in Table 6. The angles Au–N–C(1′) and Au–N–C(1‴) are 100 and 106° respectively, whilst C(9)–N–C(1′), C(9)–N–C(1‴) and C(1′)–N–C(1‴) are 136, 102 and 88°. The corresponding angles to the mid-points of the ethynyl groups are 109, 115, 127, 97 and 84°. These values indicate that the amino hydrogen atoms are directed approximately towards neighbouring ethynyl groups. Calculation of the positions of these two atoms, assuming N–H bond lengths of 1·0 Å and H–N–H angles cf 108°, leads to H···C distances of 2·58 and 2·49 Å to C(1′) and C(1‴). The N–H···C angles are 133 and 167° so that the angle to C(1′) departs considerably from 180°.

Tertiary phosphine complexes of phenylethynylgold(I) are monomeric in benzene solution and have large dipole moments of about 6·5D. In contrast, the amine complexes are associated in solution and their dielectric constants show the presence of much less polar aggregates (Coates & Parkin, 1962). The Au–N bonds are expected to be at least as polar as the Au–P bonds, so some factor, other than dipole interactions, must be responsible for the association of the amine complexes.

Hydrogen bonds are formed by acidic hydroxyl groups with ethylenes (West, 1959), with acetylenes and also between NH groups and olefins (Schleyer, Trifan & Bacskai, 1958). In the present case, hydrogen bonds may be formed between N and the ethynyl groups C(1′)–C(2′) and C(1‴)–C(2‴), although spectroscopic evidence for this is lacking. The N–H···C distances are about the same as the N–H···N distances of 3·38 Å in solid ammonia (Olovsson & Templeton, 1959). The interaction may be linked with the angle Au–N–C(9) being greater than tetrahedral and with the distortion of the angle Au–C(1)–C(2) to 174°.

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References

Arai, G. J. (1962). *Rec. Trav. chim. Pays-Bas*, **81**, 307.

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.

Coates, G. E. & Parkin, C. (1962). *J. Chem. Soc.* p. 3220.

Corfield, P. W. R. & Shearer, H. M. M. (1966*a*). *Acta Cryst.* **20**, 502.

Corfield, P. W. R. & Shearer, H. M. M. (1966*b*). *Acta Cryst.* **21**, 957.

Cruickshank, D. W. J., Pilling, D. E., Bujosa, A., Lovell, F. M. & Truter, M. R. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p. 32. Oxford: Pergamon Press.

Elliott, N. & Pauling, L. (1938). *J. Amer. Chem. Soc.* **60**, 1846.

James, R. W. (1948). *The Crystalline State*, Vol. II, p. 149. London: Bell.

Olovsson, I. & Templeton, D. H. (1959). *Acta Cryst.* **12**, 832.

Orgel, L. E. (1960). *An Introduction to Transition-Metal Chemistry*. London: Methuen.

Pauling, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.

Rosenzweig, A. & Cromer, D. T. (1959). *Acta Cryst.* **12**, 709.

Rundle, R. E. (1954). *J. Amer. Chem. Soc.* **76**, 3101.

Schleyer, P. von R., Trifan, D. S. & Bacskai, R. (1958). *J. Amer. Chem. Soc.* **80**, 6691.

Sutton, L. E. (1965). *Tables of Interatomic Distances, Supplement*. London: The Chemical Society.

Thomas, L. H. & Umeda, K. (1957). *J. Chem. Phys.* **26**, 293.

West, R. (1959). *J. Amer. Chem. Soc.* **81**, 1614.

Acta Cryst. (1967). **23**, 162

The Crystal Structure of Thomsenolite

By G. Cocco, P. C. Castiglione and G. Vagliasindi

Centro Nazionale di Cristallografia del C.N.R., Istituto di Mineralogia dell'Università di Perugia, Italy

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The determination of the crystal structure of thomsenolite, $NaCaAlF_6.H_2O$, has been carried out with integrating Weissenberg data. The mineral is monoclinic: space group $P2_1/c$; $a_0 = 5{\cdot}583 \pm 0{\cdot}004$, $b_0 = 5{\cdot}508 \pm 0{\cdot}005$, $c_0 = 16{\cdot}127 \pm 0{\cdot}006$ Å and $\beta = 96°26' \pm 3'$; $Z = 4$. The final R value is 9·0%. Fundamentally, the structure is made up by sheets subparallel to {001}, resulting from Ca^{2+} bonded to four $[AlF_6]^{3-}$ octahedra and by chains parallel to [001] of alternating Ca polyhedra and $[AlF_6]^{3-}$ octahedra. Sodium is surrounded by the unusual number of eight neighbouring fluorine atoms. The proposed structure is in good agreement with the physical properties of the mineral.

Introduction

Thomsenolite is a monoclinic hydrated aluminofluoride of sodium and calcium: $NaCaAlF_6.H_2O$, dimorphous with pachnolite for which the structure was recently announced but has not yet been published (Gerhard, 1966).

