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The Crystal Structures of Synthetic Spodiosites. Ca_2VO_4Cl and Ca_2AsO_4Cl[1]

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The crystal structures of Ca_2VO_4Cl and Ca_2AsO_4Cl isomorphous with the spodiosite analogs Ca_2PO_4Cl and Ca_2CrO_4Cl have been determined. Both compounds crystallize in the orthorhombic system space group D_{2h}^{11}-Pbcm, with four molecules per unit cell. The cell constants are as follows: for Ca_2VO_4Cl, $a = 6.311$ (5), $b = 7.140$ (5), $c = 11.052$ (5) Å; for Ca_2AsO_4Cl, $a = 6.318$ (2), $b = 7.108$ (2), $c = 11.058$ (3) Å. Refinement of the atomic coordinates was carried out by full-matrix least-squares procedures (final R is 0.021 for Ca_2VO_4Cl and 0.023 for Ca_2AsO_4Cl). The structures are made up of discrete XO_4^{3-} tetrahedra held together by calcium ions. The XO_4^{3-} tetrahedra are significantly distorted from ideal tetrahedral symmetry in all four crystals.

Introduction

The syntheses and crystal structure determination of Ca_2PO_4Cl and Ca_2CrO_4Cl have been reported previously.[2] These compounds are isomorphous with the mineral spodiosite, Ca_2PO_4F.[3] Recently, two new analogs of spodiosite, Ca_2VO_4Cl and Ca_2AsO_4Cl, have been prepared.[4] The determination of the crystal structures of Ca_2PO_4Cl and Ca_2CrO_4Cl showed that both the PO_4^{3-} and CrO_4^{3-} tetrahedra are significantly distorted from the ideal symmetry and that the distortion of the chromate tetrahedron is significantly greater than that of the phosphate. This effect was attributed to electronic ordering in the CrO_4^{3-}, in which the single d electron occupies the d_{z^2} orbital in a fashion analogous to the Jahn–Teller effect.[5] In VO_4^{3-} there are no electrons in the d orbitals (ground state), and AsO_4^{3-} also has a closed-shell electronic configuration. The absence of unpaired electrons should exclude the possibility of electronic ordering of the type apparently present in the chromate, and any additional distortion in Ca_2VO_4Cl and Ca_2AsO_4Cl as compared to the phosphate tetrahedron would presumably be due to size effects.

The analysis of the crystal structures of Ca_2VO_4Cl and Ca_2AsO_4Cl was undertaken to make possible detailed comparisons of the XO_4^{3-} ions in the spodiosite series.

Experimental Section

Preparation.—Single crystals of Ca_2VO_4Cl and Ca_2AsO_4Cl were grown from a melt containing excess $CaCl_2$. The starting materials were thoroughly mixed, fired overnight in platinum crucibles at 900° in air, and cooled at 14°/hr to 300–400°. Well-formed, colorless, needlelike crystals of Ca_2VO_4Cl and Ca_2AsO_4Cl were obtained. This stoichiometry is based on data reported previously.[4]

Crystal Data.—Single-crystal photographic studies with precession and Weissenberg cameras confirmed that these compounds are isostructural with Ca_2PO_4Cl and Ca_2CrO_4Cl. Crystal data for the four spodiosite phases are given in Table I.

The lattice constants of Ca_2AsO_4Cl were determined by least-squares refinement of the setting angles of 12 reflections measured on a Picker full-circle automatic diffractometer with manual control; each reflection was carefully centered. The lattice constants of Ca_2VO_4Cl were computed from higher order powder reflections obtained using a Norelco diffractometer.

Collection and Treatment of X-Ray Intensity Data. Ca_2VO_4Cl.—A single crystal of Ca_2VO_4Cl was ground to spherical shape (radius 0.018 ± 0.001 cm). Complete three-dimensional X-ray intensity data were collected on a PAILRED automatic single-crystal diffractometer, using graphite-monochromatized Mo Kα radiation. The integrated intensity was measured by an ω scan of 1°/min over a 3.2° range, and background was counted for 24 sec on each side of the peak.

The intensities of 912 reflections in the levels $h0l$ to $h9l$ were measured. Integrated intensities were calculated from the function

$$I_{\text{net}} = I_{\text{measd}} - \frac{(B_1 + B_2)}{2}\left(\frac{T}{t_{\text{B}}}\right)$$

where I_{measd} is the total count, B_1 and B_2 are the background counts, T is the total time spent scanning the reflection, and t_{B} is the time spent for each background count. Of the 912 reflections, 799 were accepted as statistically above background (*i.e.*, I_{net} was positive). The data were corrected for Lorentz and polarization factors in the usual way. In the case of the vanadate where the incident beam was monochromatized (monochromator angle 3.078°), the corrections for Lorentz and polarization effects are those given by Ladell.[6] A spherical crystal absorption correction was applied using the linear absorption coefficient $\mu_{\text{Mo K}\alpha} = 44.8$ cm^{-1} and $\mu R = 0.80$; the transmission factor range was 3.15–2.55.[7]

A standard reflection checked each day for intensity drift did not change more than 1–2% during the entire data collection period.

Ca_2AsO_4Cl.—A single crystal of Ca_2AsO_4Cl was ground into a small spherical shape of radius 0.016 ± 0.001 cm. Three-dimensional X-ray data were collected on a Picker full-circle automatic diffractometer using zirconium-filtered Mo Kα radiation.

The intensities of 1390 independent reflections were recorded in one octant using the θ–2θ scan technique. All independent reflections to $2\theta = 80°$ were measured. The peaks were scanned at 1° 2θ/min for 100 sec, and backgrounds were estimated by

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[1] Work supported by Army Research Office (Durham) Contract No. DA-31-124-ARO(D)-71 and National Institutes of Health Grant No. DE 02577.

[2] M. Greenblatt, E. Banks, and B. Post, *Acta Crystallogr.*, **23**, 166 (1967).

[3] H. Berman, C. Frondel, and C. Palache, "Dana's System of Mineralogy," Vol. II, Wiley, New York, N. Y., 1951, p 848.

[4] E. Banks, M. Greenblatt, and R. W. Schwartz, *Inorg. Chem.*, **7**, 1230 (1968).

[5] E. Banks, M. Greenblatt, and B. R. McGarvey, *J. Chem. Phys.*, **47**, 3772 (1967).

[6] J. Ladell, *Trans. Amer. Crystallogr. Ass.*, **1**, 110 (1965).

[7] "International Tables for X-Ray Crystallography," Vol. II, Kynoch Press, Birmingham, England, 1962, p 302.

TABLE I

CRYSTAL DATA

	Ca_2PO_4Cl	Ca_2VO_4Cl	Ca_2CrO_4Cl	Ca_2AsO_4Cl
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Pbcm	Pbcm	Pbcm	Pbcm
a, Å	6.185 ± 0.002	6.311 ± 0.005	6.259 ± 0.005	6.318 ± 0.002
b, Å	6.983 ± 0.002	7.140 ± 0.005	7.124 ± 0.005	7.108 ± 0.002
c, Å	10.816 ± 0.004	11.052 ± 0.005	10.99 ± 0.005	11.058 ± 0.003
Density (measd), g cm^{-3}	2.995	3.06	3.14	3.42
Density (X-ray), g cm^{-3}	2.993	3.07	3.14	3.41
No. of molecules per unit cell	4	4	4	4
Color	Colorless	Colorless	Dark green	Colorless
Habit	Needles elongated along *c*	Needles elongated along *c*	Needles elongated along *b*	Needles elongated along *c*

TABLE II

ATOMIC POSITIONAL PARAMETERS IN $Ca_2VO_4Cl^a$

		x	*y*	*z*
Ca(1)	4(c)	0.6218 (1)	$^1/_4$	0
Ca(2)	4(d)	0.1395 (1)	0.4717 (1)	$^1/_4$
Cl	4(d)	0.4886 (1)	0.1944 (1)	$^1/_4$
V	4(c)	0.1266 (1)	$^1/_4$	0
O(1)	8(e)	0.0345 (2)	0.7308 (2)	0.3762 (1)
O(2)	8(e)	0.7103 (2)	0.5652 (2)	0.5285 (1)

TABLE III[a]

ATOMIC THERMAL PARAMETERS IN $Ca_2VO_4Cl^b$

A. Anisotropic Thermal Factors

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca(1)	0.0028 (1)	0.0030 (1)	0.00204 (3)	0	0	0.00052 (3)
Ca(2)	0.0059 (1)	0.0033 (1)	0.00116 (3)	−0.0004 (1)	0	0
Cl	0.0079 (1)	0.0090 (1)	0.00175 (4)	0.0038 (1)	0	0
V	0.0022 (1)	0.0023 (1)	0.00076 (3)	0	0	−0.00011 (2)
O(1)	0.0046 (3)	0.0053 (2)	0.0012 (1)	0.0011 (2)	0.0005 (1)	0
O(2)	0.0047 (2)	0.0031 (2)	0.0024 (1)	−0.0006 (1)	0	0.0003 (1)

