	52	54	0.01
13	32	36	0.08
14	17	12	0.10
17	19	21	-3.12
19	30	27	-3.04
	H 4 8		
0	122	126	-3.07
2	49	48	-3.09
8	25	26	0.05
10	67	70	0.05
12	75	72	0.07
	H 4 9		
1	59	56	-3.10
3	68	66	-3.08
5	44	42	-3.08
7	65	66	0.08
9	62	63	0.06
11	34	34	0.01
13	32	33	0.08
19	26	22	-3.03
	H 4 10		
0	138	132	-3.08
2	59	58	-3.10
6	20	15	-0.02
8	40	41	0.03
10	71	69	0.05
12	56	58	0.08
16	24	25	-3.07
	H 4 11		
1	45	39	-3.09
3	46	50	-3.07
5	27	28	-3.06
7	46	49	0.09
9	45	47	0.07
11	22	19	0.01
13	25	25	0.09
	H 4 12		
0	71	73	-3.05
2	25	25	-3.06
10	37	38	0.08
12	44	43	0.09
	H 4 13		
1	38	40	-3.10
3	44	43	-3.07
7	41	48	0.08
9	42	43	0.07
	H 4 14		
0	62	63	-3.05
2	25	26	-3.07
	H 5 0		
1	43	49	-3.08
2	53	59	-3.08
3	80	86	0.05
4	21	26	0.06
5	67	68	0.02
6	23	23	0.09
7	17	12	-3.00
8	43	44	-3.11
10	102	109	-3.10
11	16	14	0.16
12	40	39	-3.11
13	24	23	-3.10
14	33	32	0.08
15	76	77	-3.08
17	23	24	-3.13
20	36	39	0.08
22	16	22	0.10
23	20	21	0.04
	H 5 1		
0	8	13	0.22
2	41	40	0.01
3	85	85	0.04
4	48	49	-3.08
5	38	40	-3.07
6	44	47	0.05
7	71	67	-3.09
8	75	71	0.06
9	14	8	0.27
10	29	27	-3.04
11	37	36	-3.11
12	43	40	-3.08
13	50	48	-3.07
16	35	37	-3.10
17	41	38	0.06
18	37	39	-3.07
19	31	36	0.08
20	18	19	-3.09
22	29	34	0.08
	H 5 2		
1	46	50	-3.09
2	66	70	-3.09
3	79	79	0.05
4	36	36	0.04
5	39	39	0.04
6	25	25	0.08
7	12	11	-2.99
8	15	13	-3.03
10	91	89	-3.09
11	34	32	0.07
12	33	30	-3.10
14	21	18	0.14
15	67	66	-3.07
17	24	25	-3.13
20	34	36	0.08
22	23	27	0.08
23	17	17	0.06
	H 5 3		
0	29	31	0.09
1	21	25	0.07
2	19	22	0.01
3	60	62	0.05
4	30	29	-3.04
5	35	35	-3.07
6	48	46	0.04
7	77	73	-3.10
8	72	67	0.07
10	33	31	-3.06
11	39	37	-3.11
12	49	47	-3.09
13	47	45	-3.07
16	35	37	-3.10
17	41	41	0.06
18	33	32	-3.06
19	38	39	0.08
22	35	36	0.07
	H 5 4		
1	43	44	-3.08
2	56	55	-3.07
3	70	71	0.06
4	28	28	0.05
5	41	42	0.04
6	18	19	0.10
8	25	27	-3.09
10	85	82	-3.09
11	20	20	0.10
12	31	29	-3.13
13	20	19	-3.09
14	28	23	0.11
15	67	65	-3.07
17	20	21	-3.13
20	31	34	0.09
22	19	22	0.10
	H 5 5		
0	23	22	0.12
1	12	11	0.15
2	20	19	0.02
3	55	55	0.05
4	42	40	-3.07
5	35	33	-3.07
6	37	36	0.05
7	43	42	-3.07
8	56	55	0.08
9	16	12	0.17
10	21	21	-3.02
11	25	26	-3.10
12	35	28	-3.05
13	45	42	-3.07
16	28	29	-3.10
17	28	29	0.08
18	36	35	-3.07
19	23	29	0.10
20	17	17	-3.09
22	22	26	0.09
	H 5 6		
1	34	33	-3.06
2	45	43	-3.05
3	58	55	0.07
4	18	19	0.07
5	35	34	0.04
6	20	19	0.10
8	27	27	-3.09
10	67	66	-3.08
11	19	16	0.13
12	28	25	-3.13
13	15	17	-3.08
14	24	21	0.11
15	59	57	-3.06
17	19	17	-3.12
20	27	31	0.09
	H 5 7		
0	26	23	0.11
1	17	19	0.09
3	40	39	0.07
4	28	23	-3.03
5	29	27	-3.06
6	36	35	0.05
7	48	45	-3.08
8	51	48	0.08
10	26	24	-3.04
11	26	26	-3.11
12	33	34	-3.08
13	34	33	-3.06
16	25	25	-3.09
17	32	32	0.07
18	27	26	-3.05
19	27	29	0.09
	H 5 8		
1	28	28	-3.06
2	40	37	-3.05
3	45	43	0.08
4	17	18	0.07
5	22	21	0.07
6	15	17	0.11
10	51	50	-3.07
11	24	21	0.09
12	18	17	-3.09
15	47	44	-3.05
20	25	25	0.10
	H 5 9		
0	23	22	0.10
1	16	16	0.10
3	30	28	0.09
4	28	21	-3.03
5	25	22	-3.04
6	26	25	0.07
7	32	31	-3.06
8	40	37	0.09
10	18	17	-3.02
11	18	17	-3.10

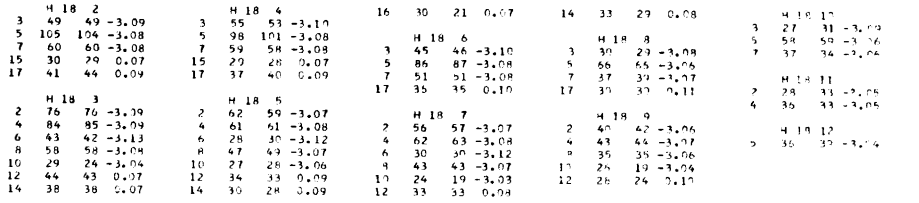
Table 2. Continued.