The unit cell of thomsenolite has been determined by Ferguson (1946); a refinement by the least-squares method on the diffractometric data gives the values below, which are similar to those obtained by Ferguson:

$a_0 = 5{\cdot}583 \pm 0{\cdot}004$ Å	$Z=4$
$b_0 = 5{\cdot}508 \pm 0{\cdot}005$	$D_{obs} = 2{\cdot}981$ g.cm^{-3}
$c_0 = 16{\cdot}127 \pm 0{\cdot}006$	$D_x = 2{\cdot}974$ g.cm^{-3}
$\beta = 96°26' \pm 3'$	Space group: $P2_1/c$

Experimental

A suitable small crystal of thomsenolite from Ivigtut, Greenland, has been cut into a subspherical shape with an average radius of about 0·5 mm.

Intensity data were obtained from integrating Weissenberg photographs (Cu $K\alpha$ radiation) about the a axis, from zero up to fifth layer. Four film packs for each layer were used with two different time exposures in order to cover a very large range of intensities; these last were measured by a microdensitometer. The intensity data for 938 independent reflexions were collected, of which 203 were indistinguishable from the film background. The absorption correction was applied for $\mu R = 3{\cdot}6$.

Geometrical and polarization corrections were applied in the usual way, while the final scale factor adjustment to the structure amplitudes was made during the refinement on the 1620 IBM computer.

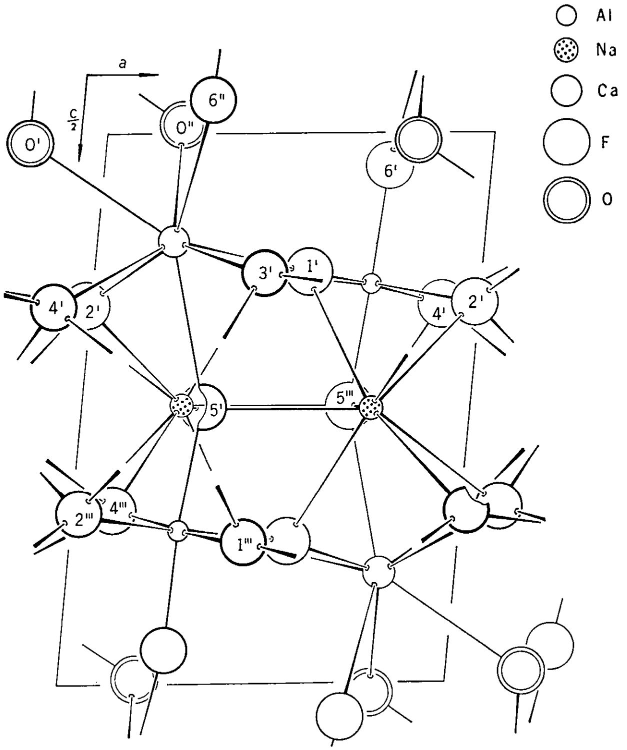

Fig. 1. Projection of the structure of thomsenolite along the b axis.

Structure determination and refinement

A three-dimensional Patterson synthesis was computed with corrected F^2's for the observed reflexions; an approximate reduction of the different layers to the same scale had been previously made by the Wilson method. The highest peak was assumed to be a Ca–Ca vector, and the next in order of height were assigned to Ca–Al and Ca–Na vectors. The expected Al–F_6 octahedral coordination, in agreement with known features of the cryolite structure (Nàray-Szabò & Sasvàri, 1938). allowed the localization of some of the F atoms, whose vectors had already been ascertained in the Patterson synthesis.

A series of three-dimensional Fourier syntheses, with phases first calculated from Ca, Al, Na and two fluorine atoms, and on successive stages with the addition of the remaining fluorine and the oxygen atoms, yielded trial positions for all the atoms of the mineral.

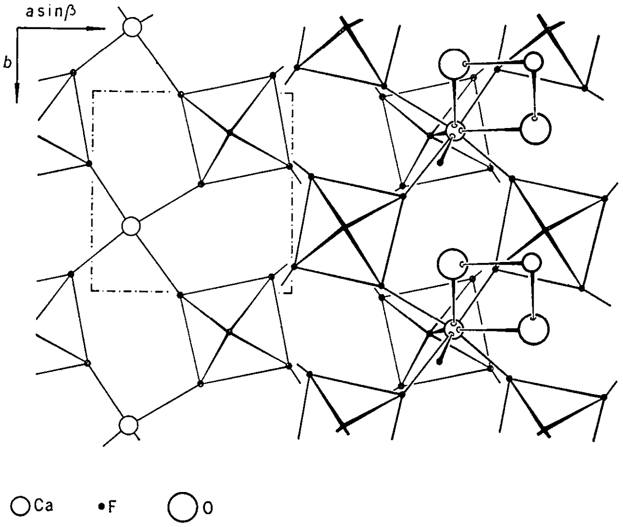

Fig. 2. Simplified projection of thomsenolite along the c axis; $c=\frac{1}{2}$. Al and Na are not represented. Unit cell in dashed line. Sheets of Ca–$(AlF)_6$ octahedra are shown at two levels. On the right are shown the Ca atoms binding oxygen atoms.

