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The Crystal Structure of Pirssonite, $CaNa_2(CO_3)_2.2H_2O$*

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The crystal structure of pirssonite, $CaNa_2(CO_3)_2.2H_2O$, has been determined from three-dimensional X-ray diffraction data. The crystals are orthorhombic, space group *Fdd*2, with eight molecules in the unit cell with dimensions $a=11{\cdot}32$, $b=20{\cdot}06$, $c=6{\cdot}00$ Å. The calcium atom occupies a square antiprism site, on the twofold axis, and the sodium atom has a distorted octahedral coordination. The CO_3 group is nearly regular. The Na polyhedra are connected by edges to form two cross-diagonal series of chains, which are connected three-dimensionally by common corners and by the Ca and C coordination polyhedra.

Introduction

In 1948 Evans examined pirssonite by X-ray methods and determined the lattice constants and the space group, in order to include these data in *Dana's System of Mineralogy*. In a paper on the saline minerals of the Green River formation, Mrose (1962) gave an accurate determination of the *d* spacings of the mineral and the corresponding indices. Infrared studies on pirssonite among several carbonate minerals were carried out by Huang & Kerr (1960) and later by Adler & Kerr (1963).

Experimental

Like the ones studied by Evans, the crystals used for the present structure determination come from Searles Lake, San Bernardino, California. Well formed and transparent crystals, suitable for X-ray examination, with size up to some millimeters, were ground to a spherical shape. The nearly perfect sphere chosen for the X-ray investigation was 0·616 mm in diameter. The unit-cell dimensions and measured density are those reported by Evans (1948).

Crystal data

($\lambda(\text{Mo } K\alpha)=0{\cdot}7107$ Å)

Chemical formula: $CaNa_2(CO_3)_2.2H_2O$,

Orthorhombic, $a=11{\cdot}32\pm0{\cdot}02$, $b=20{\cdot}06\pm0{\cdot}02$, $c=6{\cdot}00\pm0{\cdot}02$ Å.

$V=1363$ Å^3.

$D_m=2{\cdot}352$ g.cm^{-3}, $Z=8$, $D_x=2{\cdot}367$ g.cm^{-3}

$F(000)=976$.

Space group: *Fdd*2.

Absorption coefficient for X-rays: $\mu=10{\cdot}4$ cm^{-1}, $\mu R=0{\cdot}32$.

The density of 2·352 g.cm^{-3}, given by Evans, was measured by Pratt (1896).

Intensity data were collected at room temperature on an integrating precession camera, around the *b* axis; layer-lines from 0*kl* to 6*kl* and from *hk*0 to *hk*3 were recorded, and converted to a common relative scale by means of the exposure times and of the common reflexions. Of the total of 620 independent reflexions within the range recorded, 139 were below the observational limit. Intensities obtained from the optical densities were measured by the aid of a microdensitometer for the eleven levels, each recorded by a series of five differently exposed films. The corrections for Lorentz-polarization and absorption factors were made by a program written by Catani & Zanazzi (1965) for the IBM 1620 computer.

Determination of the structure

The general position in *Fdd*2 being 16-fold, the Ca atom must lie in a special position, namely on the two-

Table 1. *Final atomic parameters with their standard deviations*

	x/a	$\sigma(x)$	y/b	$\sigma(y)$	z/c	$\sigma(z)$	B	$\sigma(B)$
Ca	0·0000		0·0000		0·0000	0·0004	0·52 Å^2	0·02 Å^2
Na	0·4347	0·0003	0·1124	0·0001	0·0073	0·0007	1·51	0·04
O(1)	0·5052	0·0004	0·3839	0·0002	0·8706	0·0010	0·94	0·06
O(2)	0·6291	0·0004	0·4062	0·0002	0·1419	0·0009	1·05	0·07
O(3)	0·6171	0·0004	0·3018	0·0002	0·0119	0·0010	0·98	0·06
O(4)	0·3580	0·0005	0·4937	0·0002	0·6875	0·0010	1·39	0·07
C	0·5834	0·0005	0·3638	0·0002	0·0090	0·0013	0·63	0·07
H(1)	0·611		0·273		0·280		5·00	
H(2)	0·527		0·235		0·464		5·00	

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Table 2. *Observed and calculated structure factors*