12	26	23	-3.06
13	32	30	-3.05
16	19	19	-3.09
17	23	22	0.09
18	24	23	-3.05
19	23	23	0.10
	H	5	10
1	23	22	-3.05
2	28	27	-3.03
3	38	36	0.09
5	24	22	0.06
8	22	21	-3.09
10	43	44	-3.07
11	16	10	0.16
13	15	15	-3.09
14	19	17	0.11
15	40	40	-3.05
	H	5	11
0	19	16	0.13
3	25	23	0.09
4	22	19	-3.03
6	23	20	0.08
7	24	23	-3.04
8	32	31	0.10
13	25	23	-3.04
	H	5	12
2	21	23	-3.03
3	30	26	0.10
5	18	13	0.09
10	30	28	-3.04
	H	5	13
0	20	15	0.12
4	20	13	-3.00
6	21	16	0.08
7	21	21	-3.05
8	23	24	0.11
	H	5	14
3	22	20	0.11
	H	6	0
1	167	165	0.01
3	311	306	0.02
5	209	205	0.02
6	20	19	-3.08
7	77	72	0.04
9	80	80	0.05
10	26	26	0.07
11	56	54	-3.11
13	55	55	-3.09
14	20	21	-3.05
15	55	55	-3.10
17	52	52	-3.09
19	21	18	-3.12
	H	6	1
2	106	96	0.01
4	223	225	0.03
5	19	21	0.05
6	157	153	0.03
8	32	28	0.11
9	19	21	-3.06
12	27	25	-3.06
13	22	25	0.09
14	19	20	-3.09
16	79	79	-3.09
18	39	37	-3.09
21	25	24	0.10
	H	6	2
1	120	124	0.01
2	9	8	0.05
3	166	164	0.03
5	131	126	0.03
6	14	15	-3.07
7	39	37	0.07
9	94	91	0.04
10	24	26	0.07
11	19	20	-3.07
12	17	18	-3.07
13	34	32	-3.05
14	18	21	-3.05
15	39	41	-3.08
17	58	55	-3.10
19	25	23	-3.12
	H	6	3
2	119	116	0.01
4	245	251	0.03
5	18	19	0.06
6	163	157	0.03
8	46	44	0.07
12	38	38	-3.09
14	31	33	-3.11
16	78	74	-3.09
17	23	25	-3.04
18	33	31	-3.08
21	21	23	0.11
	H	6	4
1	98	100	0.01
3	178	179	0.03
5	140	142	0.03
6	14	14	-3.07
7	56	56	0.05
9	70	69	0.06
10	21	23	0.07
11	33	33	-3.10
13	43	43	-3.07
15	45	44	-3.09
17	47	47	-3.09
19	24	17	-3.11
20	19	19	-3.04
	H	6	5
2	45	46	0.02
4	129	129	0.05
6	101	101	0.04
8	34	33	0.08
10	23	19	-0.01
13	20	21	0.10
16	68	64	-3.08
18	34	32	-3.09
21	19	21	0.11
	H	6	6
1	63	64	0.02
3	138	139	0.04
5	112	113	0.03
6	13	13	-3.06
7	55	54	0.04
9	59	58	0.06
10	19	19	0.08
11	26	28	-3.09
13	40	38	-3.07
14	19	16	-3.04
15	43	41	-3.09
17	40	38	-3.08
	H	6	7
2	65	66	0.01
4	142	143	0.04
6	105	105	0.04
8	37	37	0.07
12	31	32	-3.09
14	25	24	-3.10
16	51	53	-3.08
17	18	21	-3.03
18	23	23	-3.07
	H	6	8
1	36	40	0.03
3	76	78	0.06
5	70	71	0.05
7	36	35	0.06
9	48	50	0.07
10	17	16	0.09
13	25	23	-3.03
15	24	28	-3.07
17	35	32	-3.08
	H	6	9
2	34	34	0.02
4	87	89	0.06
6	47	48	0.06
8	33	33	0.07
16	44	42	-3.07
18	25	21	-3.07
	H	6	10
1	36	36	0.03
3	85	86	0.05
5	75	76	0.04
7	40	40	0.05
9	28	32	0.09
13	36	32	-3.07
15	35	28	-3.08
	H	6	11
2	24	23	0.03
4	60	62	0.07
6	50	51	0.07
8	22	23	0.09
	H	6	12
3	40	41	0.09
5	36	35	0.07
7	22	22	0.08
9	29	30	0.08
	H	6	13
2	26	24	0.03
4	57	57	0.06
6	43	45	0.07
8	22	20	0.09
	H	6	14
3	37	37	0.08
	H	7	0
1	64	75	-3.11
2	106	109	0.04
3	36	35	0.05
5	11	10	0.21
6	91	89	-3.09
7	83	81	-3.08
9	32	32	-3.10
11	81	76	0.05
12	73	70	-3.08
13	18	22	0.04
14	27	24	-3.05
15	27	27	0.01
16	23	24	0.07
17	30	28	0.05
18	41	42	0.07
19	32	31	0.08
23	33	38	-3.06
	H	7	1
0	91	100	0.05
1	71	76	-3.09
2	36	36	-3.10
3	31	33	-3.09
4	103	103	-3.10
5	89	86	0.04
6	16	12	0.04
7	16	16	3.12
8	21	20	0.07
9	68	65	-3.08
11	59	59	-3.09
12	25	24	-3.07
13	19	16	0.12
14	52	52	0.07
16	66	64	0.06
19	36	34	0.08
21	35	40	0.07
24	17	18	-3.07
	H	7	2
1	58	62	-3.10
2	89	91	0.04
3	38	35	0.05
5	33	32	0.06
6	86	82	-3.09
7	83	80	-3.08
9	29	28	-3.09
11	55	53	0.07
12	64	62	-3.08
13	16	12	0.08
14	31	32	-3.08
15	17	18	0.02
17	35	31	0.04
18	33	33	0.08