Table 1. *Atomic parameters with their standard deviations*

(Positional parameters × 10^4)

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
Ca	1892	4	6745	4	992	1	1·85 Å^2	0·04 Å^2
Al	7174	6	1795	6	1390	2	1·80	0·05
Na	2542	9	1455	10	2487	3	2·82	0·09
F(1)	5511	12	4634	13	1271	4	2·55	0·12
F(2)	9887	12	3649	13	1562	4	2·60	0·12
F(3)	4406	12	126	13	1281	4	2·63	0·12
F(4)	9037	12	9173	13	1575	4	2·59	0·12
F(5)	3128	12	6983	12	2505	4	2·39	0·11
F(6)	7362	12	1672	14	301	4	2·49	0·11
O	8019	15	6585	16	65	5	2·16	0·14

The refinement of the structure was carried out by five least-squares cycles with the use of 3 × 3 and 1 × 1 block-diagonal approximations.

The computer program (Albano, Bellon, Pompa & Scatturin, 1963) applies the following weighting scheme to the observed reflexions:

$$w(hkl) = 1/(a + F_o + cF_o^2)$$

where a is twice the minimum observed F_o, and c is twice the reciprocal of the maximum observed F_o.

The final coordinates of the asymmetric unit and the isotropic thermal parameters with their standard deviations, are listed in Table 1.

The observed and calculated structure factors are shown in Table 2. The atomic scattering factors, for