B. Rms Displacement along Principal Axes of Thermal Ellipsoids (Å)

	1	2	3
Ca(1)	0.075 (2)	0.083 (1)	0.116 (1)
Ca(2)	0.085 (1)	0.091 (1)	0.110 (1)
Cl	0.101 (1)	0.104 (1)	0.171 (1)
V	0.067 (1)	0.068 (1)	0.078 (1)
O(1)	0.076 (3)	0.097 (3)	0.122 (2)
O(2)	0.083 (3)	0.101 (2)	0.123 (2)

[a] Estimated standard deviations (in parentheses) in this and following tables occur in the last significant digit in each case. [b] The form of the anisotropic temperature expression is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

counting for 10 sec at 0.8° from peak maxima. A standard reflection was measured after every 20 reflections, to check on stability of operation. Total variation in the standard intensity was less than 5% during the data collection. Deviations were erratic (*i.e.*, intensity of standard reflection fluctuated between a minimum and maximum value, probably due to instability of X-ray intensity or slight movement of the pulse-height analyzer's window or a combination of both and other operational factors). These variations were corrected by scaling the intensities as follows. We assumed a linear correction between monitored standards, and then these were scaled to the maximum standard. The total discrepancy was less than 5% between the maximum and minimum values of the intensity of standard reflection, and the average was much less.

Data reduction was carried out as described above for Ca_2VO_4Cl. For the absorption correction the linear absorption coefficient $\mu_{\text{Mo K}\alpha} = 96$ and $\mu R = 1.57$ were used. The transmission factor range was 8.51–4.31.

Of the 1390 recorded reflections, 30 were found to equal zero after data refinement, and 213 additional reflections were removed as these were too weak to be statistically reliable. The remaining 1147 observed reflections were used for the final refinement.

Refinement of the Structure. Ca_2VO_4Cl.—The structure was refined by least-squares procedures using our version of the Busing, Martin, and Levy[8] program. The atomic parameters determined for Ca_2CrO_4Cl were used as a starting point.[2] After three cycles of refinement in which anisotropic temperature factors were used and in which the scattering factors of Ca, V, and Cl were corrected for dispersion effects,[9] R $(= \Sigma||F_o| - s|F_c||/\Sigma|F_o|)$, the discrepancy factor, dropped to slightly above 8%.

It was observed in an independent experiment that crystals from this batch exhibited large extinction and multiple diffraction effects.[10] Furthermore, we noticed that F_c was systematically larger than F_o for all strong reflections, indicating large extinction effects. The structure was then refined further by applying extinction corrections to minimize the effects of both extinction and multiple diffraction in the form first suggested by Zachariasen and incorporated by Coppens and Hamilton into their least-squares program at the Brookhaven National Laboratories.[11]

After two more cycles of refinement using isotropic extinction corrections and a weighting scheme, $w = 1/[36 + 0.015F^2]$, the conventional R factor decreased to 0.021. The weighted R_w $(= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2})$ was 0.032. Plots of ΔF *vs.* F_o and *vs.* sin θ yield approximately a constant value using our

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(8) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(9) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 215, 216.

(10) B. Post, private communications.

(11) P. Coppens and W. C. Hamilton, *Acta Crystallogr.*, **A26**, 71 (1970).

TABLE IV

CALCULATED AND OBSERVED STRUCTURE FACTORS FOR Ca_2VO_4Cl[a]