19	36	37	0.06
23	29	33	-3.05
	H	7	3
0	70	72	0.06
1	53	55	-3.08
2	26	24	-3.08
3	30	32	-3.09
4	104	103	-3.10
5	80	76	0.05
7	22	22	3.13
8	16	16	0.09
9	70	68	-3.08
11	59	58	-3.09
13	17	16	0.12
14	53	53	0.06
16	65	63	0.06
19	35	36	0.07
21	39	36	0.08
	H	7	4
1	49	49	-3.10
2	75	76	0.05
3	25	24	0.07
5	17	16	0.11
6	71	71	-3.08
7	73	70	-3.08
9	26	24	-3.09
11	61	56	0.07
12	60	58	-3.08
13	19	18	0.05
14	27	25	-3.06
15	19	20	0.01
16	19	19	0.09
17	24	25	0.05
18	36	35	0.07
19	28	30	0.07
23	28	32	-3.05
	H	7	5
0	71	68	0.06
1	52	51	-3.07
2	26	25	-3.09
3	22	21	-3.07
4	66	64	-3.08
5	59	58	0.06
8	16	15	0.09
9	51	50	-3.07
10	14	11	-3.09
11	45	46	-3.08
12	24	22	-3.07
14	39	40	0.08
16	50	52	0.07
19	25	27	3.09
21	30	35	0.08
	H	7	6
1	38	38	-3.08
2	59	58	0.06
3	21	18	0.08
5	14	13	0.18
6	57	56	-3.07
7	58	56	-3.07
9	23	22	-3.08
11	51	50	0.07
12	52	51	-3.07
14	21	21	-3.05
16	18	17	0.09
17	20	22	0.06
18	33	31	0.08
19	24	25	0.08
	H	7	7
0	50	47	0.09
1	35	35	-3.05
2	20	18	-3.07
3	16	16	-3.05
4	63	59	-3.08
5	49	45	0.07
9	50	49	-3.07
11	41	42	-3.08
14	43	41	0.07
16	43	45	0.08
19	26	27	0.09
21	26	28	0.09
	H	7	8
1	26	26	-3.06
2	43	43	0.08
3	13	15	0.10
5	18	14	0.11
6	45	43	-3.05
7	48	46	-3.06
9	16	16	-3.07
11	33	32	0.10
12	40	40	-3.06
14	23	22	-3.06
17	17	19	0.06
18	19	23	0.10
19	23	24	0.08
	H	7	9
0	37	36	0.10
1	28	27	-3.04
2	15	12	-3.05
3	16	14	-3.05
4	45	42	-3.06
5	36	34	0.08
9	39	37	-3.06
11	30	31	-3.07
14	29	30	0.09
16	37	36	0.08
	H	7	10
1	23	21	-3.05
2	36	35	0.09
6	36	36	-3.05
7	40	38	-3.05
9	15	12	-3.05
11	35	35	0.08
12	30	33	-3.06
13	17	15	0.06
14	16	14	-3.02
	H	7	11
0	34	31	0.10
1	25	22	-3.03
4	32	31	-3.05
5	28	27	0.09
9	29	29	-3.04
11	25	24	-3.06
14	25	23	0.10
	H	7	12
2	28	26	0.10
6	26	27	-3.03
7	30	28	-3.03
11	23	21	0.12
12	24	24	-3.04
	H	7	13
0	24	23	0.12
1	17	17	-3.01
4	25	27	-3.05
5	20	20	0.11
9	25	25	-3.04
	H	7	14
2	22	21	0.11
	H	8	0
2	132	131	0.03
4	103	102	0.03
6	77	74	-3.13
8	142	141	-3.10
10	99	101	-3.12
12	71	70	-3.10
14	33	33	-3.08
18	21	21	0.03
20	36	36	0.08
	H	8	1
1	190	189	0.03
3	74	66	3.02
4	17	17	0.04
5	22	19	0.05
7	80	74	-3.11
8	20	22	-3.07
9	81	79	-3.10
11	94	93	-3.10
12	21	24	0.08
13	66	64	-3.08
21	28	31	0.07
	H	8	2
0	172	177	0.03
2	83	82	0.04
3	13	13	-3.10
4	83	80	0.04
6	25	24	-3.10
7	21	23	0.06
8	96	93	-3.08
10	72	71	-3.11
11	24	29	-3.08
12	69	63	-3.09
14	49	45	-3.10
19	23	25	-3.04
20	36	36	0.08
	H	8	3
1	235	213	0.03
3	75	71	0.02
4	13	11	0.06
5	17	12	0.07
7	104	99	-3.12
8	21	22	-3.07
9	91	90	-3.10
11	100	100	-3.10
13	57	54	-3.08
21	27	29	0.08
	H	8	4
0	183	189	0.03
2	97	99	3.03
4	73	73	0.04
6	44	43	-3.12
7	15	18	0.07
8	107	105	-3.09
10	81	78	-3.11
11	25	26	-3.07
12	62	58	-3.09
14	38	35	-3.09
19	20	23	-3.04
20	30	33	0.08
	H	8	5
1	115	119	0.05
3	43	42	0.03
5	23	19	0.04
7	43	41	-3.09
8	15	18	-3.05
9	57	56	-3.08
11	68	70	-3.09
12	22	20	0.08
13	55	56	-3.08
21	23	25	0.08
	H	8	6
0	146	150	0.03
2	79	80	0.04
4	65	61	0.05
6	35	35	-3.12
8	90	88	-3.09
10	67	66	-3.11
12	54	52	-3.09
14	30	29	-3.08
15	21	19	0.11
20	23	28	0.09
	H	8	7
1	129	132	0.04
3	49	48	0.02
7	62	61	-3.11
9	67	68	-3.10
11	66	70	-3.09
13	40	41	-3.07
21	20	22	0.09
	H	8	8
0	84	85	0.05
2	53	53	0.05
4	41	43	0.06
8	55	56	-3.05
10	49	42	-3.09