Table 2. *Observed and calculated structure factors*

H	K	L	FO	FC
0	0	2	24.7	-27.2
		4	65.0	-78.2
		6		.2
		8	130.6	141.2
		10	52.9	-46.0
		12	32.4	24.4
		14	22.5	-16.6
		16		-3.0
		18	24.4	-19.0
		20	24.8	21.2
0	1	1	9.3	-7.8
		2	8.4	-6.8
		3	14.4	-13.6
		4	31.0	36.2
		5	17.2	20.2
		6	7.2	-7.0
		7	17.4	17.2
		8	64.6	-73.0
		9	25.7	-25.8
		10	32.0	-30.4
		11	35.8	-32.4
		12	46.9	42.6
		13		1.4
		14	21.8	18.6
		15	10.4	8.0
		16	26.2	-20.2
		17		-4.8
		18	16.6	-12.4
		19	13.9	-10.8
		20	13.8	11.2
0	2	0	43.2	-45.4
		1	52.0	-52.6
		2		-4.2
		3	11.1	-10.6
		4	48.0	-50.4
		5	78.5	-80.4
		6	36.9	35.0
		7	51.3	66.6
		8	12.9	-13.4
		9	25.2	-27.2
		10		-3.6
		11	19.8	-19.6
		12	27.7	-26.2
		13	35.1	-30.2
		14	16.4	14.6
		15	11.1	9.0
		16	13.3	10.6
		17	15.4	-11.0
		18	12.7	8.8
		19	19.2	18.8
0	3	1	22.0	24.4
		2	7.5	-8.0
		3	11.5	-6.4
		4	10.4	-9.8
		5	24.4	-27.0
		6	8.2	9.2
		7	15.1	-15.0
		8	12.7	13.2
		9	22.5	25.4
		10		-7.0
		11	44.6	47.4
		12	7.0	-6.8
		13		4.0
		14		4.6
		15	24.4	-20.6
		16	4.0	3.0
		17	6.4	4.6
0	4	0	38.9	-38.2
		1	59.7	69.4
		2		2.6
		3	29.5	31.2
		4	13.9	-14.4
		5		-1.2
		6		-4.8
		7	30.5	-32.8
		8		-4.0
		9	27.9	29.4
		10	6.2	6.4
		11		2.4
		12	22.4	-22.0
		13	19.4	17.6
		14	5.8	5.2
		15		3.0
		16	15.3	11.2
0	5	1		-1.8
		2		-4.6
		3		-4.6
		4	17.4	-17.4
		5	8.6	9.2
		6	9.0	10.6
		7	16.4	16.6
		8	28.2	29.2
		9	8.0	-8.4
		10		-1.0
		11	23.2	-23.4
		12	19.4	-18.8
0	6	0	43.9	47.4
		1	7.8	-9.8
		2	6.7	7.0
		3		-6.4
		4	13.4	-12.8
		5	6.0	7.2
		6	10.5	-10.6
		7		2.2
		8	20.6	23.6
1	0	0		6.4
		2	25.5	18.4
		-2		-4.2
		4	34.5	-33.6
		-4	34.1	35.0
		6	53.7	52.6
		-6	11.9	12.2
		8	59.2	54.2
		-8	133.6	-142.6
		10	37.8	37.8
		-10	22.1	-23.4
		12	6.0	5.4
		-12	73.5	78.6
		14	12.7	-11.8
		-14	7.7	6.0
		-16	63.1	-60.2
		-18		-.4
		-20	24.9	19.4
1	1	0	104.8	87.0
		1		-1.4
		-1	37.2	-30.4
		2	46.9	45.0
		-2	15.0	-7.8
		3	40.4	37.4
		-3	45.6	-40.2
		4	52.8	-46.4
		-4	88.7	-83.4
		5	7.1	-7.4
		-5	21.8	19.6
1	1	6	39.3	-42.8
		-6	15.6	-15.4
		7	6.3	7.6
		-7	11.9	-13.6
		8	5.8	4.4
		-8	28.5	32.4
		9	14.4	-14.0
		-9		-1.0
		10	16.0	15.4
		-10		-5.4
		11		2.2
		-11	9.2	-8.4
		12	6.7	-5.8
		-12	27.6	-27.6
		13	5.9	5.8
		-13	7.4	-7.6
		14	9.2	-9.6
		-14	12.7	-12.6
		15	15.3	12.2
		-15	13.5	-10.8
		16	20.7	-19.8
		-16	23.4	-21.0
		-17	16.6	15.4
		-18	14.4	-11.2
		-19	8.8	7.8
		-20	11.9	11.0
1	2	0	44.5	-38.4
		1	46.7	43.0
		-1	22.1	-21.0
		2	11.6	-9.2
		-2	24.5	-21.6
		3	26.5	24.6
		-3	58.7	55.6
		4	53.6	53.0
		-4	37.5	36.0
		5	21.6	21.2
		-5	78.7	81.6
		6	6.4	-3.2
		-6	13.2	12.4
		7	55.8	61.0
		-7	11.3	10.8
		8	50.9	-57.4
		-8	12.2	12.2
		9	10.7	13.4
		-9	31.5	-34.0
		10	30.4	-32.2
		-10	5.3	5.6
		11	49.8	-53.8
		-11		.4
		12	32.0	32.8
		-12		-.0
		13		1.2
		-13	8.5	7.6
		14	10.5	10.2
		-14	11.4	-11.0
		15	32.4	32.0
		-15	20.2	18.4
		16	20.8	-20.0
		-16	11.0	9.2
		-17		-1.2
		-18	9.1	8.4
		-19	16.6	-12.8
1	3	0	40.7	-40.4
		1	18.1	-16.8
		-1	71.5	74.2
		2	31.2	33.0
		-2		3.6
		3	76.7	-83.8
		-3	55.0	55.0
		4	7.1	-9.0
		-4		.0
		5	16.6	16.8
		-5	32.5	-31.6
		6		-2.6
		-6	16.5	17.6
		7	29.2	31.8
		-7	11.4	-11.8
		8	10.0	-11.2
		-8	19.3	-22.6
		9	6.3	-5.6
		-9	11.9	12.4
		10	15.2	18.0
		-10	8.4	7.4
		11	14.0	-14.8
		-11	24.3	28.4
		12	13.1	-13.4
		-12	8.1	-10.2
		13		4.4
		-13		7.0
		14		.4
		-14	8.0	7.6
		15	14.3	-13.4
		-15		-.2
		16		.0
		-16		-1.0
		-17	12.8	-12.2
1	4	0	38.5	-39.0
		1	15.0	-15.0
		-1	13.2	-12.8
		2		1.6
		-2	8.8	7.6
		3	12.6	12.4
		-3		-6.8
		4	28.6	30.0
		-4	21.1	21.4
		5	26.6	-30.0
		-5	25.2	-27.8
		6	13.2	-14.6
		-6	7.5	-7.6
		7	33.6	-36.8
		-7	37.2	-39.4
		8	28.9	-32.0
		-8		5.0
		9		1.6
		-9	25.9	28.2
		10		.0
		-10	11.7	13.0
		11	29.1	31.8
		-11	24.5	28.6
		12		4.8
		-12		-5.4
		13		.8
		-13	17.5	-18.0
		14		-.6
		-14		-3.8
		15	18.3	-16.8
		-15	24.4	-25.0
		16	6.3	-5.6
		-16	8.1	6.4
1	5	0	18.0	-17.6
		1	10.3	12.0
		-1	30.8	-34.2
		2		-2.0
		-2	21.3	-22.8
1	5	3	17.4	18.8
		-3		-3.4
		4	18.8	20.2
		-4	39.5	42.8
		5	10.5	11.8
		-5		2.6
		6		-7.6
		-6		6.6
		7	19.3	-22.4
		-7	12.4	14.6
		8	11.7	13.8
		-8	8.4	-8.4
		9		3.2
		-9	10.7	-12.2
		10		-3.8
		-10	7.6	-7.6
		11		1.2
		-11		-1.8
		12		-.4
		-12	14.5	16.2
		13	9.0	8.0
		-13	9.5	-7.8
		-14	5.4	5.4
1	6	0		-2.8
		1	7.2	-6.8
		-1		1.0
		2		-1.2
		-2	11.1	11.4
		3	8.6	-8.8
		-3		2.2
		4		-3.8
		-4	9.8	10.0
		5	9.0	9.2
		-5		-3.0
		6		-.0
		-6	11.6	-13.0
		7		2.8
		-7		3.6
		8	14.0	18.2
		-8	20.7	-24.8
		9	5.5	-4.8
		-9	3.9	-4.8
		10	19.3	18.8
		-10		.2
2	0	0	91.6	-89.4
		2	39.7	-35.8
		-2	10.5	8.0
		4	106.2	-110.2
		-4	48.6	-44.8
		6	72.0	74.8
		-6	51.1	44.2
		8	10.5	-8.0