H	K	L	FO	FC	AC	BC
0	0	4	159.3	159.3	157.0	-27.1
		8	126.0	119.4	113.8	36.2
0	2	2	97.7	88.0	-16.2	86.5
		6	74.5	68.1	68.0	4.4
0	4	0	122.5	113.1	-113.1	
		4	85.5	87.8	67.4	-56.2
		8	44.8	34.5	-29.4	-18.1
0	6	2	72.6	66.9	65.6	13.0
		6	62.8	62.7	55.2	29.7
0	8	0	313.7	356.7	356.7	
		4	89.0	88.4	83.5	-29.0
		8	64.7	62.1	62.1	.9
0	10	2	164.2	160.7	143.0	73.3
		6	125.2	120.8	118.6	23.0
0	12	0		11.8	11.8	
		4	61.1	59.0	-3.8	-58.9
0	14	2	49.5	40.7	18.3	36.4
		6	45.3	43.3	43.3	1.5
0	16	0	136.1	141.7	141.7	
		4	93.9	99.7	99.7	1.7
0	18	2	46.7	53.9	47.8	-24.8
		6	49.6	49.4	43.7	23.0
0	20	0	109.6	110.4	110.4	
		4	65.5	64.6	62.9	-14.9
0	22	2	53.2	49.9	8.3	49.2
0	24	0	54.2	53.1	53.1	
		4	32.5	32.0	30.5	-9.7
0	26	2	62.9	63.2	57.0	-27.4
1	1	1	97.2	90.7	71.5	-55.8
		3	35.3	34.5	27.8	20.4
		5		15.7	15.0	4.6
		7	56.4	60.1	52.4	29.4
1	3	1	46.2	43.7	40.0	17.7
		3	112.5	111.5	35.8	-105.6
		5	24.0	19.9	-.9	19.9
		7	31.9	30.6	6.1	-30.0
1	5	1	100.6	101.7	53.4	-86.5
		3	226.5	239.0	130.2	200.4
		5	105.0	106.6	86.7	-62.1
		7	43.4	41.0	31.0	26.8
1	7	1	112.1	114.8	100.4	-55.7
		3	91.2	88.4	85.6	-22.2
		5	48.2	43.0	38.2	19.7
		7	27.7	27.5	17.0	-21.6
1	9	1	108.7	105.0	-15.4	-103.9
		3	33.2	28.1	-8.6	-26.8
		5	24.7	21.3	-7.0	20.1
		7	37.7	40.8	21.8	34.5
1	11	1	71.4	70.4	52.8	46.6
		3	44.9	43.1	32.3	-28.6
		5	25.2	24.3	24.3	.3
		7	28.9	30.0	13.4	-26.8
1	13	1	28.4	34.3	28.3	-19.3
		3	123.1	133.3	24.2	131.1
		5	79.6	83.1	38.4	-73.7
		7	33.4	32.7	28.2	16.6
1	15	1	122.5	127.4	119.6	43.9
		3	112.0	113.4	84.4	-75.7
		5	61.7	59.4	36.5	46.9
		7	44.9	43.9	39.2	-19.8
1	17	1		16.2	-15.1	-6.0
		3	49.0	46.7	32.8	-33.2
		5	46.3	44.4	16.9	41.1
		7	25.7	27.4	25.8	9.2
1	19	1	24.6	24.4	-10.7	21.9
		3	37.7	36.0	.6	-36.0
		5		10.4	-1.3	10.3
		7	34.4	34.6	-5.6	-34.1
1	21	1	58.2	61.4	52.8	-31.3
		3	67.8	75.1	25.9	70.5
		5	52.0	54.2	33.2	-42.9
1	23	1	59.4	66.2	53.1	39.6
		3	48.1	51.1	37.3	-34.9
		5	32.1	33.6	31.5	11.7
1	25	1	25.0	16.0	11.3	-11.3
		3	28.2	26.8	20.6	17.2
		5	33.7	31.0	31.0	-1.3
1	27	1	24.4	21.2	20.3	-6.0
		3	23.2	20.7	-1.7	-20.6
2	0	2	263.8	275.5	257.3	-98.4
		6	109.2	110.4	103.1	39.4
2	2	0	119.0	112.7	112.7	
		2	201.9	200.3	178.8	90.2
		4	78.6	79.8	78.9	11.9
		6	83.8	81.0	80.9	2.9
		8	49.1	48.8	48.8	-1.0
2	4	0	34.0	30.3	-30.3	
		2	74.0	65.4	28.0	59.1
		4	69.1	67.5	-64.6	-19.5
		6	46.0	44.7	11.3	-43.2
		8		2.4	-2.3	-.5
2	6	0	42.0	41.0	41.0	
		2	45.0	47.3	-29.4	-37.0
		4	71.4	72.8	72.7	4.4
		6	36.4	32.0	-32.0	-.4
		8	31.9	37.4	37.4	1.1
2	8	0	169.1	180.8	-180.8	
		2	181.3	185.5	174.4	-63.3
		4	18.2	18.7	-.2	18.7
		6	85.3	87.9	83.4	27.7
		8	25.8	23.5	-16.1	-17.1
2	10	0	163.2	162.4	162.4	
		2	86.1	89.0	82.5	-33.4
		4	78.9	78.2	76.7	15.1
		6	25.4	21.9	18.6	11.5
		8	57.0	57.5	57.5	-.2
2	12	0	85.8	88.1	88.1	
		2	55.5	49.4	42.4	25.4
		4	18.7	22.0	17.4	13.4
		6	35.7	35.1	23.4	-26.1
		8	30.1	27.0	23.4	13.4
2	14	0		1.4	1.4	
		2	74.5	73.9	-72.4	15.0
		4	63.5	60.2	60.2	-1.0
		6	47.4	49.3	-32.3	-37.3
		8	23.7	26.3	26.3	1.6
2	16	0		16.0	-16.0	
		2	90.0	91.4	88.6	-22.5
		4	21.1	21.5	10.4	18.8