Table 2. Continued.

12	40	39	-3.08
14	29	29	-3.09
19	22	19	-3.03
20	23	23	0.09
	H 8 9		
1	85	85	0.06
3	31	29	0.03
7	36	34	-3.09
9	41	42	-3.08
11	50	51	-3.08
13	34	36	-3.06
	H 8 10		
0	95	91	0.04
2	59	58	0.04
4	34	36	0.06
6	26	26	-3.11
8	62	63	-3.08
10	46	45	-3.10
12	32	32	-3.07
	H 8 11		
1	61	61	0.07
3	21	21	0.04
7	26	22	-3.07
9	28	32	-3.07
11	34	36	-3.06
13	27	27	-3.05
	H 8 12		
0	46	44	0.08
2	32	28	0.08
4	26	25	0.08
8	30	32	-3.03
10	24	22	-3.06
12	26	23	-3.06
	H 8 13		
1	54	55	0.07
7	24	24	-3.09
9	28	30	-3.07
	H 8 14		
0	32	38	0.07
2	29	26	0.08
	H 10 0		
1	41	42	0.05
3	78	75	-3.10
5	239	236	-3.11
7	140	138	-3.11
9	36	36	-3.13
10	21	21	-3.07
11	53	56	0.04
13	44	40	-0.01
15	65	62	0.04
17	55	52	0.09
	H 10 1		
2	111	109	-3.09
4	95	94	-3.09
6	77	75	-3.13
8	131	126	-3.11
9	16	16	0.08
10	62	60	-3.09
12	92	86	0.04
14	65	63	0.05
16	36	38	0.05
	H 10 2		
1	46	47	0.04
3	16	14	-2.94
5	188	184	-3.10
7	112	110	-3.10
9	44	44	-3.14
11	33	32	0.07
13	23	23	-0.01
15	51	50	0.04
17	55	55	0.09
	H 10 3		
2	117	119	-3.10
4	125	125	-3.10
6	83	83	-3.13
8	125	121	-3.11
10	44	41	-3.07
12	91	88	0.04
14	73	69	0.05
16	38	36	0.05
17	20	19	0.11
	H 10 4		
1	25	25	0.08
3	51	50	-3.09
5	175	178	-3.10
7	105	107	-3.10
9	30	32	-3.13
11	39	40	0.05
13	29	29	-0.01
15	46	49	0.04
17	46	49	0.09
	H 10 5		
2	69	74	-3.07
4	69	68	-3.07
5	14	13	-3.08
6	49	51	-3.13
8	90	92	-3.10
10	55	54	-3.09
12	62	61	0.06
14	45	47	0.07
16	31	32	0.06
	H 10 6		
1	15	18	0.10
3	49	51	-3.09
5	139	143	-3.09
7	88	91	-3.10
9	23	26	-3.13
11	33	35	0.06
13	20	23	-0.01
15	45	43	0.05
17	41	44	0.10
	H 10 7		
2	81	82	-3.08
4	91	91	-3.09
6	56	58	-3.13
8	73	76	-3.09
10	31	30	-3.05
12	60	62	0.05
14	49	50	0.06
16	24	27	0.06
	H 10 8		
3	24	25	-3.05
5	97	99	-3.08
7	63	63	-3.09
9	23	22	-3.14
11	19	19	0.09
15	29	29	0.06
17	39	39	0.10
	H 10 9		
2	51	54	-3.06
4	58	60	-3.07
6	35	34	-3.13
8	56	58	-3.08
10	27	30	-3.06
12	37	40	0.07
14	38	36	0.08
16	21	21	0.07
	H 10 10		
3	42	42	-3.10
5	86	93	-3.08
7	56	57	-3.09
11	32	26	0.06
15	29	26	0.06
	H 10 11		
2	42	42	-3.05
4	42	43	-3.06
6	21	23	-3.12
8	39	40	-3.07
10	26	24	-3.05
12	29	30	0.09
14	25	26	0.09
	H 10 12		
5	52	54	-3.05
7	33	36	-3.06
	H 10 13		
2	42	39	-3.06
4	44	42	-3.07
6	23	21	-3.12
8	27	30	-3.06
	H 12 0		
2	113	113	-3.11
4	112	110	-3.09
6	73	71	0.03
8	151	146	0.05
10	58	56	0.02
12	35	33	0.03
14	51	47	0.07
16	29	30	-3.07
20	42	41	-3.06
	H 12 1		
1	185	192	-3.10
3	16	10	2.98
5	22	21	0.04
7	28	26	-0.02
9	56	52	0.05
11	104	100	0.06
13	59	58	0.06
21	35	33	-3.07
	H 12 2		
0	96	98	-3.12
2	85	86	-3.10
4	100	98	-3.08
6	40	42	0.04
8	122	116	0.07
10	40	37	0.03
12	29	29	0.03
14	57	56	0.06
20	41	40	-3.06
	H 12 3		
1	187	198	-3.10
3	19	17	3.05
5	24	21	0.04
7	44	43	-0.01
9	62	60	0.04
11	110	104	0.06
13	54	51	0.07
	H 12 4		
0	106	108	-3.13
2	87	91	-3.10
4	89	90	-3.08
6	49	50	0.04
8	117	118	0.06
10	46	44	0.02
12	30	27	0.03
14	48	46	0.07
18	28	24	-3.06
20	34	36	-3.06
	H 12 5		
1	131	136	-3.09
9	38	38	0.06
11	81	81	0.07
13	53	51	0.07
	H 12 6		
0	85	88	-3.12
2	71	75	-3.10
4	78	79	-3.07
6	40	42	0.04
8	103	102	0.07
10	36	38	0.02
12	30	24	0.03
14	42	39	0.08