		-8	84.4	-88.0
		10	13.1	-12.4
		-10	7.0	6.4
		12	41.4	-38.0
		-12	7.0	-7.0
		-14	26.2	24.6
		-16		-1.8
		-18	13.9	10.0
		-20	36.0	-27.6
2	1	0	24.6	-20.0
		1	37.9	33.8
		-1	51.0	-41.8
		2		1.8
		-2	42.7	35.6
		3	52.9	50.4
		-3	28.7	-25.4
		4	40.4	-39.2
		-4	24.9	-24.2
		5	40.2	-44.0
		-5	35.1	25.8
		6	14.2	-13.6
		-6	49.6	-50.2
		7	30.6	-31.6
		-7		.4
		8	20.1	19.6
		-8	51.0	-58.2
		9	16.5	17.6
		-9	19.0	14.6
		10	50.8	51.0
		-10	11.7	13.2
		11	30.2	27.8
		-11	20.8	19.8
		12	23.0	-22.4
		-12	27.7	22.0
		13		-1.2
		-13		-1.8
		14	27.4	-26.4
		-14		.0
		15	6.8	-6.2
		-15		-3.8
		-16	34.8	-29.8
		-17	14.2	11.4
		-18		-2.0
		-19	8.7	8.0
2	2	0	109.7	101.2
		1	70.0	67.2
		-1	84.4	-121.6
		2	37.0	33.8
		-2	41.0	-38.4
		3	58.3	54.0
		-3	12.8	12.4
		4	26.5	-26.4
		-4	33.1	-31.8
		5	21.2	22.8
		-5	25.2	24.0
		6	24.6	-26.4
		-6	10.6	9.0
		7	25.1	-25.6
		-7	23.3	24.2
		8	38.2	42.4
		-8	48.7	53.2
		9	42.6	46.2
		-9	41.1	-46.0
		10		-5.8
		-10	9.6	-10.8
		11	14.2	-14.2
		-11	8.0	7.2
		12		-3.0
		-12	6.8	-8.0
		13	18.0	17.2
		-13	27.5	-27.0
		14		1.8
		-14	11.5	-11.0
		15	19.5	18.6
		-15	12.8	11.6
		-16	7.1	6.0
		-17	8.9	8.8
		-18		-2.6
		-19	13.0	9.4
2	3	0	12.3	-12.2
		1	20.2	21.2
		-1	8.6	-9.4
2	3	2	15.8	-18.2
		-2	12.8	10.4
		3	33.7	-34.0
		-3	9.6	-8.6
		4	19.8	21.8
		-4	11.4	11.0
		5	6.4	7.0
		-5	33.1	31.2
		6		-.4
		-6	21.2	-24.2
		7	35.0	36.0
		-7	21.1	21.0
		8	6.1	-6.0
		-8	11.7	12.4
		9	6.8	8.4
		-9	52.0	-65.0
		10	7.3	-9.0
		-10	6.1	6.8
		11	40.8	-43.4
		-11	30.2	-33.6
		12		4.0
		-12	8.3	-8.8
		13	12.3	-12.0
		-13	24.6	24.8
		14		3.4
		-14	6.7	-6.2
		15	8.7	9.4
		-15	14.5	13.8
		-16	11.7	10.6
		-17	31.4	-27.8
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		2	8.3	9.0
		-2		-.8
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		-3		4.2
		4	10.9	11.4
		-4		-2.2
		5	33.8	-34.6
		-5	19.3	-19.6
		6	17.7	-18.2
		-6	10.2	-9.4
		7	15.2	16.2
		-7	21.8	-22.4
		8	12.7	13.8
		-8	30.6	32.0
		9		-2.0
		-9	32.1	36.2
		10	6.2	6.2
		-10		.2
		11		-1.2
		-11		2.2
		12		-.0
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		13	20.4	-19.2
		-13	4.9	4.8
		14	6.7	-6.6
		-14	4.1	-3.6
		-15		-1.2
		-16	10.4	8.8
2	5	0	8.9	-9.2
		1		-1.0
		-1		4.4
		2		2.4
		-2		1.6
		3	14.7	16.8
		-3	11.4	-13.2
		4	13.7	14.8
		-4	10.6	10.8
		5	7.4	-8.8
		-5	8.9	-8.4
		6	8.2	9.8
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		7	18.6	-19.4
		-7		-.6
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		-8	12.0	13.0
		9		-3.0
		-9	18.8	20.8
		10	17.3	-18.0
		-10	7.6	7.8
		11	22.6	24.8
		-11		2.4
		12	5.1	5.6
		-12	10.8	-12.4
		-13	4.6	-5.6
		-14	3.6	-4.4
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		1		1.0
		-1		-4.2
		2	17.9	-20.0
		-2	10.8	12.0
		3	5.5	6.0
		-3	8.4	-8.6
		4		.2
		-4	4.9	5.8
		5		-2.0
		-5	4.3	4.2
		6	10.2	12.8
		-6		-3.0
		7	3.5	-4.2
		-7	7.4	7.8
		8	8.0	-7.2
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		-14		-2.6
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		-18	5.3	-4.4
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		6	12.6	12.0
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3	1	7	9.4	8.8
		-7	14.5	-15.6
		8		1.8
		-8	5.5	-4.4
		9	9.9	10.0
		-9	31.3	35.8
		10		-2.4
		-10	8.1	7.4
		11	15.4	-14.4
		-11	33.0	35.6
		12		2.2
		-12	22.7	23.0
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		-13	21.9	-23.8
		14	17.2	-16.2
		-14	15.9	15.2
		15		-.2
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		-18	7.2	-6.8
3	2	0	18.8	-17.4
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		-1	40.3	-37.4
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		3	40.4	41.2
		-3	16.4	-16.2
		4	9.1	-7.8
		-4	10.1	8.8
		5	20.5	-21.4
		-5	11.1	-9.4
		6	9.1	-9.8
		-6	9.1	-10.6
		7	33.5	-41.2
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		-8	38.5	-41.8
		9	12.2	-12.4
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		11	25.9	27.6
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		12		-1.2
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		-14	7.4	-7.6
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		4	12.0	12.8
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		5	14.1	14.8
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		-6	7.7	-7.4
		7	8.2	9.0
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		8	3.7	4.4
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		9	24.2	-25.4
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		11	6.1	-5.4
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		12		.8
		-12	5.0	-4.8
		13	5.6	4.6
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		-14		2.2