		6	55.9	57.7	56.3	12.6
		8		17.6	15.6	8.1
2	18	0	105.6	112.6	112.6	
		2	43.0	44.6	17.0	-41.2
		4	42.9	45.8	45.2	7.3
		6		17.1	-16.1	5.9
		8	46.6	50.3	50.2	-2.5
2	20	0	31.4	26.8	-26.8	
		2	63.3	60.5	59.9	8.3
		4		23.5	14.8	18.3
		6	40.8	39.8	39.0	-7.8
2	22	0		8.2	8.2	
		2	29.1	30.3	30.3	1.5
		4	59.5	54.5	54.5	-1.2
		6		10.8	9.2	-5.7
2	24	0		22.2	-22.2	
		2	46.0	41.8	41.2	-6.9
		4	31.3	32.1	-32.1	-.4
		6	32.2	32.4	32.4	1.0
2	26	0	66.5	72.5	72.5	
		2		10.1	10.0	-1.6
		4	27.2	28.6	28.4	3.5
		6		7.1	-.9	-7.0
2	28	0	31.5	28.3	-28.3	
		2	53.0	51.4	51.4	.7
		4		11.5	1.4	11.4
3	1	1	126.4	125.2	120.7	33.2
		3	68.6	60.7	-46.3	-39.2
		5	42.2	44.6	17.6	41.0
		7	29.6	31.4	30.5	7.6
3	3	1	121.5	121.1	112.4	-45.2
		3	137.3	128.3	-16.6	127.2
		5	127.1	128.0	43.0	-120.6
		7	33.4	34.5	8.9	33.3
3	5	1	152.6	159.6	-15.6	158.8
		3	34.5	31.3	29.6	-10.1
3	5	5	80.8	78.5	76.9	15.6
		7	31.2	31.2	19.8	-24.1
3	7	1	179.8	192.5	191.9	-15.2
		3	107.8	99.2	82.9	-54.4
		5	57.0	58.1	58.1	2.0
		7	48.3	54.1	36.0	40.4
3	9	1	61.1	58.8	33.9	48.0
		3	40.0	39.5	-20.4	-33.8
		5	44.0	43.1	21.0	37.6
		7		26.6	23.2	-13.1
3	11	1	37.4	33.7	12.1	-31.4
		3	48.1	46.1	15.0	43.6
		5	58.3	58.7	32.6	-48.8
		7		19.1	2.5	18.9
3	13	1	119.7	124.1	13.9	123.3
		3	97.1	94.3	27.3	-90.3
		5	63.3	61.3	31.2	52.8
		7		33.3	18.4	-27.7
3	15	1	92.4	92.4	86.8	31.6
		3	30.1	31.5	31.0	-5.8
		5	41.9	42.4	35.6	-23.0
		7	33.6	37.6	34.2	15.6
3	17	1	88.7	87.4	83.0	27.4
		3	30.8	32.9	22.8	23.7
		5	54.7	56.9	56.6	5.6
		7	37.6	42.2	42.2	-1.0
3	19	1	69.3	69.8	-1.5	-69.8
		3	30.3	28.4	-16.5	23.1
		5	39.0	41.8	6.5	-41.3
		7	30.4	36.3	-10.8	34.7
3	21	1	33.2	38.9	-3.5	38.7
		3	57.1	57.7	24.7	-52.1
		5	43.3	44.4	26.8	35.4
		7		14.9	-2.3	-14.7
3	23	1	46.2	45.1	45.1	.1
		3	54.7	55.2	41.5	36.4
		5	53.5	55.0	48.0	-26.8
		7		27.6	23.9	13.9
3	25	1	55.6	54.3	52.2	14.9
		3		1.4	.8	1.1
		5		22.2	22.1	-2.2
		7	24.0	26.5	26.3	-3.2
3	27	1	44.0	40.4	28.7	-28.5
		3		10.2	1.9	10.0
		5		23.3	13.0	-19.3
4	0	0	105.7	99.2	-99.2	
		4	48.3	43.6	10.0	42.4
		8	49.3	49.1	38.6	-30.4
4	2	0	189.5	198.3	198.3	
		4	109.7	104.3	101.9	22.1
		6	50.6	54.7	54.5	4.7
		8	42.3	39.0	36.4	13.9
4	4	0	22.0	27.6	27.6	
		2	11.7	10.5	9.7	-3.9
		4	101.0	97.5	95.7	18.7
		6		4.6	3.4	3.1
		8	48.7	53.1	51.3	13.9
4	6	0	121.9	129.1	-129.1	
		2	97.0	97.0	90.7	34.5
		4	75.6	74.1	-71.7	-18.6
		6	60.0	60.7	40.6	-45.1
		8	35.0	31.5	-29.9	-10.0
4	8	0	129.0	135.3	135.3	
		2	55.0	49.6	-48.7	9.4
		4	67.0	64.6	51.0	39.7
		6		12.9	-11.8	-5.2
		8	66.0	70.8	70.8	1.0
4	10	0	109.0	108.5	108.5	
		2	131.0	129.3	75.1	-105.3
		4	52.5	51.6	51.2	6.3
		6		15.9	13.3	8.8
		8		23.6	21.7	9.2
4	12	0	20.9	20.0	20.0	
		2	43.4	43.9	43.8	3.3
		4	138.6	141.2	136.0	37.8
		6		20.2	17.8	9.6
		8	40.6	44.5	44.4	3.5
4	14	0	52.3	54.1	-54.1	
		2	74.2	76.9	74.3	19.8
		4	29.9	33.5	-31.2	-12.3
		6	41.5	45.1	31.2	-32.6
		8		21.5	-20.0	-8.0
4	16	0	71.8	77.4	77.4	
		2	27.1	33.7	-33.0	6.6
		4		3.6	-.7	3.5
		6		5.3	-5.3	.2
		8	51.0	52.3	52.2	2.8
4	18	0	20.8	23.7	23.7	
		2	101.4	101.7	99.4	-21.4