18	22	23	-3.06
20	31	32	-3.05
	H 12 7		
1	128	135	-3.09
7	32	25	-0.02
9	45	47	0.04
11	80	77	0.07
13	40	39	0.08
	H 12 8		
0	45	47	-3.11
2	54	53	-3.08
4	60	61	-3.06
8	74	73	0.09
14	40	37	0.08
	H 12 9		
1	94	94	-3.07
9	30	29	0.06
11	62	61	0.08
13	38	33	0.08
	H 12 10		
0	56	53	-3.12
2	53	52	-3.09
4	49	52	-3.05
6	27	29	0.05
8	71	72	0.08
14	24	24	0.10
	H 12 11		
1	71	70	-3.06
11	46	46	0.10
	H 12 12		
0	23	20	-3.10
2	27	28	-3.06
4	42	40	-3.04
8	43	44	0.11
	H 12 13		
1	61	59	-3.06
	H 14 0		
3	97	99	0.02
5	173	172	0.05
7	87	86	0.05
11	41	40	-3.08
15	39	39	-3.09
17	70	68	-3.06
	H 14 1		
2	129	128	0.05
4	117	117	0.04
6	33	33	-0.03
8	58	60	0.08
10	55	53	0.08
12	51	47	-3.05
14	54	49	-3.06
16	30	31	-3.11
	H 14 2		
3	60	63	0.02
5	149	145	0.06
7	75	71	0.06
11	24	25	-3.05
15	29	31	-3.07
17	72	69	-3.06
	H 14 3		
2	127	130	0.05
4	121	126	0.03
6	38	38	-0.02
8	65	62	0.07
10	43	41	0.10
12	55	51	-3.06
14	56	53	-3.07
16	31	29	-3.11
	H 14 4		
3	70	70	0.02
5	142	143	0.06
7	74	72	0.06
11	25	30	-3.07
15	32	32	-3.08
17	67	62	-3.06
	H 14 5		
2	93	97	0.06
4	81	82	0.05
6	21	20	-0.04
8	53	52	0.08
10	50	49	0.08
12	42	38	-3.04
14	40	39	-3.05
16	26	25	-3.10
	H 14 6		
3	58	59	0.02
5	125	123	0.06
7	64	64	0.06
11	26	26	-3.06
15	27	30	-3.08
17	58	54	-3.05
	H 14 7		
2	94	94	0.06
4	85	86	0.04
6	27	26	-0.03
8	45	49	0.08
10	31	33	0.11
12	45	43	-3.06
14	44	41	-3.06
	H 14 8		
3	32	32	0.04
5	95	92	0.08
7	50	48	0.08
17	47	46	-3.05
	H 14 9		
2	68	68	0.08
4	54	57	0.06
8	42	41	0.09
10	34	32	0.10
12	31	31	-3.03
14	35	32	-3.04
	H 14 10		
3	39	37	0.03
5	86	85	0.07
7	46	45	0.08
	H 14 11		
2	53	53	0.09
4	46	40	0.07
8	28	31	0.10
10	29	27	0.11
12	28	25	-3.03
	H 14 12		
5	57	55	0.10
7	34	30	0.10
	H 14 13		
2	45	45	0.09
4	36	35	0.07
	H 16 0		
2	76	78	0.04
4	116	116	0.05
6	29	28	-3.08
8	121	120	-3.08
10	58	58	-3.13
12	44	41	-3.12
14	37	33	-3.05
18	30	27	0.07
	H 16 1		
1	119	122	0.06
9	67	66	-3.11
11	139	135	-3.09
13	41	43	-3.07
15	38	31	0.09
21	23	19	0.12
	H 16 2		
0	28	29	0.06
2	64	64	0.05
4	105	105	0.05
8	104	101	-3.07
10	48	46	-3.12
12	40	37	-3.12
14	38	38	-3.06
18	28	22	0.09
	H 16 3		
1	123	127	0.06
9	59	57	-3.11
11	105	104	-3.09
13	43	39	-3.06
15	33	32	0.08
	H 16 4		
0	39	42	0.04
2	63	66	0.05
4	92	94	0.06
6	22	20	-3.06
8	99	100	-3.07
10	46	47	-3.12
12	34	33	-3.12
14	30	32	-3.05
18	22	23	0.08
	H 16 5		
1	89	95	0.07
9	47	48	-3.10
11	80	84	-3.08
13	37	39	-3.06
	H 16 6		
0	40	40	0.03
2	55	55	0.05
4	77	79	0.06
8	85	86	-3.07
10	39	39	-3.12
12	28	28	-3.11
14	26	28	-3.04
	H 16 7		
1	87	95	0.07
9	48	47	-3.10
11	73	74	-3.07
13	30	31	-3.05
15	28	25	0.10
	H 16 8		
0	22	22	0.05
2	41	41	0.07
4	61	61	0.07
8	66	65	-3.05
10	27	26	-3.11
	H 16 9		
1	69	70	0.08
9	26	31	-3.09
11	57	58	-3.05
13	27	27	-3.05
	H 16 10		
0	38	30	0.03
2	38	40	0.06
4	46	49	0.08
8	58	60	-3.06
10	24	25	-3.11
	H 16 11		
1	54	54	0.10
11	41	43	-3.05
	H 16 12		
2	25	23	0.10
4	35	37	0.10
8	37	39	-3.03
	H 18 0		
3	67	67	-3.11
5	119	119	-3.09
7	69	69	-3.39
11	29	25	0.07
15	28	34	0.06
17	44	43	0.09
	H 18 1		
2	75	76	-3.08
4	81	80	-3.09
6	40	41	-3.13
8	59	59	-3.08
10	32	30	-3.06
12	40	41	0.08
14	35	35	0.07