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		2		.2
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		5	15.3	15.8
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		6		-3.8
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		7	17.3	18.6
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		8		3.0
		-8		-4.2
		9	14.8	15.8
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		10	13.4	15.0
		-10	7.6	9.4
		11	21.2	-22.6
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		12	6.7	6.6
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		1		-4.6
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		-4	19.0	-20.6
		5		-.2
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		-7		-3.6
		8		-2.4
		-8		2.4
		9	8.0	-6.4
3	5	-9	17.8	20.2
		10	9.1	8.8
		-10		-.4
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		2	17.3	-16.8
		-2		-1.4
		3	8.4	9.6
		-3		2.0
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		-4		.0
		5	4.8	5.8
		-5		-.6
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		-4		-1.4
		6	29.3	-28.6
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		10	15.6	-14.2
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		7		-2.8
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		9	32.5	32.2
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		11	5.1	-5.8
		-11		-4.6
		12	6.1	5.6
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		-16	26.4	24.2
		-17	22.1	-16.6
		-18	21.6	-13.6
4	2	0	22.1	-20.4
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		-2	25.8	22.6
		3	11.0	-12.6
		-3	22.8	-21.4
		4	9.0	-8.2
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		5	44.2	-44.8
		-5	23.1	-22.6
		6	6.3	6.4
		-6	19.9	-20.4
		7		2.2
		-7	12.2	-11.8
		8		4.0
		-8	17.3	-18.2
		9		-3.6
		-9	37.1	40.0
		10	3.9	4.2
		-10	13.3	15.0
		11		1.6
		-11		-4.4
		12	7.8	-6.2
		-12	4.9	4.6
		13	16.2	-12.4
		-13	5.8	-7.0
		-14		1.8
		-15	9.5	-9.2
4	3	0	10.1	-11.0
		1		-.0
		-1	20.7	-20.0
		2		1.0
		-2	15.8	18.6
		3	28.2	28.2
		-3	31.5	-31.2
		4	7.9	7.4
		-4		-5.2
		5	5.3	-5.6
		-5	9.1	11.0
		6		-.4
		-6		-5.0
		7	25.7	-27.4
		-7	17.6	17.8
		8	9.5	-11.0
		-8		-.2
		9	19.7	-21.0
		-9	17.7	19.6
		10	11.0	12.2
		-10	6.6	8.4
		11	23.1	23.6
		-11		-3.2
		12		1.8
		-12		-3.0
		13	15.0	13.2
		-13	6.5	-6.4
		-14	3.1	3.4
4	4	0	13.8	-15.0
		1	7.3	-7.8
		-1	28.2	-26.8
		2		-4.4
		-2	13.8	15.0
		3	18.8	18.2
		-3	10.3	10.6
		4	6.2	-7.2
		-4	5.4	-5.6
		5	18.3	21.4
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		6	4.5	4.8
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		7		-1.6
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		-10	4.6	6.0
		11	1.8	-2.0
		-11	8.5	-9.4
		-12	3.1	-3.4
4	5	0		-2.0
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		-1		2.4
		2	5.9	6.2
		-2	4.6	-5.8
		3	11.8	-15.4
		-3		.4
		4	4.6	-5.6
		-4		-4.0
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		-5	4.5	3.6
		6	17.6	-16.4
		-6	14.6	-17.6
		7	11.5	9.8
		-7	7.1	7.4
		-8	12.9	-11.8
		-9	24.5	-23.0
		-10	8.5	8.4
5	0	0		5.0
		2	46.6	44.8
		-2		.2
		4	7.5	-6.8
		-4	16.4	-17.6
		6	20.0	-19.0
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		8		3.0
		-8	11.0	-12.2
		-10	28.3	31.8
		-12		5.8
		-14	11.7	-14.0
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5	1	0		-1.4
		1	46.3	-39.8
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		2	39.7	36.6
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		4		5.8
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		7	6.1	6.4
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		-12	22.2	-25.6
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5	2	0		-1.0
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		2	19.7	-20.0
		-2		-.2
		3	12.2	-11.4
		-3	20.2	18.8
		4		3.6
		-4	11.0	9.8
		5	6.6	-7.4
		-5		1.0
		6	6.0	7.2
		-6		-.8
		7	9.5	9.2
		-7	11.1	-9.4
		8	4.3	4.2
		-8	6.8	9.6
		9	26.3	20.8
		-9	17.7	-19.8
		10	22.9	-18.8
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		11		-9.4
		-11	12.4	12.6
		12		-7.4
		-12		-6.4
		-13	9.3	12.2
		-14	4.5	7.4
5	3	0		.4
		1	34.2	33.0
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		2	10.5	-11.0
		-2	15.4	15.8
		3	26.9	-26.6
		-3		1.0
		4		2.0
		-4	8.8	-9.0
		5		-.4
		-5	30.8	-31.6
		6	5.5	6.4
		-6		-6.6
		7		2.0
		-7	20.0	24.0
		8	4.8	-5.0
		-8	5.1	5.6
		9		1.8
		-9	25.1	25.4
		-10		1.2
		-11	13.9	14.6
		-12		-4.8
		-13	10.8	-13.0
5	4	0	4.8	-6.0
		1	25.1	-21.4
		-1		-7.6
		2	8.3	-8.4
		-2		3.6
		3	20.7	18.0
		-3		-5.2
		4		-.6
		-4		.4
		5	15.6	15.0
		-5		-.4
		6	3.0	3.6
		-6		-.2
		7	16.1	-15.8
		-7		3.2