K	L	FOBS	FCALC
0	2	77	78
0	4	228	228
0	6	33	34
0	8	187	189
0	10	9	9
0	12	86	87
0	14	3	3
0	16	80	80
0	20	43	43
2	2	125	123
2	3	20	20
2	4	39	41
2	5	19	18
2	6	104	104
2	7	29	30
2	8	89	90
2	9	5	5
2	10	80	82
2	11	12	11
2	12	39	38
2	13	3	4
2	14	59	60
4	2	63	60
4	3	37	36
4	4	109	106
4	5	67	66
4	6	48	48
4	7	37	37
4	8	117	116
4	9	62	62
4	10	36	37
4	11	22	21
4	12	63	63
4	13	34	34
4	14	25	25
6	2	110	119
6	3	11	11
6	4	41	43
6	5	24	25
6	6	95	95
6	7	9	9
6	8	47	48
6	9	10	10
6	10	70	70
6	11	6	5
6	12	17	17
6	13	16	15
6	14	50	49
8	3	23	25
8	4	28	29
8	5	20	20
8	6	57	56
8	7	36	35
8	8	43	43
8	9	28	27
8	10	54	53
8	11	19	19
8	12	32	32
8	13	15	15
8	14	46	45
H = 1			
K	L	FOBS	FCALC
0	0	36	35
0	2	10	11
0	4	58	56
0	6	8	10
0	8	24	25
0	10	14	14
0	12	11	11
0	14	10	10
0	16	16	16
0	18	9	9
1	0	35	34
1	1	61	59
1	2	18	17
1	3	21	22
1	4	41	42
1	5	62	62
1	6	7	7
1	7	9	9
1	8	12	12
1	9	42	43
1	11	10	10
1	12	12	13
1	13	25	25
2	0	14	14
2	1	37	36
2	2	90	88
2	3	54	53
2	4	90	88
2	5	35	35
2	6	60	61
2	7	29	29
2	8	16	15
2	9	17	17
2	10	43	44
2	11	26	26
2	12	39	40
2	13	18	18
3	0	61	57
3	1	40	39
3	3	32	31
3	4	26	25
3	5	40	41
3	6	13	13
3	7	18	18
3	8	11	12
3	9	28	28
3	10	21	21
3	11	16	16
3	12	6	6
3	13	20	21
4	0	54	51
4	2	10	9
4	3	20	20
4	5	23	24
4	6	8	8
4	8	32	33
4	9	8	7
4	10	3	4
4	11	11	11
4	13	11	11
5	0	47	48
5	1	16	17
5	2	5	6
5	3	20	21
5	4	45	46
5	7	22	23
5	8	21	22
5	9	6	6
5	10	11	11
5	11	15	15
5	12	16	16
5	13	5	5
6	0	14	16
6	1	27	29
6	3	46	48
6	4	10	9
6	5	39	39
6	7	28	28
6	8	14	14
6	9	20	20
6	10	6	5
6	11	33	33
6	13	24	24
7	0	23	24
7	2	22	24
7	3	15	16
7	4	17	18
7	6	23	24
7	7	15	15
7	8	16	16
7	9	5	4
7	10	22	22
7	11	13	12
7	12	8	8
8	0	29	30
8	2	10	11
8	4	15	16
8	5	6	6
8	6	11	11
8	7	14	14
8	8	23	23
8	9	16	16
8	10	9	9
8	12	10	10
8	13	6	6
9	2	15	18
9	3	4	4
9	4	16	17
9	5	9	9
9	6	13	13
9	7	11	10
9	8	17	17
9	9	8	7
9	10	8	8
9	13	7	6
H = 2			
K	L	FOBS	FCALC
0	0	45	43
0	2	78	75
0	4	31	28
0	6	40	39
0	8	40	41
0	10	15	15
0	12	10	9
0	14	8	8
0	16	26	26
1	0	109	108
1	1	60	59
1	2	115	115
1	3	65	63
1	4	127	128
1	5	36	36
1	6	90	92
1	7	50	52
1	8	71	73
1	9	26	27
1	10	63	64
1	11	33	34
1	12	64	65
1	13	21	21
2	0	109	108
2	1	44	43
2	2	19	17
2	3	10	11
2	4	22	23
2	5	35	35
2	6	24	24
2	7	11	11
2	8	46	48
2	9	31	32
2	10	23	23
2	11	5	5
2	13	16	16
3	0	87	87
3	1	33	31
3	2	146	146
3	3	41	40
3	4	97	96
3	5	29	29
3	6	112	111
3	7	27	27
3	8	48	49
3	9	18	18
3	10	74	74
3	11	23	23
3	12	42	42
3	13	17	16
4	0	27	25
4	1	30	29
4	3	28	28
4	4	18	18
4	7	40	41
4	8	14	14
4	9	10	9
4	11	20	20
4	12	9	10
5	0	96	97
5	1	31	31
5	2	43	43
5	3	19	19
5	4	105	106
5	5	24	25
5	6	40	40
5	7	19	19
5	8	79	79
5	9	24	24
5	10	34	34
5	11	11	11
5	12	72	71
5	13	15	15
6	0	9	9
6	1	33	34
6	3	11	11
6	4	26	27
6	5	22	22
6	7	19	19
6	9	29	29
6	10	8	8
6	11	5	6
6	12	7	8
6	13	13	13
7	0	38	39
7	1	7	7
7	2	84	87
7	3	8	8
7	4	43	44
7	5	15	15
7	6	77	77
7	8	30	29
7	9	9	9
7	10	63	63
7	11	6	6
7	12	28	28
7	13	9	8
8	0	3	4
8	1	8	7
8	2	25	25
8	3	6	6
8	4	11	11
8	6	18	17
8	8	5	5
8	9	7	6
8	10	9	9
8	11	5	5
8	12	17	16
9	0	67	74
9	2	28	29
9	3	7	7
9	4	73	74
9	6	25	25
9	7	5	4
9	8	61	60
9	9	5	4
9	10	20	20
9	11	7	7
9	12	53	52
H = 3			
K	L	FOBS	FCALC
0	0	38	40
0	2	97	96
0	4	95	95
0	6	62	62
0	8	47	47
0	10	37	38
0	12	63	63
0	14	22	22
0	16	34	34
0	18	14	14
1	0	20	18
1	1	19	18
1	2	19	18
1	3	30	29
1	4	26	27
1	6	8	7
1	7	29	30
1	11	18	18
1	12	20	20
2	0	13	10
2	1	7	7
2	2	37	35
2	3	4	4
2	4	34	32
2	5	20	21
2	6	25	24
2	7	6	7
2	8	13	12
2	9	11	12
2	10	13	12
2	12	13	9
2	13	9	9
3	1	21	20
3	2	31	30
3	3	31	31
3	4	23	23
3	5	21	21
3	6	19	19
3	7	20	20
3	8	10	10
3	9	12	12
3	10	8	7
3	11	19	19
3	13	13	13
4	0	25	24
4	1	41	40
4	2	21	20
4	3	61	61
4	4	52	52
4	5	39	38
4	6	16	16
4	7	44	44
4	8	20	19
4	9	23	23
4	10	14	14
4	11	39	39
4	12	31	32
4	13	26	25
5	0	12	12
5	1	12	12
5	2	18	18
5	4	12	12
5	5	6	5
5	6	9	9
5	9	10	10
5	12	18	18
6	0	33	34
6	1	10	10
6	2	21	20
6	3	3	3
6	4	13	12
6	5	7	6
6	6	23	22
6	7	15	15
6	8	19	19
6	10	23	23
6	11	6	5
7	0	17	17
7	2	22	21
7	4	7	6
7	5	15	16
7	6	19	19
7	7	8	8
7	8	15	15
7	9	9	9
7	10	15	15
7	12	5	5
7	13	10	10
8	1	21	21
8	2	24	23
8	3	29	29
8	4	6	6
8	5	31	30
8	6	18	18
8	7	15	15
8	8	6	6
8	9	19	19
8	10	12	11
8	11	20	20
8	13	22	21
9	0	10	10
9	1	7	7
9	4	14	15
9	5	4	3
9	8	7	7
9	9	9	8
9	10	5	5
9	11	4	4
9	12	10	10
H = 4			
K	L	FOBS	FCALC
0	0	72	72
0	2	75	75
0	4	102	102
0	6	68	68
0	8	61	60
0	10	55	56
0	12	65	66
0	14	43	43
0	16	40	40
0	18	31	31
1	0	22	22
1	2	20	21
1	3	22	22
1	4	16	16
1	5	3	3
1	6	14	14
1	7	19	20
1	8	19	20
1	9	5	5
1	10	5	5
1	11	15	15
2	0	30	28
2	1	32	33
2	2	155	156
2	3	32	32
2	4	52	52
2	5	19	19
2	6	125	126
2	7	32	33
2	8	17	14
2	9	18	18
2	10	92	93
2	11	20	21
2	12	24	22
3	0	29	30
3	1	22	22
3	2	21	21
3	3	18	17
3	4	9	8
3	5	10	10
3	6	6	9
3	7	22	22
3	8	7	8
3	9	13	12
3	11	11	12
3	12	15	16
4	0	87	86
4	1	10	10
4	2	59	59
4	3	6	7
4	4	99	100
4	5	7	7
4	6	50	50
4	8	65	66
4	9	12	12
4	10	38	39
4	11	6	7
4	12	63	63
5	2	17	17
5	4	16	16
5	5	9	10
5	6	10	10
5	7	8	8
5	8	10	9
6	0	47	47
6	1	42	42
6	2	61	61
6	3	35	35
6	4	57	57
6	5	28	28
6	6	57	57
6	7	40	39
6	8	42	42
6	9	30	30
6	10	50	50
6	11	25	25
6	12	44	43
7	0	5	6
7	1	10	9
7	2	16	16
7	3	8	7
7	4	18	18
7	5	6	6
7	6	13	13
7	9	13	13
7	10	10	10
7	11	8	8
7	12	15	14
8	0	69	69
8	1	11	11
8	2	42	42
8	3	19	19
8	4	71	70
8	5	18	17
8	6	36	36
8	7	11	10
8	8	54	53
8	9	10	9
8	10	28	28
8	11	16	16
8	12	46	45
9	0	11	11
9	3	3	3
9	5	10	10
9	7	8	7
9	8	7	6
9	9	5	4
9	10	5	4
H = 5			
K	L	FOBS	FCALC
0	0	50	50
0	2	16	15
0	4	59	60
0	6	22	22
0	8	26	25
0	10	24	25
0	12	26	25
0	14	21	21
0	16	10	10
0	18	13	13
1	0	24	24
1	1	33	33
1	2	11	11
1	3	39	39
1	4	12	12
1	5	29	29
1	6	10	10
1	7	32	32
1	8	18	19
1	9	21	21
1	10	11	11
1	11	27	27
2	0	14	12
2	1	7	7
2	2	19	19
2	3	19	20
2	4	13	10
2	6	11	11
2	7	17	17
3	0	13	13
3	1	20	20
3	2	32	31
3	3	13	13
3	4	17	17
3	5	11	11
3	6	25	24
3	7	18	18
3	8	6	6
3	9	14	14
3	10	20	20
3	11	10	9
4	1	27	26
4	2	12	12
4	3	20	19
4	4	18	18
4	5	37	37
4	6	9	10
4	7	8	7
4	8	8	7
4	9	28	28
4	10	7	6
4	11	10	10
5	0	39	38
5	1	17	17
5	2	20	20
5	3	26	25
5	4	18	17
5	5	24	25
5	6	16	16
5	7	14	14
5	8	35	34
5	9	15	14
5	10	9	10
5	11	19	19
6	2	21	21
6	3	14	14
6	5	5	5
6	6	15	15
6	7	9	9
6	8	9	10
6	10	9	9
6	11	10	10
7	1	11	11
7	2	22	21
7	4	11	12
7	6	20	19
7	7	5	6
7	9	12	12
7	10	18	18
8	0	20	20
8	1	9	8
8	3	14	14
8	4	13	13
8	5	13	13
8	7	8	8
8	8	8	8
8	9	6	7
8	10	9	10
8	11	8	10
9	0	31	30
9	1	8	8
9	2	14	14
9	4	23	22
9	6	13	13
9	7	8	8
9	8	27	26
9	9	6	5
9	10	11	11
H = 6			
K	L	FOBS	FCALC
0	0	38	38
0	2	38	38
0	4	28	27
0	6	33	33
0	8	30	31
0	10	27	27
0	12	19	19
0	14	19	19
0	16	18	19
1	0	106	106
1	1	21	21
1	2	62	63
1	3	13	13
1	4	67	67
1	5	30	30
1	6	51	51
1	8	77	78
1	9	24	24
2	1	9	8
2	3	6	5
2	5	6	6
2	7	6	6
2	9	7	6
3	0	55	55
3	1	33	32
3	2	61	60
3	3	22	22
3	4	30	30
3	5	26	26
3	6	59	59
3	7	23	24
3	8	53	53
3	9	27	27
4	0	15	15
4	1	27	27
4	2	15	15
4	3	24	23
4	4	9	9
4	5	22	21
4	6	13	13
4	7	23	23
4	8	12	13
4	9	20	20
5	0	90	88
5	2	56	56
5	3	13	13
5	4	63	63
5	6	46	45
5	8	65	65
6	0	10	10
6	1	5	4
6	2	9	9
6	4	12	13
6	6	9	8
6	8	8	8
7	0	30	30
7	1	10	9
7	2	68	67
7	3	6	7
7	4	18	17
7	5	5	6
7	6	64	63
7	7	19	19
7	8	27	27
7	10	56	56
8	0	7	7
8	1	15	15
8	2	7	7
8	3	13	12
8	4	7	8
8	5	11	11
8	6	6	6
8	7	14	14
8	8	7	6
8	9	13	13
9	0	51	50
9	3	9	10
9	4	43	43
9	6	27	26
9	8	48	47
9	9	5	6
H = 7			
K	L	FOBS	FCALC
0	0	29	30
0	2	13	14
0	4	24	24
0	6	7	7
0	8	16	16
0	12	9	9
0	16	9	9
1	1	6	6
1	2	6	6
1	3	9	10
1	4	21	21
1	5	5	6
1	6	6	6
1	7	6	7
2	0	35	35
2	1	19	19
2	2	34	34
2	3	13	13
2	4	31	31
2	5	23	23
2	6	35	36
2	7	8	8
3	0	10	10
3	2	5	5
3	3	8	8
3	4	12	13
3	5	7	7
3	6	4	4
4	0	19	19
4	1	4	3
4	2	5	5
4	3	5	6
4	4	19	18
4	5	9	8
4	6	4	4
4	7	9	8
5	0	13	13
5	1	5	4
5	2	8	8
5	3	12	12
5	5	12	12
5	6	6	7
6	0	9	9
6	1	27	27
6	2	18	18
6	3	24	24
6	4	7	7
6	5	30	30
6	6	15	15
6	7	19	19
7	0	9	9
7	1	5	5
7	2	4	4
7	6	5	4
8	0	6	6
8	1	11	12
8	2	11	11
8	3	11	11
8	4	9	9
8	5	9	10
8	7	12	11
9	0	10	10
9	1	6	6
9	2	5	5
9	4	4	4
9	6	4	4
9	7	5	6
H = 8			
K	L	FOBS	FCALC
0	0	74	76
0	2	20	21
0	4	77	77
0	6	22	22
0	8	66	67
0	10	19	20
0	12	59	59
0	14	20	20
1	0	13	14
1	1	20	19
1	2	6	7
1	3	11	11
2	0	50	50
2	2	57	58
3	0	29	29
4	0	62	62
4	1	18	18
5	0	13	12
5	1	15	16
5	2	8	7
5	3	11	11
6	0	30	30
7	0	12	12
7	3	9	9
8	0	36	36
8	1	10	14
9	0	5	5
9	2	15	15
H = 9			
K	L	FOBS	FCALC
0	0	23	23
0	4	13	13
0	6	7	6
0	8	13	13
0	10	9	8
H = 10			
K	L	FOBS	FCALC
0	2	12	11
0	4	7	7
0	6	9	8
0	8	6	6
H = 11			
K	L	FOBS	FCALC
0	0	26	27
0	2	12	12
0	4	16	17
0	6	10	10