Table 2. Continued.



eters including isotropic thermal vibrations, the occupation number of Cr_3 and an isotropic extinction coefficient. An R value of 0.063, based on the total data set (hkl and $\bar{h}kl$) was obtained when correction was made for anomalous dispersion and secondary extinction during the refinements. Since the crystal was very symmetric, the values of the average path lengths in the crystal, used to calculate the extinction correction, are approximately the same for reflexions hkl and $\bar{h}kl$. Hence, mean values of F_{hkl} and $F_{\bar{h}kl}$ could be calculated, giving a final data set consisting of 1679 independent reflexions. After one more cycle of refinement, the R value dropped to 0.052. Anisotropic temperature coefficients were calculated and a few cycles of refinement were performed in which these coefficients were varied together with the atomic coordinates, the occupation number of Cr_3 and the extinction coefficient, while the scale factors were held constant. The shifts of the parameters were then less than 10 % of the standard deviations and the R value had dropped to 0.038. A weighting scheme according to Cruickshank was used in the refine-

Table 3. Atomic coordinates, expressed as fractions of the cell edges. Standard deviations are given within parentheses.

Atom	Occupation number	x	y	z
Zr_1	1	0.05643(5)	0.12439(14)	0
Zr_2	1	0.04063(5)	0.62585(14)	0
Cr_1	1	0.37323(10)	0.16138(15)	0
Cr_2	1	0.36038(9)	0.59065(16)	0
Cr_3	0.475	0.1958(2)	0.8730(4)	0
O_1	1	0.0691(3)	0.1257(7)	0.2998(5)
O_2	1	−0.0528(3)	0.3736(8)	0.3015(5)
O_3	1	0.2442(5)	0.1119(8)	0
O_4	1	0.2307(4)	0.6376(10)	0
O_5	1	0.3573(8)	0.2767(9)	0
O_6	1	0.3449(8)	0.4769(10)	0
O_7	1	0.1044(6)	0.2772(7)	0
O_8	1	0.0886(6)	0.7794(8)	0
O_9	1	0.0956(7)	0.9689(8)	0
O_{10}	1	0.0990(7)	0.4759(8)	0
O_{11}	0.475	0.2755(8)	0.8710(15)	0.1843(15)
O_{12}	0.300	−0.3078(14)	0.1241(38)	0

ments, yielding a weighted R value of 0.046. The final R value based on the comparatively weak structure factors $F_{k=2n+1}$ (685) was 0.052 whereas that based on the stronger structure factors $F_{k=2n}$ (994) was 0.033. In the final cycles of refinement the occupation number of Cr_3 was 0.476 and O_{11} was assigned the same value. Moreover, the occupation number of O_{12} (water of crystallization) was assigned the value 0.30, corresponding to the results of the water analysis. The contributions from these oxygen atoms to the structure factors are small and, accordingly, a refinement of their occupation numbers would have been arbitrary.

In Table 2 the observed and calculated structure factors and the phase angles of the reflexions are listed. The resulting atomic coordinates, together with the standard deviations, and the anisotropic temperature coefficients are given in Tables 3 and 4, respectively.

Table 4. Anisotropic thermal parameters for $Zr_4(OH)_6(CrO_4)_5H_2O$. The temperature factor is $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$. Standard deviations are given within parentheses.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zr_1	0.00173(3)	0.00083(5)	0.00313(7)	0.00000(6)	0	0
Zr_2	0.00104(2)	0.00070(4)	0.00317(7)	0.00009(5)	0	0
Cr_1	0.00122(5)	0.00114(10)	0.00273(15)	−0.00011(5)	0	0
Cr_2	0.00115(5)	0.00127(10)	0.00298(15)	0.00000(5)	0	0
Cr_3	0.00094(9)	0.00097(12)	0.00465(26)	−0.00009(15)	0	0
O_1	0.0025(2)	0.0037(4)	0.0028(4)	0.0008(3)	−0.0004(2)	0.0009(6)
O_2	0.0024(2)	0.0034(3)	0.0032(4)	−0.0004(3)	0.0006(2)	−0.0001(7)
O_3	0.0015(2)	0.0005(7)	0.0090(9)	−0.0003(3)	0	0
O_4	0.0010(2)	0.0014(8)	0.0114(11)	0.0006(3)	0	0
O_5	0.0043(5)	0.0003(7)	0.0216(24)	−0.0007(4)	0	0
O_6	0.0036(5)	0.0019(9)	0.0203(23)	−0.0002(5)	0	0
O_7	0.0011(3)	0.0006(7)	0.0124(19)	0.0002(3)	0	0
O_8	0.0008(3)	0.0002(6)	0.0139(20)	0.0005(3)	0	0
O_9	0.0020(4)	0.0013(8)	0.0099(17)	−0.0001(4)	0	0
O_{10}	0.0019(3)	0.0009(7)	0.0101(16)	0.0003(4)	0	0
O_{11}	0.0032(5)	0.0037(7)	0.0122(17)	0.0003(7)	−0.0039(8)	−0.0013(16)
O_{12}	0.0003(7)	0.0051(19)	0.0270(74)	−0.0005(16)	0	0

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The most important distances and angles in $Zr_4(OH)_6(CrO_4)_5H_2O$ are to be found in Table 5. The zirconium atoms Zr_1 and Zr_2 constitute together with the coordinated oxygen atoms O_7, O_8, O_9, and O_{10} infinite chains lying in the xy plane and running along the b axis.

The sequence of zirconium atoms in the chains is Zr_1, Zr_1, Zr_2, Zr_2 . . . , these atoms being joined by double oxygen or hydroxide bridges in the same way as in the structures of $Zr(OH)_2CrO_4$[1] and $Hf(OH)_2SO_4H_2O$.[7] In the same plane as the chains, and at coordination distances from Zr_1 and Zr_2, there are two further oxygen atoms, O_3 and O_4. These oxygen atoms are coordinated to Cr_1 and Cr_2, respectively, and, together with the oxygen atoms mentioned

Table 5. Distances (in Å) and angles in $Zr_4(OH)_6(CrO_4)_5H_2O$. Standard deviations are given within brackets.