		4		6.4	4.7	-4.4
		6	59.2	62.8	61.7	11.7
		8		4.0	3.3	2.3
4	20	0		13.2	-13.2	
		2		16.4	15.7	4.6
		4	55.2	53.3	52.2	10.7
		6		10.0	9.1	4.1
		8	25.0	22.2	19.4	-10.7
4	22	0		13.8	13.8	
		2	68.8	68.9	68.7	-5.0
		4		8.7	8.1	-3.1
		6		26.7	25.9	-6.4
		8		1.3	-.5	1.2
4	24	0	44.4	44.4	44.4	
		2		17.9	-17.6	3.3
		4	42.5	39.3	38.5	7.7
		6		3.0	-2.8	1.1
		8	29.6	36.4	36.4	-.2
4	26	0		7.5	-7.5	
		2	41.1	40.8	40.1	-7.6
		4		10.7	-9.1	-5.7
		6	36.9	38.3	38.3	-.6
4	28	0	61.8	57.6	57.6	
		2		2.8	-1.9	2.1
		4	41.4	36.9	36.7	3.6
5	1	1	158.7	160.6	-.5	-160.6
		3	32.9	29.3	19.6	21.8
		5	37.9	35.2	21.2	-28.1
		7	36.0	35.8	1.3	35.8
5	3	1	114.8	116.5	-29.5	112.7
		3	126.4	109.1	86.9	-65.9
		5	89.0	90.1	56.1	70.5
		7	41.1	43.2	20.9	-37.8
5	5	1	63.4	59.8	50.3	32.4
		3		12.3	11.5	4.5
		5	43.3	42.2	-6.5	-41.7
		7		16.9	16.8	1.7
5	7	1	124.5	126.9	114.1	55.6
		3	33.4	29.9	29.7	3.0
		5	32.5	35.2	32.8	12.7
		7	48.9	48.9	47.3	-12.4
5	9	1	92.1	92.7	71.8	-58.7
		3	80.9	72.2	69.0	21.4
		5	57.6	54.1	51.9	-15.2
		7	42.8	44.2	37.5	23.4
5	11	1	67.3	72.0	-27.8	-66.4
		3	99.6	90.4	21.2	-87.9
		5	70.4	71.0	3.3	70.9
		7	38.0	40.2	16.2	-36.8
5	13	1	64.4	59.7	35.0	-48.4
		3	49.5	53.0	37.7	37.2
		5	34.0	42.7	9.1	-41.7
		7		15.7	1.0	15.7
5	15	1		13.4	6.2	-11.9
		3	52.0	50.4	24.7	43.9
		5	39.0	41.5	40.2	-10.5
		7		14.4	10.6	-9.8
5	17	1	97.6	102.7	83.0	-60.4
		3	54.2	54.5	50.2	21.3
		5	51.6	48.0	41.1	-24.7
		7	43.3	50.7	35.6	36.1
5	19	1	61.6	60.8	37.9	47.5
		3	44.9	46.7	16.8	-43.6
		5	40.7	46.1	8.8	45.3
		7	36.5	42.8	37.4	-20.8
5	21	1	32.7	28.7	-14.0	-25.1
5	21	3	33.1	36.0	6.1	35.5
		5	42.2	44.0	-4.5	-43.8
		7		9.2	-7.1	-5.8
5	23	1		8.9	8.1	3.6
		3	47.7	46.1	46.1	1.4
		5	38.7	41.9	35.5	22.3
		7		16.5	13.4	-9.6
5	25	1	59.3	56.2	44.7	-34.1
		3	39.7	43.1	41.6	-11.1
		5		16.8	16.8	.2
		7		30.0	22.3	20.1
5	27	1	53.5	50.9	23.6	45.1
		3		31.0	16.6	-26.2
		5		36.4	8.6	35.4
		7	35.4	44.3	33.8	-28.7
6	0	2	80.3	73.4	-62.8	-37.9
		6		17.2	12.9	11.4
6	2	0	155.5	156.2	156.2	
		2	72.2	66.3	33.6	-57.1
		4	70.0	68.6	66.0	-18.6
		6		23.2	-.8	23.2
		8	30.2	38.4	38.3	2.5
6	4	0	50.2	47.6	47.6	
		2	175.6	181.6	164.6	76.6
		4	71.6	67.8	65.3	18.2
		6	95.6	97.9	97.9	1.2
		8		7.9	7.8	1.4
6	6	0	110.1	108.1	108.1	
		2	103.1	103.8	-101.0	23.9
		4	96.0	89.0	87.4	-16.8
		6	37.6	37.4	-30.0	-22.3
		8		25.7	25.6	-1.8
6	8	0	54.2	55.5	55.5	
		2	35.6	29.4	-4.7	-29.0
		4	41.7	36.3	-30.6	-19.6
		6	32.5	34.8	29.6	18.3
		8		13.9	5.1	12.9
6	10	0	90.7	96.3	96.3	
		2	33.5	31.6	24.0	20.6
		4	25.1	27.0	19.1	-19.1
		6		24.8	24.0	6.1
		8	31.8	37.4	37.4	-1.7
6	12	0		1.7	1.7	
		2	121.3	120.1	108.9	50.7
		4	22.3	19.8	19.7	-2.1
		6	77.9	78.7	78.7	-1.4
		8		13.0	-8.6	-9.8
6	14	0	77.6	76.3	76.3	
		2		16.9	12.4	-11.5
		4	86.0	82.6	81.8	-11.6
		6		21.3	3.3	21.0
		8		19.4	19.4	-.4
6	16	0	51.9	49.0	-49.0	
		2	37.7	29.7	25.0	-16.1
		4	42.0	41.0	-36.0	-19.6
		6	39.0	35.9	33.6	12.7
		8		24.2	-22.7	-8.5
6	18	0	78.4	82.8	82.8	
		2	31.8	29.8	.4	29.8
		4	29.6	31.6	31.3	-4.3
		6		21.1	21.0	-1.6
		8	40.8	44.0	44.0	1.0
6	20	0	63.7	62.2	62.2	