Ca^{2+}, Na^{+}, Al^{3+}, F^{-} and O, used in the calculations of structure factors, were taken from a paper by Hanson, Herman, Lea & Skillman (1964).

The final reliability index for all the truly observed reflexions is $R = 9{\cdot}0\%$.

Discussion

Distances and bond angles with their standard deviations are given in Tables 3 and 4. The projection along the y axis, of half the unit cell of thomsenolite, is shown in Fig. 1

Ca is bonded to six F and two O atoms, forming an almost equilateral distorted square antiprism. The distances Ca–F range from 2·288 to 2·463 Å, and Ca–O distances are 2·488 and 2·508 Å respectively. Of course the angular values of the Ca coordination cover a wide range.

Al shows the known regular octahedral coordination with F. Distances and bond angles fall within the limits

Table 3. *Interatomic distances and their standard deviations*

$'\ x, y, z$
$''\ \bar{x}, \bar{y}, \bar{z}$
$'''\ \bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$
$^{\mathrm{iv}}\ x, \frac{1}{2}-y, \frac{1}{2}+z$

Ca–F(1′)	2·330 ±	0·007 Å	Na–F(1‴)	2·389 ±	0·007 Å
F(2′)	2·288	0·007	F(2′)	2·321	0·008
F(3′)	2·347	0·007	F(2‴)	2·654	0·008
F(4′)	2·355	0·006	F(3′)	2·419	0·007
F(5′)	2·463	0·005	F(4′)	2·631	0·008
F(6″)	2·340	0·006	F(4‴)	2·367	0·008
O′	2·488	0·007	F(5′)	2·484	0·008
O″	2·508	0·008	F(5‴)	2·433	0·008
Al–F(1′)	1·817	0·007	Al –F(4′)	1·785	0·007
F(2′)	1·822	0·007	F(5‴)	1·811	0·006
F(3′)	1·798	0·007	F(6′)	1·772	0·006

Table 4. *Bond angles and their standard deviations*

F(1′)-Ca-	F(2′)	90·2 ±	0·2°	F(1‴)-Na-	F(2′)	162·7 ±	0·3°
	F(3′)	82·6	0·2		F(2‴)	59·0	0·2
	F(4′)	144·8	0·2		F(3′)	110·5	0·3
	F(5′)	72·2	0·2		F(4′)	120·5	0·3
	F(6″)	96·9	0·2		F(4‴)	84·1	0·3
	O″	71·6	0·2		F(5′)	61·8	0·2
	O′	140·7	0·3		F(5‴)	71·8	0·2
F(2′)	F(3′)	145·1	0·2	F(2′)	F(2‴)	110·1	0·3
	F(4′)	83·1	0·2		F(3′)	86·7	0·3
	F(5′)	74·8	0·2		F(4′)	60·5	0·3
	F(6″)	141·2	0·2		F(4‴)	79·9	0·3
	O″	77·1	0·2		F(5′)	126·7	0·3
	O′	77·5	0·3		F(5‴)	120·3	0·3
F(3′)	F(4′)	83·5	0·2	F(2‴)	F(3′)	125·6	0·3
	F(5′)	70·5	0·2		F(4′)	69·4	0·2
	F(6″)	73·7	0·2		F(4‴)	75·4	0·3
	O″	131·2	0·3		F(5′)	59·4	0·2
	O′	127·4	0·3		F(5‴)	129·6	0·3
F(4′)	F(5′)	72·6	0·2	F(3′)	F(4′)	76·5	0·2
	F(6″)	109·9	0·3		F(4‴)	158·3	0·3
	O″	138·8	0·3		F(5′)	69·0	0·3
	O′	71·3	0·2		F(5‴)	61·6	0·2
F(5′)	F(6″)	143·6	0·2	F(4′)	F(4‴)	110·6	0·3
	O″	133·4	0·3		F(5′)	67·8	0·2
	O′	136·5	0·2		F(5‴)	137·4	0·3
F(6″)	O″	69·4	0·3	F(4‴)	F(5′)	132·6	0·3
	O′	73·0	0·2		F(5‴)	111·2	0·3
O″	O′	69·4	0·3	F(5′)	F(5‴)	89·4	0·3
F(1′)-Al-	F(2′)	86·6 ±	0·3°	F(2′)—Al -	F(6′)	91·8 ±	0·3°
	F(3′)	90·4	0·3				
	F(4′)	174·1	0·4	F(3′)	F(4′)	94·7	0·4
	F(5‴)	87·2	0·3		F(5‴)	87·2	0·3
	F(6′)	90·8	0·3		F(6′)	91·7	0·3
F(2′)	F(3′)	175·4	0·3	F(4′)	F(5‴)	89·9	0·3
	F(4′)	88·2	0·3		F(6′)	92·1	0·3
	F(5‴)	89·2	0·3	F(5‴)	F(6′)	177·8	0·4