Within the ZrO_7 pentagonal bipyramids				
axial oxygens:	Zr_1-2O_1	2.069(3)	Zr_2-2O_2	2.079(3)
equatorial oxygens:	Zr_1-O_3	2.191(5)	Zr_2-O_4	2.216(5)
	Zr_1-O_7	2.160(10)	Zr_2-O_7	2.144(8)
	Zr_1-O_8	2.138(8)	Zr_2-O_8	2.169(10)
	Zr_1-O_9	2.172(11)	Zr_2-O_{10}	2.157(10)
	Zr_1-O_9'	2.179(9)	Zr_2-O_{10}'	2.137(9)
	$O_1-Zr_1-O_1$	171.8(2)°	$O_2-Zr_2-O_2$	172.2(2)°
	$O_3-Zr_1-O_7$	79.5(4)°	$O_4-Zr_2-O_8$	70.9(4)°
	$O_7-Zr_1-O_8$	67.1(3)°	$O_8-Zr_2-O_7$	66.8(3)°
	$O_8-Zr_1-O_9'$	73.7(4)°	$O_7-Zr_2-O_{10}$	78.7(4)°
	$O_9'-Zr_1-O_9$	66.4(4)°	$O_{10}-Zr_2-O_{10}$	67.8(4)°
	$O_9-Zr_1-O_3$	73.4(4)°	$O_{10}'-Zr_2-O_4$	75.8(4)°
ax.–eq.:	O_1-O_3	2.905(5)	O_2-O_4	2.934(5)
	O_1-O_7	2.950(10)	O_2-O_7	3.062(8)
	O_1-O_8	3.049(8)	O_2-O_8	2.972(11)
	O_1-O_9	2.990(11)	O_2-O_{10}	2.970(11)
	O_1-O_9'	3.097(8)	O_2-O_{10}'	3.062(9)
eq.–eq.:	O_3-O_7	2.781(13)	O_4-O_8	2.545(14)
	O_7-O_8	2.374(10)	O_8-O_7	2.374(10)
	O_8-O_9'	2.588(15)	O_7-O_{10}'	2.714(14)
	$O_9'-O_9$	2.381(17)	$O_{10}'-O_{10}$	2.395(16)
	O_9-O_3	2.608(13)	$O_{10}-O_4$	2.687(15)
Within the CrO_4 tetrahedra sharing vertices with ZrO_7				
	Cr_1-2O_2	1.683(4)	Cr_2-2O_1	1.673(4)
	Cr_1-O_3	1.645(7)	Cr_2-O_4	1.638(7)
	Cr_1-O_5	1.585(12)	Cr_2-O_6	1.564(14)
	$O_2-Cr_1-O_2$	108.5(4)°	$O_1-Cr_2-O_1$	110.8(4)°
	$O_2-Cr_1-O_3$	110.5(3)°	$O_1-Cr_2-O_4$	109.8(3)°
	$O_3-Cr_1-O_5$	107.5(5)°	$O_4-Cr_2-O_6$	106.4(6)°
	$O_5-Cr_1-O_2$	109.9(4)°	$O_6-Cr_2-O_1$	109.9(4)°
Within the CrO_4 tetrahedra sharing an edge with ZrO_7				
	Cr_3-O_8	1.786(10)	$O_8-Cr_3-O_9$	94.0(4)°
	Cr_3-O_9	1.752(10)	$O_9-Cr_3-O_{11}$	113.9(7)°
	Cr_3-2O_{11}	1.571(10)	$O_{11}-Cr_3-O_8$	113.5(7)°
			$O_{11}-Cr_3-O_{11}$	107.7(7)°
Other distances				
	$O_{12}(H_2O)-O_8$	2.87(3)		
	$O_{12}(H_2O)-O_9'$	2.77(3)		
	Zr_1-Zr_1	3.641(3)		
	Zr_1-Zr_2	3.592(3)		
	Zr_2-Zr_2	3.564(4)		

earlier, they form planar five-membered rings around the zirconium atoms. In addition there are two further oxygen atoms, O_1, and O_2, which are coordinated to both zirconium and chromium (Cr_1, Cr_2), situated in axial positions

with respect to the five-membered oxygen rings. All the zirconium atoms are thus sevenfold coordinated. The coordination polyhedra are pentagonal bipyramids, which have the ideal symmetry D_{5h}. The chains, which are related to each other by an n glide plane perpendicular to the y axis, are connected in the x and z directions through the chromate groups (Cr_1, $2O_2$, O_3, O_5) and (Cr_2, $2O_1$, O_4, O_6). Two chains of condensed pentagonal bipyramids, connected in the z direction by chromate tetrahedra, are outlined in perspective in Fig. 1.

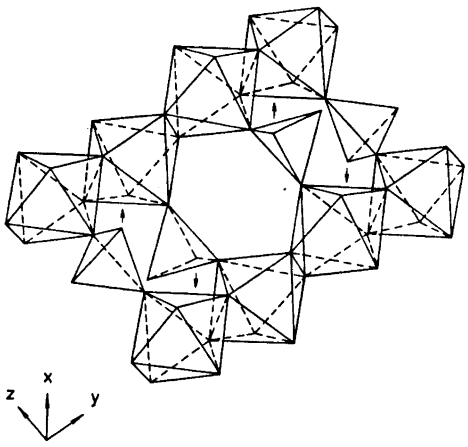


Fig. 1. Connection of the pentagonal bipyramids in two Zr–O chains by Cr–O tetrahedra. Only the oxygen atoms are depicted. The arrows indicate in which way the chains are connected to other chains in the x direction.

The two chains are connected to other chains through the O_3 and O_4 atoms in the chromate tetrahedra, in the directions indicated by the arrows. The chain-connecting chromate tetrahedra thus share three vertices with ZrO_7 bipyramids belonging to three different chains.

The chromate groups corresponding to the remaining chromium atoms, Cr_3, have two oxygen atoms, O_8 and O_9, in common with a bipyramid (Zr_1). They share an edge with the Zr_1 polyhedron, and do not take part in chain-connection, since the O_{11} atoms are coordinated only to Cr_3. The infinite chains can therefore be formulated approximately as $[Zr_4(OH)_6CrO_4]_n^{8n+}$, which is in accordance with the results obtained by Lundgren.[2] A formula unit of $Zr_4(OH)_6(CrO_4)_5H_2O$ is shown in Fig. 2, the interatomic distances being indicated. In order to complete the oxygen coordination around all the zirconium atoms, two additional O_9 atoms have been included in the figure. The condensed chromate tetrahedra (Cr_3) and the water molecules (O_{12}) are situated above or below Zr_1 in the x direction. They are situated in holes in the structure and are randomly distributed between these holes. As a consequence, Zr_1 is not structurally equivalent to Zr_2.