		2	49.4	44.6	41.1	17.3
		4		10.9	5.2	-9.6
		6	40.5	40.5	40.1	-5.4
		8		14.0	10.6	9.1
6	22	0	46.5	48.3	48.3	
		2		17.2	-17.2	-.5
		4	47.8	60.7	60.2	-7.9
		6		7.1	-5.9	4.0
		8		16.6	16.5	1.9
6	24	0		9.1	-9.1	
		2	48.7	47.7	47.7	.4
		4		19.4	19.4	.0
		6	42.1	42.6	42.1	6.5
		8		9.6	-9.2	-2.9
6	26	0	61.6	59.1	59.1	
		2		23.8	-23.7	-2.1
		4	29.3	25.8	25.8	-.5
		6		10.2	-9.7	3.0
6	28	0	32.4	35.6	35.6	
		2	34.6	26.6	26.6	.0
		4		8.0	.0	-8.0
		6	31.2	25.3	25.3	.8
7	1	1	103.0	106.9	54.8	91.8
		3	82.3	90.7	41.9	-80.4
7	3	1	42.3	39.1	-9.6	-37.9
		3	57.6	61.3	38.2	47.9
7	5	1	54.9	50.7	14.4	-48.6
		3	83.7	88.3	80.8	-35.5
7	7	1	48.9	47.3	-25.6	-39.8
		3	69.2	65.6	45.6	47.2
7	9	1	134.8	142.8	132.9	52.2
		3	74.7	69.4	51.7	-46.3
7	11	1	90.0	90.8	37.6	-82.6
		3	82.9	76.9	6.5	76.6
7	13	1	32.4	35.1	-18.8	-29.6
		3	52.0	47.6	47.2	5.8
7	15	1	26.8	25.3	-9.9	-23.3
		3	55.5	51.3	46.7	21.3
7	17	1	68.5	71.2	63.3	32.5
		3	78.9	69.8	28.0	-63.9
7	19	1	58.5	61.6	51.2	-34.2
		3	70.5	65.9	44.4	48.7
7	21	1	28.0	22.0	-6.2	21.1
		3	35.8	25.9	20.0	-16.4
7	23	1		4.4	1.0	-4.3
		3		11.3	10.5	4.3
7	25	1	49.8	48.9	43.1	23.1
		3	55.6	47.9	37.5	-29.8
7	27	1	42.9	43.8	16.9	-40.4
		3	48.3	41.8	29.3	29.8
8	0	0	148.6	154.9	154.9	
8	2	0	33.5	32.1	-32.1	
		2	30.8	26.9	12.3	23.9
8	4	0	137.2	133.5	133.5	
		2	24.2	20.7	20.5	2.6
8	6	0		5.5	-5.5	
		2	101.8	99.7	99.7	-.8
8	8	0	32.7	31.4	31.4	
		2		11.6	7.5	-8.8
8	10	0	31.9	27.5	-27.5	
		2	49.9	49.2	41.4	26.5
8	12	0	92.6	97.5	97.5	
		2		10.1	6.9	-7.4
8	14	0		14.3	14.3	
		2	85.3	87.4	84.7	21.7
8	16	0	55.4	52.5	52.5	
		2		12.9	-12.1	-4.5
8	18	0		13.7	-13.7	
		2		24.2	1.6	-24.1
8	20	0	79.0	82.5	82.5	
		2		23.5	20.1	-12.1
8	22	0		15.6	-15.6	
		2	53.5	55.3	41.8	36.2
8	24	0	59.5	60.6	60.6	
		2		1.1	.4	1.0
8	26	2	49.8	44.1	37.2	-23.7
8	28	2		18.6	16.3	-9.0
9	1	1	103.4	108.6	91.9	-57.9
		3	50.6	55.1	36.0	41.7
9	3	1	24.1	20.1	19.[illegible]	-3.3
		3	21.4	23.9	-3.2	-23.7
9	5	1	18.7	19.5	16.1	11.0
		3	52.0	58.8	39.2	43.8
9	7	1	41.8	40.3	16.6	36.7
		3	39.9	36.7	20.5	-30.4
9	9	1	113.3	117.6	55.2	-103.8
		3	40.1	37.8	19.4	[illegible]
9	11	1	67.5	69.6	61.5	12.5
		3	44.9	43.3	39.1	-18.6
9	13	1	58.5	57.0	7.6	56.5
		3		18.1	6.2	17.0
9	15	1	58.7	58.5	34.6	48.6
9	15	3	57.4	52.0	13.2	-50.3
9	17	1	57.0	58.3	11.4	-57.2
		3	29.2	25.1	16.0	19.4
9	19	1	45.4	47.7	39.3	27.1
		3	54.6	46.9	38.5	-26.7
9	21	1	39.7	42.9	40.5	14.0
		3	33.4	27.7	21.6	17.4
9	23	1	26.4	25.7	4.7	25.3
		3		24.3	-9.7	-22.3
9	25	1	39.7	36.1	13.2	-33.6
		3	49.6	38.4	10.9	36.8
9	27	1	41.3	42.6	41.8	8.1
		3	30.6	28.4	20.3	-19.9
10	0	2	85.7	93.9	75.8	-55.5
10	2	0		17.4	17.4	
		2	59.9	54.9	-53.5	12.4
10	4	0		14.8	-14.8	
		2	97.0	101.2	99.5	18.7
10	6	0	63.4	60.5	60.5	
		2	80.4	83.4	83.2	5.3
10	8	0	33.7	37.0	-37.0	
		2	60.9	63.3	47.7	-41.6
10	10	0	31.8	32.4	32.4	
		2	45.4	44.2	-37.3	-23.8
10	12	0	23.5	19.0	19.0	
		2	59.1	64.9	64.9	1.5
10	14	0	57.2	53.4	53.4	
		2		20.5	2.1	20.4
10	16	0		17.3	17.3	
		2	60.6	60.6	58.5	-15.7
10	18	0	26.7	19.7	19.7	
		2		26.1	-7.7	-24.9
10	20	0	19.0	21.4	-21.4	