[a] Scale factor is 10.54; $F_o = F_0/\text{scale factor}$.

TABLE V

ATOMIC POSITIONAL PARAMETERS IN Ca_2AsO_4Cl

		x	*y*	*z*
Ca(1)	4(c)	0.6252 (1)	1/4	0
Ca(2)	4(d)	0.1384 (1)	0.4764 (1)	1/4
Cl	4(d)	0.4958 (1)	0.2007 (1)	1/4
As	4(c)	0.12909 (3)	1/4	0
O(1)	8(e)	0.0297 (2)	0.7352 (2)	0.3774 (1)
O(2)	8(e)	0.7100 (2)	0.5669 (2)	0.5272 (1)

weighting scheme. The standard deviation of an observation of unit weight is 0.8439. The isotropic extinction parameter which multiplies F_c is 1.320 (41) × 10^{-4} cm^{-1}. The largest extinction correction is equal to 0.29 for (004) in Ca_2VO_4Cl. The atomic parameters and their estimated standard deviations are listed in Tables II and III. Calculated and observed structure factors are listed in Table IV.

The refinement of the crystal structure of Ca_2AsO_4Cl proceeded in much the same way. Starting with the positional parameters of Ca_2VO_4Cl, three cycles of least-squares refinement yielded $R = 0.071$. Two more cycles of refinement with isotropic extinction corrections gave a discrepancy coefficient of 0.023. The weighted R_w value was 0.024, using the weighting scheme $w = 1/(\sigma_I^2 + 0.004F^2)$ where σ_I is the fractional standard deviation in the intensity of each reflection calculated by the function

$$\sigma_I = \left[\left|I_{\text{measd}} + \left(\frac{B_1 + B_2}{2}\right)\left(\frac{T}{t_B}\right)\right|\right]^{1/2} \Big/ |I_{\text{net}}|$$

TABLE VI

ATOMIC THERMAL PARAMETERS IN Ca_2AsO_4Cl

A. Anisotropic Thermal Factors

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca(1)	0.0038 (1)	0.0028 (1)	0.00202 (3)	0	0	0.00036 (3)
Ca(2)	0.0060 (1)	0.0031 (1)	0.00143 (3)	−0.0005 (1)	0	0
Cl	0.0082 (1)	0.0081 (1)	0.00185 (3)	0.0035 (1)	0	0
As	0.00308 (4)	0.00232 (3)	0.00108 (2)	0	0	−0.00009 (2)
O(1)	0.0061 (2)	0.0049 (2)	0.0013 (1)	0.0009 (2)	0.0007 (1)	0.0002 (1)
O(2)	0.0051 (2)	0.0027 (2)	0.0027 (1)	−0.0011 (2)	0	0.0003 (1)

B. Rms Displacement along Principal Axes of Thermal Ellipsoids (Å)

	1	2	3
Ca(1)	0.083 (1)	0.088 (1)	0.114 (1)
Ca(2)	0.088 (1)	0.094 (1)	0.111 (1)
Cl	0.102 (1)	0.107 (1)	0.164 (1)
As	0.0761 (6)	0.0789 (5)	0.0825 (6)
O(1)	0.084 (3)	0.103 (2)	0.123 (2)
O(2)	0.074 (3)	0.108 (2)	0.129 (2)

TABLE VII
CALCULATED AND OBSERVED STRUCTURE FACTORS FOR Ca_2AsO_4Cl[a]

H = 0

K	L	FOBS	FCALC
0	2	122	118
0	4	279	265
0	6	69	67
0	8	218	219.
0	10	39	40
2	0	182	179
2	1	13	13
2	2	164	159
2	3	22	21
2	4	76	77
2	5	17	16
2	6	131	133
2	7	28	29
2	8	116	120
2	9	6	6
2	10	103	106
2	11	12	12
2	12	58	60
2	14	71	73
4	0	223	218
4	1	75	74
4	2	85	84
4	3	34	34
4	4	143	144
4	5	62	63
4	6	68	69
4	7	31	31
4	8	146	148
4	9	54	57
4	10	55	57
4	11	18	18
4	12	84	85
4	13	32	32
4	14	35	36
6	0	112	112
6	1	4	2
6	2	147	149
6	4	69	69
6	5	16	17
6	6	119	120
6	7	12	11
6	8	71	72
6	9	6	6
6	10	89	90
6	12	32	32
6	13	10	10
6	14	59	60
8	0	73	73
8	1	39	40
8	2	70	71
8	3	29	29
8	4	55	55
8	5	24	24
8	6	67	67
8	7	38	38
8	8	67	67
8	9	28	28
8	10	62	62
8	11	22	22
8	12	47	47
8	13	17	17
8	14	48	47
10	0	60	59
10	1	15	14
10	2	79	78
10	3	30	29
10	4	46	46
10	5	17	17
10	6	69	68
10	7	20	20
10	8	46	46
10	10	56	56
10	11	24	24
10	12	29	28
12	0	43	44
12	1	15	14
12	2	57	57
12	3	13	12
12	4	36	36
12	6	51	51
12	7	20	21