The pentagonal bipyramids in $Zr_4(OH)_6(CrO_4)_5H_2O$, as well as in $Zr(OH)_2CrO_4$, deviate from the ideal D_{5h} symmetry mainly because of two reasons: One is that the double oxygen bridges, which four of the oxygen atoms in the five-membered ring take part in, cause a compression of the ring.

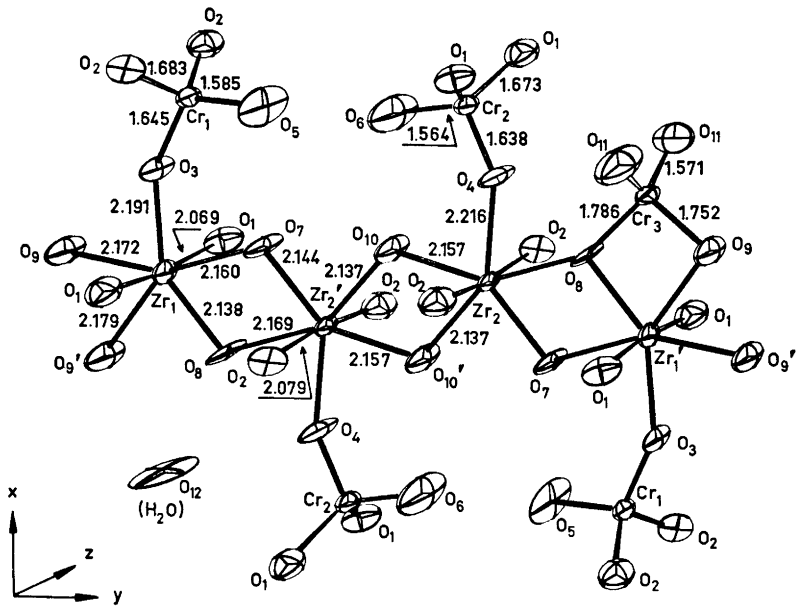


Fig. 2. One formula unit of $Zr_4(OH)_6(CrO_4)_5(H_2O)$. Distances are given in Å and the anisotropic thermal vibrations are outlined.

The other reason is that the axially situated oxygen atoms are involved in chain-connection, resulting in a distortion of the bipyramids due to packing restrictions.

The short distances between the bridging oxygen atoms (O_7, O_8, O_9, O_{10}), 2.37 – 2.40 Å, are in agreement with the corresponding distances in $Zr(OH)_2CrO_4$ (2.35 Å), $Hf(OH)_2SO_4H_2O$ (2.33 Å) and $Zr_2(OH)_2(SO_4)_3(H_2O)_4$ (2.34 Å).[8] The distances between zirconium and the non-bridging oxygen atoms in the five-membered rings (2.19 and 2.22 Å) are longer than the other equatorial oxygen – zirconium distances (*cf.* Table 5), although they are shorter than the corresponding distance (2.26 Å) in $Zr(OH)_2CrO_4$. This fact might be explained by the enhanced packing restrictions that are imposed by the more complicated structure of $Zr(OH)_2CrO_4$.

As can be seen from Table 5, the differently connected chromate tetrahedra are also distorted, the extent of distortion being less for those sharing three vertices with ZrO_7 polyhedra. The shortest Cr – O distances (1.56 and 1.59 Å) are between chromium and those oxygen atoms that are not connected to zirconium atoms. In the tetrahedra that share an edge with a polyhedron, two very long distances of 1.79 and 1.75 Å are found between chromium (Cr_3) and the shared oxygen atoms (O_8, O_9). Moreover, the $O_8 - Cr_3 - O_9$ angle is 94.0°. This large deviation from the tetrahedral angle, together with the long Cr – O distances, can be explained by the fact that the O_8 and O_9 oxygen atoms are each coordinated to two zirconium atoms as well as to one chromium atom.

The same is noted in $Zr(OH)_2CrO_4$, where the corresponding distance and angle are 1.76 Å and 99.2°, respectively.

The distances between O_{12} (water of crystallization) and two hydroxide oxygen atoms in the ZrO_7 pentagonal bipyramid are 2.77 and 2.87 Å, which imply hydrogen bonding (*cf.* Table 5).

The analyses of different products in the $ZrO_2 - CrO_3 - H_2O$ system show that the chromium and water content can vary slightly without changing the structure. This will be discussed in a forth-coming paper on the above-mentioned system.

The author would like to thank Professor Georg Lundgren for his support and great interest in this work. She is also indebted to Dr. Susan Jagner for revising the English text. Financial support, provided by the *Swedish Natural Science Research Council* (NFR, Contract No. 2318) and by *Chalmers University of Technology*, the latter to cover the costs of the computer work, is gratefully acknowledged.

REFERENCES

1. Mark, W. *Acta Chem. Scand.* **26** (1972) 3744.
2. Lundgren, G. *Arkiv Kemi* **13** (1958) 59.
3. Briggs, S. H. C. *J. Chem. Soc.* **1929** 242.
4. Kolthoff, I. M. and Sandell, E. B. *Textbook of Quantitative Inorganic Analysis*, 3rd Ed., McMillan, New York 1952, p. 717.
5. *International Tables for X-Ray Crystallography*, 2nd Ed., Kynoch Press, Birmingham 1965, Vol. I.
6. Lindgren, O. *Computer Programmes in Use at the Department of Inorganic Chemistry, Göteborg. To be published.*
7. Hansson, M. *Acta Chem. Scand.* **23** (1969) 3541.
8. McWhan, D. B. and Lundgren, G. *Inorg. Chem.* **5** (1966) 284.

Received June 20, 1972.