		2	55.8	57.2	57.2	-.9
10	22	2		11.8	10.5	5.3
10	24	2	45.4	45.3	44.7	-7.1
10	26	2		20.5	20.2	3.3
10	28	2	24.6	28.5	28.5	-1.3
11	1	1	79.4	81.3	80.3	12.5
		3	26.9	33.2	26.0	-20.7
11	3	1	61.1	57.9	56.0	14.9
		3		20.1	13.5	14.9
11	5	1	58.7	57.9	-10.8	56.9
		3		8.1	8.1	-.5
11	7	1	78.4	78.4	49.0	-61.2
		3	25.2	29.7	21.9	20.0
11	9	1	53.6	51.2	18.1	47.9
		3	40.1	44.9	2.1	-44.9
11	11	1	52.4	51.2	47.5	19.2
		3	51.8	50.8	50.0	-8.8
11	13	1	32.1	33.4	14.8	29.9
		3	32.6	33.0	27.0	-18.9
11	15	1	51.7	47.3	27.2	-38.7
		3	29.9	31.1	3.3	30.9
11	17	1	47.7	48.9	21.7	43.8
		3		9.6	1.3	-9.5
11	19	1	41.9	37.5	29.0	-23.8
		3		17.1	17.1	-.8
11	21	1	25.1	26.2	26.2	-.2
		3	46.3	44.2	43.3	-9.1
11	23	1	32.3	28.6	12.0	-26.0
		3	44.3	39.2	18.2	34.7
11	25	1	35.0	32.1	8.3	31.0
		3		18.5	-11.1	-14.8
11	27	3		17.9	17.8	-2.2
12	0	0	61.1	57.8	57.8	
12	2	0	34.9	28.3	-28.3	
		2	64.8	74.8	73.6	-13.3
12	4	0		6.8	6.8	
		2	27.7	27.0	-25.8	-7.8
12	6	0	51.8	46.7	46.7	
		2	48.0	54.2	49.4	22.2
12	8	0	102.5	107.5	107.5	
		2		17.2	8.2	15.1
12	10	0		8.1	-8.1	
		2	49.4	46.9	30.7	-35.5
12	12	0		10.8	10.8	
		2	24.7	20.5	-20.0	-4.5
12	14	0		1.1	-1.1	
		2	54.9	57.5	54.8	17.5
12	16	0	68.3	71.1	71.1	
		2	28.6	28.9	24.9	14.6
12	18	2	42.5	43.2	42.2	-9.1
12	20	2		26.8	-26.7	1.7
12	22	2	54.8	60.2	60.2	2.1
12	24	2		6.9	1.3	6.8
12	26	2		15.9	15.3	-4.4
12	28	2		15.2	-15.1	1.7
13	1	1	36.9	38.2	22.5	-30.9
		3	26.8	36.7	36.7	1.6
13	3	1	29.7	28.3	27.9	5.0
		3	53.6	68.7	67.1	-14.8
13	5	1	29.8	25.7	7.6	-24.6
		3	34.1	38.4	13.5	36.0
13	7	1	66.1	68.0	37.6	56.6
		3	40.8	46.0	19.1	-41.8
13	9	1		20.0	12.2	-15.9
		3		27.6	25.5	10.5
13	11	1	29.1	24.8	16.4	-18.6
		3	30.4	28.9	26.7	-11.0
13	13	1	56.3	56.5	35.1	-44.3
		3	55.7	59.7	41.2	43.2
13	15	1	35.3	32.4	5.8	31.9
		3	29.4	30.8	26.1	-16.3
13	17	1	34.7	34.5	17.1	-30.0
		3		21.7	16.4	14.2
13	19	1	24.1	23.9	23.5	-4.5
		3		12.4	5.4	-11.2
13	21	1	27.7	25.7	20.0	-16.2
		3	43.0	41.9	28.1	31.1
13	23	1	36.6	32.8	16.5	28.4
		3	52.2	49.3	44.9	-20.3
13	25	3		12.8	10.6	-7.2
14	0	2	47.6	52.8	52.8	2.0
14	2	0	87.6	83.6	83.6	
		2		26.0	-4.7	-25.6
14	4	0		4.9	-4.9	
		2		20.6	2.3	20.5
14	6	0	40.4	38.6	38.6	
		2		20.5	-16.5	12.2
14	8	0	39.3	38.3	38.3	
		2	58.5	67.5	67.5	-.9
14	10	0	76.4	71.3	71.3	
		2		2.4	2.4	.2
14	12	0	42.1	35.9	-35.9	
		2	30.5	34.2	24.5	23.9
14	14	2		12.9	11.4	-6.1
14	16	2	31.5	36.2	35.6	-6.7
14	18	2		10.1	3.9	9.3
14	20	2		24.1	21.0	11.9
14	22	2		8.3	-7.7	-3.1
14	24	2	23.3	24.0	24.0	.6
15	1	1	22.7	22.9	19.9	11.3
		3		15.2	9.0	-12.2
15	3	1	39.3	39.1	35.5	-16.3
		3	38.7	47.2	38.1	27.9
15	5	1	36.4	33.0	18.7	27.2
		3	54.5	65.1	43.7	-48.2
15	7	1	33.3	31.7	-9.5	-30.2
		3	27.9	35.3	17.1	30.9
15	9	1	47.2	46.7	46.3	-5.8
		3		12.6	11.4	5.3
15	11	1	35.4	33.3	23.2	-23.9
		3	28.9	26.7	-1.5	26.7
15	13	1	36.4	34.2	14.8	30.8
		3	48.2	49.5	38.5	-31.1
15	15	1	25.2	22.3	7.1	-21.1
		3	38.7	42.0	33.7	25.1
15	17	1	34.1	29.0	29.0	1.4
		3		22.0	6.7	-21.0
15	19	1	15.5	18.1	16.8	[illegible]
		3		17.1	8.9	[illegible]
15	21	3	40.3	33.6	17.7	-28.6
15	23	3	32.6	29.5	23.8	17.4