H = 1

K	L	FOBS	FCALC
0	2	36	38
0	4	35	32
0	6	29	30
0	8	44	45
0	10	33	33
0	12	6	6
0	14	21	20
1	2	50	48
1	3	23	24
1	4	65	63
1	5	63	62
1	6	34	34
1	7	10	10
1	8	33	32
1	9	41	42
1	10	21	21
1	11	10	10
1	12	27	27
1	13	25	25
1	14	15	14
2	0	11	9
2	1	35	33
2	2	119	117
2	3	48	47
2	4	69	68
2	5	30	30
2	6	82	84
2	7	26	27
2	8	5	5
2	9	15	15
2	10	63	64
2	11	23	23
2	12	26	27
2	13	14	15
2	14	40	41
3	0	32	30
3	1	40	39
3	2	18	18
3	3	32	31
3	5	38	39
3	6	32	33
3	7	18	19
3	8	11	10
3	9	26	27
3	10	35	36
3	11	15	15
3	12	19	20
3	13	19	19
3	14	31	31
4	0	74	73
4	1	10	10
4	2	19	17
4	3	20	20
4	4	17	17
4	5	23	24
4	6	15	15
4	8	48	49
4	9	10	10
4	10	15	15
4	11	11	11
4	12	14	14
4	13	12	11
4	14	8	7
5	0	67	67
5	1	20	20
5	2	30	30
5	3	25	25
5	4	62	64
5	5	9	9
5	6	19	20
5	7	25	26
5	8	37	38
5	9	8	8
5	10	7	8
5	11	18	18
5	12	26	27
5	13	6	7
6	0	29	29
6	1	32	32
6	2	28	28
6	3	46	47
6	5	38	39
6	6	25	25
6	7	29	29
6	8	24	25
6	9	21	22
6	10	24	24
6	11	31	32
6	12	4	5
6	13	23	23
6	14	17	16
7	2	40	41
7	3	18	19
7	4	5	4
7	6	37	38
7	7	18	19
7	10	31	31
7	11	16	15
7	12	5	4
7	14	25	25
8	0	50	50
8	1	11	11
8	2	5	4
8	4	30	30
8	6	10	3
8	7	9	8
8	8	37	38
8	9	10	10
8	12	17	18
8	14	3	4
9	0	25	25
9	2	7	7
9	3	9	8
9	4	28	29
9	5	6	3
9	8	26	26
9	11	9	9
9	12	26	26
9	14	6	4
10	0	26	26
10	1	10	9
10	2	5	4
10	3	18	17
10	4	16	16
10	5	18	18
10	7	6	6
10	8	23	22
10	9	9	8
10	10	7	5
10	11	15	14
10	12	12	12
11	0	7	7
11	2	34	34
11	4	8	6
11	6	27	28
11	10	19	19
12	0	15	14
12	1	19	18
12	2	7	6
12	3	8	8
12	4	10	9
12	5	11	11
12	6	6	5

H = 2

K	L	FOBS	FCALC
0	0	40	39
0	2	83	82
0	4	36	34
0	6	48	47
0	8	36	37
0	10	19	19
0	12	6	6
0	14	13	12
1	0	150	149
1	1	58	57
1	2	149	148
1	3	63	62
1	4	161	160
1	5	36	36
1	6	121	122
1	7	49	50
1	8	101	104
1	9	25	25
1	10	86	87
1	11	32	32
1	12	84	85
1	13	20	20
1	14	64	63
2	0	107	104
2	1	40	38
2	2	25	25
2	3	9	9
2	4	18	18
2	5	34	34
2	6	31	31
2	7	8	8
2	8	44	45
2	9	29	29
2	10	26	26
2	13	15	15
2	14	25	24
3	0	130	127
3	1	39	38
3	2	178	174
3	3	44	43
3	4	132	131
3	5	33	33
3	6	136	137
3	7	30	30
3	8	79	81
3	9	21	22
3	10	93	94
3	12	63	63
3	13	18	18
3	14	67	66
4	0	29	28
4	1	29	28
4	2	5	6
4	3	29	29
4	4	20	19
4	6	8	9
4	7	39	39
4	8	14	15
4	9	9	8
4	10	6	5
4	11	21	21
4	12	11	10
4	13	5	4
4	14	7	6
5	0	125	124
5	1	32	32
5	2	78	77
5	3	22	22
5	4	129	129
5	5	26	27
5	6	70	71
5	7	20	20
5	8	97	99
5	9	25	25
5	10	55	56
5	11	14	13
5	12	83	83
5	13	17	16
5	14	44	43
6	0	7	7
6	1	34	34
6	2	11	12
6	3	15	15
6	4	28	29
6	5	24	25
6	6	7	7
6	7	20	20
6	9	29	29
6	11	7	8
6	12	8	8
6	13	15	15
7	0	64	64
7	1	14	14
7	2	108	110
7	3	13	13
7	4	67	68
7	5	19	20
7	6	96	97
7	7	4	5
7	8	50	49
7	9	15	14
7	10	77	77
7	11	8	8
7	12	41	42
7	13	12	12
7	14	59	59
8	1	12	12
8	2	22	22
8	4	15	15
8	6	14	14
8	7	8	8
8	8	6	5
8	9	10	9
8	10	8	8
8	12	18	18
9	0	91	92
9	1	6	6
9	2	48	48
9	4	91	91
9	5	5	5
9	6	42	42
9	8	73	73
9	9	9	8
9	10	32	32
9	12	60	60
10	1	7	7
10	2	5	4
10	4	20	20
10	5	8	6
10	6	5	5
10	7	14	14
10	8	9	7
10	10	6	7
10	12	10	10
11	2	64	64
11	4	32	32
11	6	61	61
11	8	27	27
12	3	13	12
12	4	10	9
12	5	6	4

H = 3

K	L	FOBS	FCALC
0	0	62	64
0	2	71	71
0	4	119	120
0	6	38	39
0	8	65	65
0	10	21	21
0	12	76	76
0	14	10	10
1	0	6	5
1	1	21	20
1	2	10	10
1	3	34	32
1	4	41	40
1	5	5	5
1	6	18	18
1	7	31	30
1	8	16	16
1	10	15	15
1	11	17	19
1	12	29	28
1	13	6	5
1	14	16	15
2	0	15	15
2	1	9	9
2	2	62	57
2	4	60	59
2	5	21	21
2	6	46	45
2	7	5	6
2	8	12	11
2	9	13	13
2	10	28	28
2	12	26	26
2	13	10	9
2	14	22	21
3	0	25	21
3	1	20	20
3	2	53	51
3	3	28	27
3	4	41	42
3	5	19	18
3	6	38	39
3	7	19	19
3	8	9	9
3	9	11	11
3	10	22	21
3	12	14	14
3	13	11	11
3	14	15	15
4	0	53	52
4	1	38	37
4	3	56	56
4	4	80	82
4	5	35	34
4	7	41	41
4	8	41	41
4	9	21	21
4	11	36	36
4	12	48	48
4	13	22	22
5	0	10	9
5	1	15	15
5	2	4	4
5	4	29	28
5	5	12	11
5	6	10	9
5	7	8	7
5	9	13	13
5	9	12	13
5	10	10	10
5	13	7	6
5	14	11	11
6	0	16	17
6	2	38	38
6	4	10	9
6	5	10	9
6	6	39	39
6	7	9	9
6	8	8	7
6	10	34	34
6	12	12	11
6	13	4	5
6	14	30	30
7	1	7	6
7	2	34	33
7	4	11	10
7	5	16	16
7	6	30	30
7	7	7	5
7	9	12	12
7	10	22	22
7	12	4	5
7	13	10	10
7	14	19	18
8	0	18	18
8	1	24	24
8	2	32	32
8	3	30	30
8	4	27	27
8	5	33	33
8	6	25	26
8	7	17	17
8	8	9	10
8	9	22	22
8	10	16	16
8	11	21	21
8	12	14	13
8	13	22	22
8	14	11	11
9	0	22	22
9	1	9	8
9	2	8	8
9	4	27	27
9	5	8	6
9	8	15	15
9	9	10	9
9	12	17	16
10	0	6	5
10	1	21	20
10	2	22	22
10	3	9	9
10	4	7	6
10	5	15	15
10	6	22	22
10	7	14	14
10	9	19	19
10	10	19	19
10	11	6	6
11	0	9	9
11	1	5	4
11	2	12	12
11	6	14	14
11	7	5	5
12	1	7	7
12	2	17	16
12	3	11	9

H = 4

K	L	FOBS	FCALC
0	0	100	100
0	2	105	105
0	4	131	132
0	6	·95	96
0	8	82	82
0	10	76	76
0	12	81	82
0	14	58	57
1	0	23	23
1	1	8	7
1	3	22	22
1	4	10	10
1	7	20	20
1	8	21	20
1	10	8	5
1	11	15	15
2	0	57	53
2	1	30	29
2	2	188	188
2	3	30	29
2	4	79	80
2	5	17	17
2	6	152	155
2	7	30	30
2	8	36	35
2	9	16	16
2	10	113	114
2	11	20	19
2	12	39	39
2	13	12	11
2	14	83	82
3	0	35	37
3	1	17	16
3	2	31	32
3	3	15	14
3	5	7	7
3	6	18	17
3	7	17	17
3	8	14	14
3	11	10	10
3	12	10	9
3	13	5	5
4	0	110	111
4	1	12	12
4	2	87	87
4	4	125	127
4	5	10	10
4	6	75	76
4	8	83	85
4	9	13	14
4	10	57	57
4	12	77	77
4	14	42	42
5	0	8	8
5	2	8	9
5	4	8	8
5	5	11	12
5	7	6	5
5	8	14	14
5	9	7	6
5	12	5	4
5	13	7	6
6	0	62	61
6	1	41	41
6	2	89	91
6	3	36	35
6	4	74	74
6	5	29	28
6	6	83	83
6	7	40	39
6	8	52	52
6	9	29	29
6	10	68	68
6	11	26	25
6	12	52	51
6	13	19	19
6	14	56	54
7	1	9	8
7	2	18	18
7	3	5	5
7	4	10	10
7	5	8	8
7	6	15	15
7	9	12	12
7	10	14	13
7	11	6	6
7	12	7	8
7	13	6	5
7	14	8	8
8	0	88	88
8	1	6	7
8	2	55	55
8	3	14	14
8	4	92	92
8	5	14	13
8	6	48	47
8	7	8	6
8	8	68	68
8	9	7	6
8	10	36	35
8	11	12	11
8	12	59	58
8	13	10	9
8	14	28	27
9	0	18	18
9	2	7	5
9	4	10	8
9	5	10	10
9	[illegible]	7	5
9	8	11	11
9	9	7	5