quoted in the literature. The average value for the Al–F distances is 1·80 Å, with 1·772 as minimum and 1·822 Å as maximum. The angular values F–Al–F are not far from 90° and 180°.

The coordination around the Na may be referred to a distorted triangular prism having six F lying at the corners, and there are two more F atoms beyond two of the prism faces. The distances Na–F range from 2·321 to 2·654 Å with an average of 2·46 Å.

The unusual number (eight) of F atoms neighbouring Na, which is usually 6 or 7, together with some unusually high Na–F distances, implies that Na is contained in the coordination polyhedron by electrostatic forces which are weaker than usual. This assumption may be confirmed by the Na thermal parameter (2·8 Å^2), which is the highest of the whole structure.

The structure on the whole may be described thus: Ca polyhedra are linked by F [F(1), F(2), F(3), F(4)] to four Al octahedra forming undulating sheets at $\frac{1}{8}$, $\frac{3}{8}$, $\frac{5}{8}$ and $\frac{7}{8}$ *c* nearly parallel to (001) (Fig. 2). Within these sheets lie the strong Ca–F bonds, so determining the perfect cleavage of the mineral and its somewhat pearly luster on {001}.

Ca polyhedra also form chains with the F(5) and F(6) of the same Al octahedra which develop nearly parallel to the *c* axis at about $\frac{3}{4}$ and $\frac{1}{4}$ *b*, close to $\frac{1}{4}$ and $\frac{3}{4}$ *a* respectively. The chains in two adjoining cells are connected by a Ca–F bond for each Ca and by pairs of oxygen atoms around the center at $0,\frac{1}{2},0$. Such chains yield the distinct cleavage {110}.

On the whole the thomsenolite structure is not very compact and the distribution of its atoms in the cell is rather homogeneous, so giving a clear explanation of its low hardness ($H=2$) and low birefringence.

References

ALBANO, V., BELLON, P. L., POMPA, F. & SCATTURIN, V. (1963). *Ric. Sci.* 3A, 1067.

FERGUSON, R. B. (1946). *Trans. Roy. Soc. Canada*, **40**, 11.

GERHARD, F. B., JR. (1966). *Acta Cryst.* **21**, A52.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.

NÁRAY-SZABÓ, S. V. & SASVÁRI, K. (1938). *Z. Kristallogr.* **99**, 27.

Acta Cryst. (1967). **23**, 166

The Crystal Structures of the Spodiosite Analogs, Ca_2CrO_4Cl and Ca_2PO_4Cl*†

BY MARTHA GREENBLATT, E. BANKS AND B. POST

Departments of Chemistry and Physics, Polytechnic Institute of Brooklyn, Brooklyn, New York, U.S.A. and Brookhaven National Laboratories, Upton, New York, U.S.A.

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Both calcium chromate(V) chloride (Ca_2CrO_4Cl) and calcium phosphate chloride (Ca_2PO_4Cl) crystallize in the orthorhombic system, space group *Pbcm*, with four molecules per unit cell. The dimensions of the unit cell are: $a=6·259\pm0·005$, $b=7·124\pm0·005$, $c=10·990\pm0·005$ Å for $CaCrO_4Cl$, and $a=6·185\pm0·002$, $b=6·983\pm0·002$, $c=10·816\pm0·004$ Å for $CaPO_4Cl$. The crystal structures of both compounds have been determined from full data in three dimensions. X-ray reflection intensities were measured with scintillation counters. Refinement of the atomic coordinates was carried out by full-matrix least-squares procedures. The structures are made up of discrete CrO_4^{3-} and PO_4^{3-} tetrahedra which appear to be held together primarily by calcium ions. The indicated distortion of the CrO_4^{3-} tetrahedra is considerably greater than that of the PO_4^{3-} tetrahedra. This is in agreement with measurements of infrared absorption which show substantially more splitting of vibrational bands of the chromate compound than of the phosphate.

Introduction

Recently the syntheses of compounds of composition Ca_2CrO_4Cl and Ca_2PO_4Cl, as well as their strontium analogs, have been reported (Banks & Jaunarajs, 1965). X-ray diffractometric studies indicated that the dimensions of the unit cells of these phases were close to those of chlorospodiosite (ideally Ca_2PO_4Cl) (Palache, Berman & Frondel, 1951). The Ca_2CrO_4Cl compound is of particular interest, since in it the chromium appears to be in the 5+ state.

The analysis of the crystal structures of Ca_2CrO_4Cl and Ca_2PO_4Cl was undertaken to make possible detailed comparisons of the atomic parameters in the two

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