fold axis. A three-dimensional Patterson synthesis was computed from the observed reflexions. Some vector peaks due to the contribution of Ca, Na and one O were recognized in this synthesis, these atoms accounting for about 50% of the electrons in the structure.

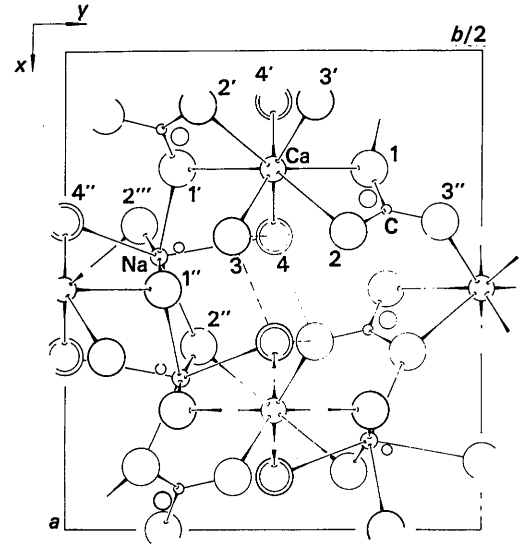

Fig. 1. Projection of the structure along the *c* axis. Large circles indicate oxygen atoms and double circles indicate water molecules. Dashed lines represent hydrogen bonds. For clarity some Na and C atoms close to the diamond glide planes at $\frac{1}{8}b$ and $\frac{3}{8}b$ are drawn without any bond.

The reliability index *R* was 0·33 at this stage. The four missing atoms (three oxygen atoms and the carbon atom) were found in two subsequent electron density syntheses, from which improved parameters were obtained for the remaining atoms. The contribution of all the non-hydrogen atoms decreased the *R* value to 0·14.

The atomic scattering factors used for the calculations of the structure factors are the ones given by Cromer & Waber (1965) for Ca, Na, O and C, and the ones reported in *International Tables for X-ray Crystallography* (1962) for H.

The refinement of the structure was carried out by the method of least squares with a program devised by Albano, Bellon, Pompa & Scatturin (1963). This program uses 3 × 3 blocks for the positional parameters and 1 × 1 blocks for the individual isotropic temperature factors. The quantity minimized is $\Sigma w(|F_o|-|F_c|)^2$. The weight of the reflexions was calculated from Cruickshank's formula. The individual thermal parameters were at first 0·5 Å^2 for Ca, 0·8 Å^2 for Na and C, and 1·0 Å^2 for oxygen. The refinement was ended after the completion of the eighth cycle, with a final *R* value of 0·057 for all the observed reflexions.

The two hydrogen atoms were placed at calculated positions, and their contribution was included in the last two cycles of refinement, with isotropic temperature factors of 5·0 Å^2. The coordinates of these atoms were not allowed to refine, but the bond lengths and the water angle are reasonable.