H = 5

K	L	FOBS	FCALC
0	0	66	68
0	4	79	81
0	6	8	8
0	8	40	40
0	10	15	14
0	12	37	37
0	14	15	14
1	0	49	49
1	1	31	31
1	2	30	29
1	3	36	36
1	4	17	17
1	5	27	26
1	6	26	25
1	7	30	30
1	8	38	38
1	9	20	20
1	10	24	24
1	11	25	24
1	12	14	14
1	13	17	17
1	14	15	15
2	0	7	6
2	1	9	7
2	2	5	5
2	3	19	19
2	4	29	29
2	6	5	5
2	7	17	17
2	8	14	14
2	10	9	8
2	11	15	14
2	12	26	25
2	14	11	10
3	0	38	38
3	1	24	24
3	2	47	48
3	3	19	19
3	4	10	9
3	5	17	17
3	6	38	38
3	7	21	21
3	8	25	25
3	9	17	17
3	10	31	31
3	11	14	13
3	12	6	5
3	13	12	12
3	14	19	19
4	0	24	23
4	1	26	26
4	3	20	20
4	4	38	38
4	5	36	36
4	7	8	8
4	8	21	20
4	9	28	28
4	10	3	3
4	11	10	10
4	12	27	26
4	13	22	22
5	1	17	18
5	2	6	5
5	3	23	23
5	4	32	31
5	5	22	22
5	6	5	4
5	7	14	14
5	8	44	44
5	9	14	14
5	10	6	6
5	11	17	17
5	12	24	24
5	13	14	14
5	14	5	4
6	0	9	9
6	2	33	34
6	3	15	16
6	4	16	16
6	5	8	8
6	6	25	26
6	7	11	10
6	10	16	16
6	11	12	12
6	12	6	4
6	13	5	5
7	1	14	15
7	2	35	36
7	3	4	5
7	4	4	4
7	5	10	10
7	6	30	31
7	7	9	9
7	8	11	11
7	9	14	14
7	10	27	27
7	13	8	8
7	14	20	19
8	0	10	10
8	1	11	11
8	2	7	8
8	3	17	18
8	5	15	15
8	6	11	11
8	7	11	11
8	9	9	8
8	10	13	13
8	11	13	13
8	12	10	9
9	0	39	40
9	2	7	4
9	4	29	29
9	5	6	5
9	6	5	5
9	8	33	33

H = 6

K	L	FOBS	FCALC
0	0	52	53
0	2	27	27
0	4	36	36
0	6	25	23
0	8	42	42
0	10	19	18
0	12	24	24
1	0	119	122
1	1	24	24
1	2	90	93
1	3	16	16
1	4	85	86
1	5	31	31
1	6	76	77
1	7	8	8
1	8	89	89
1	9	26	26
1	10	61	60
1	11	9	8
1	12	50	50
1	13	19	19
1	13	19	19
1	14	41	40
2	0	22	22
2	1	9	9
2	2	5	6
2	3	7	6
2	4	11	8
2	5	6	7
2	6	5	5
2	7	7	7
2	8	17	17
2	9	7	7
2	11	5	4
2	12	7	4
3	0	74	76
3	1	28	28
3	2	81	83
3	3	23	20
3	4	51	51
3	5	24	24
3	6	77	77
3	7	21	20
3	8	·68	68
3	9	24	23
3	10	71	70
3	11	13	13
3	12	43	42
3	13	16	16
3	14	54	53
4	0	29	29
4	1	26	26
4	2	9	8
4	3	22	22
4	4	18	18
4	5	20	20
4	6	8	7
4	7	23	23
4	8	24	24
4	9	20	19
4	10	6	6
4	11	16	16
4	12	13	13
4	13	13	13
4	14	5	4
5	0	103	106
5	1	8	8
5	2	74	75
5	3	18	18
5	4	78	80
5	5	10	10
5	6	61	62
5	7	14	12
5	8	77	78
5	10	47	47
5	11	15	15
5	12	46	46
5	13	8	8
5	14	30	30
6	1	9	8
6	2	17	17
6	4	6	5
6	6	16	15
6	7	6	6
6	9	8	7
6	10	13	12
6	12	5	4
6	14	10	10
7	0	49	49
7	1	11	10
7	2	77	79
7	3	14	10
7	4	35	34
7	6	71	71
7	7	20	19
7	8	42	41
7	10	63	62
7	11	10	10
7	12	25	24
8	1	17	17
8	2	12	12
8	3	13	13
8	5	12	12
8	6	11	11
8	7	16	16
8	9	14	13
8	10	8	8
8	11	9	10
9	0	62	62
9	2	35	35
9	3	13	12
9	4	52	52
9	5	6	4
9	6	33	33
9	7	8	7
9	8	56	56

H = 7

K	L	FOBS	FCALC
0	2	33	33
0	4	36	36
0	6	25	25
0	8	30	30
0	10	12	13
0	12	15	16
0	14	8	7
1	0	21	21
1	2	13	14
1	3	9	8
1	5	6	5
1	6	11	12
1	7	7	7
1	8	17	17
1	10	12	12
1	11	6	6
1	14	8	7
2	0	17	17
2	1	18	18
2	2	52	53
2	3	12	13
2	4	21	20
2	5	22	22
2	6	51	51
2	7	7	7
2	8	10	9
2	9	19	18
2	10	45	45
2	11	7	7
2	12	10	9
2	13	14	14
2	14	37	37
2	14	38	37
3	0	23	23
3	1	5	2
3	2	15	15
3	5	4	1
3	6	11	12
3	8	18	17
3	10	10	11
4	0	35	36
4	2	11	10
4	3	8	9
4	4	29	30
4	5	4	5
4	6	9	10
4	7	10	10
4	8	30	30
4	9	8	8
4	10	8	8
4	11	9	9
4	12	22	22
4	14	7	7
5	0	22	22
5	3	8	8
5	4	7	6
5	5	9	9
5	6	4	3
5	8	19	19
5	10	6	5
5	11	8	6
5	12	5	5
5	13	6	5
6	0	20	20
6	1	26	26
6	2	34	34
6	3	25	25
6	4	14	14
6	5	28	29
6	6	27	28
6	7	17	18
6	8	11	11
6	9	23	23
6	10	19	20
6	11	17	17
6	12	5	4
7	0	15	15
7	1	7	6
7	2	7	6
7	4	7	4
7	6	7	5
7	7	6	4
7	8	12	13
7	9	7	7
7	10	7	6
8	0	20	20
8	1	10	9
8	2	8	7
8	3	7	8
8	4	19	20
8	5	6	6
8	7	9	9
8	8	22	23
8	9	7	8
9	0	17	16
9	1	5	4
9	4	9	8

H = 8

K	L	FOBS	FCALC
0	0	94	96
0	2	33	33
0	4	89	91
0	6	33	32
0	8	81	81
0	10	27	27
0	12	65	65
0	14	24	23
1	1	16	16
1	2	13	14
1	3	9	9
1	4	22	21
1	5	19	19
1	6	12	12
1	7	6	6
1	9	18	18
1	10	7	6
1	11	3	4
1	12	11	12
1	13	13	12
1	14	6	6
2	0	67	68
2	1	8	5
2	2	70	71
2	4	62	62
2	5	5	5
2	6	64	64
2	8	53	53
2	9	6	5
2	10	51	51
2	12	41	39
2	13	5	3
3	0	15	14
3	1	6	6
3	2	8	6
3	3	8	7
3	4	5	6
3	5	11	10
3	6	10	10
3	8	7	6
3	9	7	7
3	10	11	11
3	11	5	5
3	12	12	11
3	13	7	7
4	0	79	80
4	1	19	19
4	2	45	45
4	3	21	21
4	4	74	75
4	5	16	15
4	6	41	41
4	7	20	20
4	8	65	65
4	9	13	13
4	10	32	32
4	11	17	16
4	12	52	51
5	1	12	12
5	3	9	9
5	4	31	30
5	5	6	4
5	7	15	14
5	8	10	11
5	9	7	7
5	10	5	4
5	11	8	8
6	0	39	40
6	0	40	40
6	2	59	60
6	4	38	38
6	6	56	57
6	8	36	35
6	10	49	49
7	0	5	5
7	2	10	9
7	3	11	11
7	4	6	6
7	6	11	10
7	7	8	7
8	0	47	47
8	1	16	16
8	2	48	48
8	3	14	14
8	4	45	45
8	5	15	14
8	6	44	44
8	7	14	13
9	0	9	9
9	2	8	8

H = 9

K	L	FOBS	FCALC
0	0	14	13
0	2	11	11
0	4	9	9
0	6	13	14
0	8	7	6
0	10	13	13
1	0	13	14
1	1	15	15
1	2	11	12
1	3	17	17
1	4	29	29
1	5	11	10
1	6	13	12
1	7	18	18
1	8	13	13
1	9	10	9
1	10	11	10
1	11	15	14
1	12	23	23
2	1	8	5
2	2	20	20
2	3	10	9
2	6	16	17
2	7	10	9
2	10	11	11
2	11	8	7
3	0	9	9
3	1	16	16
3	2	29	29
3	3	20	20
3	4	21	21
3	5	17	18
3	6	25	25
3	7	15	15
3	8	6	5
3	9	13	13
3	10	18	18
3	11	16	15
4	1	10	11
4	2	9	9
4	3	7	7
4	4	5	4
4	5	13	13
4	6	8	9
4	9	12	12
4	10	7	6
5	0	12	13
5	1	11	11
5	2	7	6
5	3	4	5
5	4	25	25
5	5	8	8
5	6	7	7
5	7	8	8
5	8	15	14
5	9	12	11
6	1	7	7
6	3	10	10
6	5	7	5
6	7	11	10
6	8	6	4
7	0	8	7
7	1	6	5
7	2	27	28
7	3	8	6
7	4	5	4
7	5	12	12

H = 10

K	L	FOBS	FCALC
0	6	2	3
0	8	10	10
1	0	40	41
1	1	10	11
1	2	48	48
1	3	12	12
1	4	53	52
1	5	7	7
1	6	46	45
1	7	14	13
1	8	35	35
2	1	8	7
2	2	29	29
2	3	11	10
2	4	9	8
2	5	5	4
2	6	25	25
2	7	12	11
2	8	6	5
3	0	41	42
3	2	54	54
3	3	8	7
3	4	51	50
3	5	6	5
3	6	48	48
3	7	7	5
3	8	33	32
4	0	16	15
4	2	6	4
4	4	11	11
4	5	7	5
5	0	42	42
5	1	10	11
5	2	32	31
5	3	6	6
5	4	51	51
5	5	7	8
6	1	13	13
6	2	7	7

H = 11

K	L	FOBS	FCALC
0	0	33	33
0	2	8	8
0	4	27	27
1	2	5	4
1	3	7	6
1	4	12	11
2	0	12	13
2	2	21	20
2	4	8	7
3	0	8	7
3	2	5	4

[a] Scale factor is 3.350; $F_o = F_0$/scale factor.

The standard deviation of an observation of unit weight is 0.6668. The isotropic extinction parameter applied to F_c is 0.733 (16) × 10^{-4} cm^{-1}. The largest extinction correction is 0.35 for (004) in Ca_2AsO_4Cl. The atomic parameters are listed in Tables V and VI. Calculated and observed structure factors are listed in Table VII.

Results

The spodiosite structure projected along the *a* axis is shown in Figure 1. Interatomic distances and interbond angles for Ca_2PO_4Cl, Ca_2VO_4Cl, Ca_2CrO_4Cl, and Ca_2AsO_4Cl are listed in Table VIII. The standard deviations reported were derived from the complete variance–covariance matrices using the function and error program of Busing, *et al.*[12] The dimensions of the vanadate and arsenate tetrahedra are illustrated in Figure 2, produced by Johnson's thermal ellipsoid plot program.[13]

Discussion

The spodiosite structure is made up of discrete XO_4^{3-} tetrahedra, arranged along the *c* axis one above the other; members of each pair are related by a mirror plane at $z = ^1/_4$. They are apparently held together by the positively charged calcium ions. The coordination around both calcium ions is eight, with six nearest oxygens and two chlorines, in an irregular polyhedron. The chlorines appear to fill available holes in the structures. Evidently the spodiosite structure requires the

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(12) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(13) C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

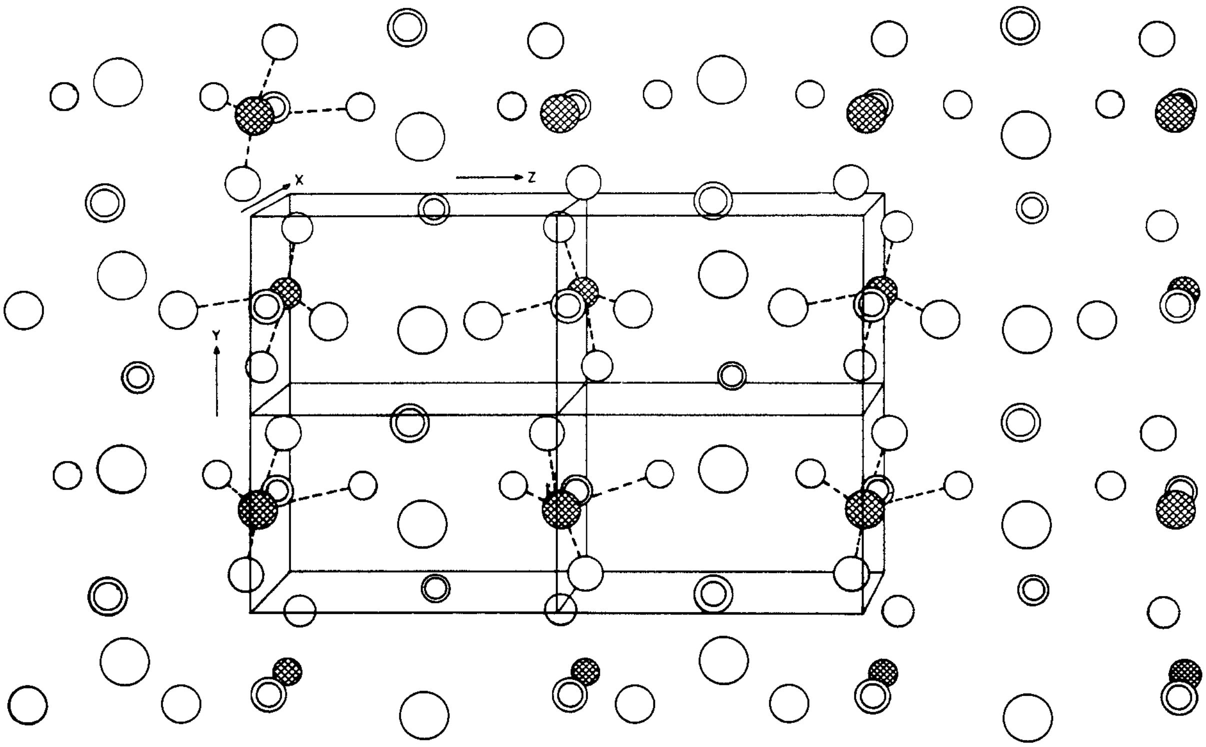

Figure 1.—The unit cell contents of Ca_2XO_4Cl projected along *a* (X = P, V, Cr, As): large open circles, Cl; atoms shaded up and down, X; double circles, Ca; smaller open circles, O. Bonds between the atoms in XO_4^{3-} tetrahedra are represented by broken lines.