Table 3. *Interatomic distances with their standard deviations*

		σ			σ
Ca-O(1)	2·455 Å	0·004 Å	Na-O(1′)	2·295 Å	0·005 Å
O(2)	2·530	0·004	O(1″)	2·284	0·007
O(3)	2·410	0·005	O(2″)	2·386	0·005
O(4)	2·472	0·006	O(2‴)	2·338	0·006
			O(4)	2·710	0·004
C—O(1)	1·278	0·008	O(4″)	2·755	0·005
O(2)	1·275	0·007			
O(3″)	1·301	0·005			

Table 4. *Bond angles with their standard deviations*

		σ			σ
O(1)-Ca-O(1′)	143·1°	0·4°	O(1′)—Na-O(1″)	89·4°	0·4°
O(2)	52·2	0·2	O(2″)	147·6	0·2
O(2′)	145·6	0·1	O(2‴)	91·1	0·2
O(3)	126·9	0·2	O(4)	72·3	0·2
O(3′)	79·2	0·2	O(4″)	75·6	0·2
O(4)	78·1	0·2	O(1″) -Na-O(2″)	90·1	0·2
O(4′)	74·2	0·2	O(2‴)	172·6	0·2
O(2)-Ca-O(2′)	140·7	0·4	O(4)	99·7	0·2
O(3)	75·0	0·2	O(4″)	75·4	0·2
O(3′)	79·7	0·2	O(2″) -Na-O(2‴)	93·4	0·4
O(4)	85·3	0·2	O(4)	75·8	0·2
O(4′)	126·3	0·2	O(4″)	135·3	0·2
O(3)-Ca-O(3′)	98·6	0·4	O(2‴)-Na-O(4)	87·4	0·2
O(4)	93·8	0·2	O(4″)	97·6	0·2
O(4′)	157·2	0·1	O(4)—Na-O(4″)	147·6	0·4
O(4)-Ca-O(4′)	81·4	0·4			
			O(1)—C—O(2)	118·4	0·4
			O(3″)	120·9	0·6
			O(2)—C—O(3″)	120·7	0·6

The final atomic parameters are given in Table 1, together with their standard deviations. The observed and calculated structure factors are listed in Table 2.

Description of the structure

The general arrangement of the atoms in pirssonite is shown in Fig. 1. The bond lengths and angles are listed in Tables 3 and 4.

The carbonate group is triangular and planar, with a mean C–O distance of 1·285 Å. The distances C–O(1) and C–O(2) are equal, whilst the C–O(3) distance is slightly longer. The corresponding angle O(1)–C–O(2) is narrower than the other two.

The calcium atom lies on the twofold axis and it is coordinated by eight oxygen atoms, at a mean distance of 2·467 Å, in an almost regular polyhedron, resembling a square antiprism. The Ca polyhedra, eight per unit cell, are independent from each other.

The coordination of Na is sixfold, in a somewhat irregular octahedron. These polyhedra are connected to each other by the sharing of one edge O(1)–O(2), so as to form an infinite diagonal chain, and by the sharing of one corner O(4) in the **b** direction. In the structure there are two sets of these chains, elongated parallel to the *ac* diagonals, that is along the directions of the two series of 'diamond' glide planes. The connexions between one chain and its two adjacent parallel ones are provided by the carbon atoms in the **c** direction, whilst along the **b** direction the connexions are through the Ca polyhedra and directly through the O(4) oxygen atoms. On the whole it can be said that the complex of Na coordination polyhedra forms a three-dimensional network, whose strength is increased by the Ca polyhedra and the CO_3 groups.

The oxygen of the water molecule is O(4), the only one not bound to the carbon atom, and its hydrogen atoms make indirect connexions between neighbour Ca atoms, by O(4)–H···O(3) hydrogen bridges. The distances from O(4) and its nearest neighbour oxygens, bound by the hydrogen atoms, are of 2·70 and 2·83 Å.

In conclusion, arising from the above considerations, a noteworthy feature of pirssonite is the massiveness of its structure. Indeed, the lack of any observed cleavage can be explained by the presence of two series of Na chains parallel to the *ac* plane, running in cross diagonal directions, by the connexions of Na polyhedra with carbon triangles in the **c** direction, and by Na–O(4)–Na and Na–O(2)–Ca bonds in the **b** direction. Also in the **b** direction there are indirect Na–Ca–Na connexions through the O(1)–O(4) edges.

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Crystal Structure of Tetramethylammonium Manganese(II) Chloride*

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The crystal structure of tetramethylammonium manganese(II) chloride has been determined by full-matrix least-squares refinement of three-dimensional Mo $K\alpha$ intensity data. The space group is $P6_3/m$ with lattice constants $a_0 = 9{\cdot}1510$, $c_0 = 6{\cdot}4940$ Å. The structure consists of infinite linear chains composed of manganese atoms bridged by three chlorine atoms, $-MnCl_3^-$–, and of disordered $[N(CH_3)_4]^+$ ions.

Introduction

The evaporation of aqueous solutions of tetramethylammonium chloride and manganous chloride (as well as the corresponding bromides) yields two differently colored crystals; the light green prisms, $[(CH_3)_4N]_2MnCl_4$, are isomorphous with the zinc and cobalt compounds reported by Morosin & Lingafelter (1959; also Wiesner, Srivastava, Kennard, DiVaira & Lingafelter, 1967) which contain discrete $MnCl_4^{2-}$ ions while the rose pink rods, $(CH_3)_4NMnCl_3$, contain infinite linear chains composed of manganese atoms bridged by three chlorine atoms, $-MnCl_3^-$–. Under ultraviolet light, both of these materials fluoresce brightly. The crystal structure of the latter compound is reported here.

Experimental

The lattice constants for tetramethylammonium manganese chloride [$a_0 = 9{\cdot}1510(9)$, $c_0 = 6{\cdot}4940(9)$] were obtained with Cu $K\alpha$ radiation (λ for $K\alpha_1 = 1{\cdot}54050$ Å) by least-squares fit of 14 high 2θ values measured on films taken with a 115 mm diameter Weissenberg

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