Table VIII

Interatomic Distances and Bond Angles[a]

	Ca_2PO_4Cl	Ca_2VO_4Cl	Ca_2CrO_4Cl	Ca_2AsO_4Cl
		Distances, Å		
Ca(1)–O(1)	2.532 (2)	2.568 (1)	2.515 (3)	2.570 (1)
Ca(1)–O(2)	2.491 (2)	2.496 (1)	2.464 (3)	2.504 (1)
Ca(2)–O(1)	2.424 (2)	2.409 (1)	2.425 (3)	2.416 (1)
Ca(2)–O(2)	2.655 (2)	2.638 (1)	2.593 (3)	2.661 (1)
Cl–Cl	3.4990 (1)	3.5729 (1)	3.5707 (2)	3.5545 (0)
Cl–O(1)	3.263 (2)	3.327 (1)	3.331 (3)	3.322 (1)
Cl–O(2)	3.191 (2)	3.243 (1)	3.227 (3)	3.239 (1)
X–O(1)	1.547 (2)	1.711 (1)	1.710 (3)	1.690 (1)
X–O(2)	1.534 (2)	1.703 (1)	1.689 (3)	1.679 (1)
O(1)–O(2′)	2.481 (2)	2.724 (2)	2.694 (4)	2.678 (2)
O(1′)–O(2′)	2.578 (2)	2.902 (2)	2.931 (4)	2.873 (2)
O(2)–O(2′)	2.477 (3)	2.713 (2)	2.670 (5)	2.672 (2)
O(1)–O(1′)	2.495 (3)	2.751 (2)	2.719 (5)	2.720 (2)
		Angles, deg		
O(1)–X–O(2′)	107.3 (1)	105.9 (1)	104.8 (1)	105.3 (1)
O(1′)–X–O(2)	107.3 (1)	105.9 (1)	104.8 (1)	105.3 (1)
O(2)–X–O(2′)	107.7 (1)	105.6 (1)	104.4 (2)	105.5 (1)
O(1)–X–O(1′)	105.7 (1)	107.0 (1)	105.3 (2)	107.2 (1)
O(1)–X–O(2)	113.6 (1)	116.4 (1)	119.2 (1)	117.1 (1)
O(1′)–X–O(2′)	113.6 (1)	116.4 (1)	119.2 (1)	117.1 (1)

presence of a large anion such as Cl^- or Br^- in these positions. Except for the mineral Ca_2PO_4F which gives its name to this structure, there are no spodiosites with these ions absent, and, significantly, no phase of this composition exists in the $Ca_3(PO_4)_2$–CaF_2 system.

Comparison of tetrahedral radii for V^{5+} and As^{5+} in these compounds with those listed by Shannon and Prewitt[14] shows a discrepancy of about 0.05 Å. We believe that this contradicts the statement by Shannon and Prewitt that radii are independent of structure type. However, these authors point out that this independence must be modified by considerations of covalency and repulsive forces. It would appear that the effect of these differences between the structures reported here and those chosen by Shannon and Prewitt as standards is sufficient to modify the apparent radii to this extent, which is significantly greater than experimental error.

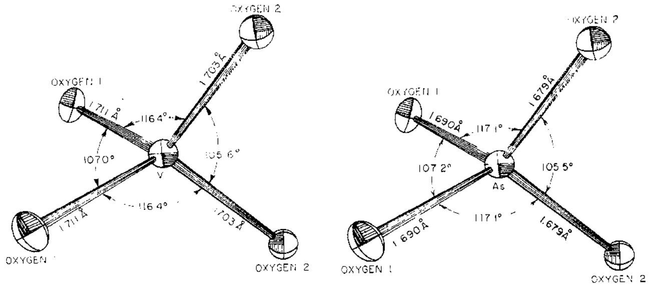

Figure 2.—Dimensions of vanadate and arsenate tetrahedra.

The tetrahedra are considerably distorted from ideal configuration for all four structures; the only element of symmetry left is a twofold axis. A significant aspect of this study is the relative distortion of XO_4^{3-} tetrahedra. It is now clear that the most significant angular distortions occur in CrO_4^{3-}. The electronic configuration of Cr(V) in CrO_4^{3-} is d^1. Results of the electron spin resonance measurements made in diluted single crystals of $Ca_2(PO_4,CrO_4)Cl$ showed that the unpaired electron is in a d_{z^2} orbital.[5] We suggested that, in addition to the distortion due to crystal lattice effects

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[14] R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, 25, 925 (1969).

clearly present in the phosphate tetrahedron, a Jahn–Teller type of electronic ordering takes place in the case of CrO_4^{3-} tetrahedron, nearly doubling the extent of distortion.

In VO_4^{3-} there is no electron in the d orbitals (ground state). Bond distances in VO_4^{3-} are similar to those in CrO_4^{3-}, but bond angles fall approximately between the values in the phosphate and chromate. The increased distortion in the vanadate tetrahedron as compared to PO_4^{3-} is tentatively attributed to the lowering of the interatomic force constants and vibration frequencies due to the increased mass. As the chromium(V) and vanadium(V) ions are not expected to differ appreciably in size the larger distortion in the CrO_4^{3-} tetrahedron appears to be electronic in nature. However, the excess distortion in VO_4^{3-} may also be due to the mixing of low-lying excited states in the d manifold. This should be investigated spectroscopically.

Similarly, in AsO_4^{3-}, there are no unpaired electrons (ground state); the crystal structure shows the distortion to be intermediate between the VO_4^{3-} and CrO_4^{3-}. On the basis of size considerations alone we might have expected the distortion of the arsenate to be smaller than that of the vanadate ion; although the differences between the distortions of the two tetrahedra are small, the arsenate is distorted to a significantly greater extent than the vanadate. The reasons are not clear.

Conclusion

Spodiosites with the general formula Ca_2XO_4Cl, with X = P, V, Cr, and As, have been prepared. Detailed crystal structure analyses of all four show that the XO_4^{3-} tetrahedra are considerably distorted from T_d symmetry. Interatomic distances are normal, and the distortions cannot be explained by considerations of crystal packing alone. The largest distortion is exhibited by the CrO_4^{3-} tetrahedron; this was attributed to electronic ordering of the lone electron in the d orbital. PO_4^{3-}, VO_4^{3-}, and AsO_4^{3-} do not contain unpaired electrons and the observed distortions are notably smaller than in CrO_4^{3-}.

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The Crystal Structure of the 1:1 Molecular Addition Compound Xenon Difluoride–Iodine Pentafluoride, $XeF_2 \cdot IF_5$

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The crystal structure of the 1:1 molecular addition compound xenon difluoride–iodine pentafluoride, $XeF_2 \cdot IF_5$, has been determined from three-dimensional X-ray data. The material crystallizes in the tetragonal system, with four molecules in a cell of dimensions $a = 7.65$ (1) and $c = 10.94$ (1) Å. A satisfactory refinement was obtained in the space group I4/m, with a final conventional R factor of 0.034 for 403 nonzero reflections. The structure has established the existence of discrete XeF_2 and IF_5 molecules, linear and square-based pyramidal, respectively. The alignment of the XeF_2 molecules, with each fluorine ligand directed toward the iodine atoms of neighboring IF_5 molecules, and the shortness of those interatomic distances (3.142 ($\sigma = 0.007$) Å) suggest that the ordered crystal lattice is largely a consequence of electrostatic attractions between the different components.

Introduction

Xenon difluoride is a fluoride ion donor[1-3] and forms salts with arsenic pentafluoride and strong fluoride ion acceptor metal pentafluorides. It also forms a 1:1 compound with iodine pentafluoride which Bartlett and Sladky[4] concluded was a molecular adduct on the basis of Raman spectroscopic evidence. The crystal structure of the compound confirms this representation, the geometry of each molecule being only slightly different from that of the "free" species.

The nature of the alignment of the molecules in the crystal lattice is consistent with coulombic attraction of negatively charged fluorine ligands of the XeF_2 molecules to the positively charged iodine atoms of nearest IF_5 molecules. This is similar to the 1:1 molecular adduct[5] $XeF_2 \cdot XeF_4$ and like the situations found[6,7] in crystalline XeF_2 and XeF_4.

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[1] F. O. Sladky, P. A. Bulliner, N. Bartlett, B. G. De Boer, and A. Zalkin, *Chem. Commun.*, 1048 (1968); F. O. Sladky, P. A. Bulliner, and N. Bartlett, *J. Chem. Soc. A*, 2179 (1969).

[2] V. M. McRae, R. D. Peacock, and D. R. Russell, *Chem. Commun.*, 62 (1969).

[3] J. G. Knowles and J. H. Holloway, *J. Chem. Soc. A*, 756 (1969).

[4] N. Bartlett and F. O. Sladky, *ibid.*, *A*, 2188 (1969).

[5] J. H. Burns, R. D. Ellison, and H. A. Levy, *Acta Crystallogr.*, **18**, 11 (1965); *J. Phys. Chem.*, **67**, 1569 (1963); "Noble-Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p 226.

[6] H. A. Levy and P. A. Agron, "Noble-Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p 221; *J. Amer. Chem. Soc.*, **85**, 241 (1963); P. A. Agron, G. M. Begun, H. A. Levy, A. A. Mason, C. G. Jones, and D. F. Smith, *Science*, **139**, 842 (1963).

[7] D. H. Templeton, A. Zalkin, J. D. Forrester, and S. M. Williamson, *J. Amer. Chem. Soc.*, **85**, 242 (1963); "Noble-Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p 203; W. C. Hamilton and J. A. Ibers, *ibid.*, p 195; J. H. Burns, P. A. Agron, and H. A. Levy, *ibid.*, p 211; *Science*, **139**, 1208 (1963); J. A. Ibers and W. C. Hamilton, *ibid.*, **139**, 106 (1963).