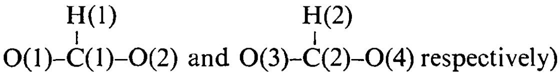
diagram, Fig. 2. Bond distances and angles for the structure are presented in Table 3. Atoms of the type Cd(1) and Cd(2) occupy centres of symmetry, on the space group special positions (*a*) and (*d*) respectively, to form a face-centred array which the formate ligands *A* and *B* (*A* and *B* refer to



$\overset{\mathrm{H(1)}}{\mathrm{O(1)–\underset{}{C}(1)–O(2)}}$ and $\overset{\mathrm{H(2)}}{\mathrm{O(3)–C(2)–O(4)}}$ respectively)

bridge in the following manner. Ligand *A* coordinates Cd(1) atoms alone, in *anti–anti* configuration, and links them into two-dimensional layers parallel to *bc*. Ligand B, which exhibits *anti–syn* configuration, bridges Cd(1) and Cd(2) atoms in planes parallel to *ab*, forming the three-dimensional polymeric lattice. Cd(1) is six-coordinate through atoms O(1^{i}) and O(2) of ligand *A* and O(4) of *B* (plus symmetry-related atoms), while Cd(2) completes its coordination sphere with O(3) from ligand *B* and coordinated water molecules O(5) and O(6). The polymer is further strengthened by the formation of hydrogen bonds between the water molecules and each of the formate oxygen atoms (Table 4).

Table 3. *Bond distances* (Å) *and angles* (°) *with standard deviations in parentheses*

Cd(1)–O(2)	2·248 (4)	C(2)–O(3)	1·224 (8)
Cd(1)–O(4)	2·301 (5)	C(2)–O(4)	1·251 (8)
Cd(1)–O(1^{i})	2·263 (4)	C(1)–H(1)	1·09
Cd(2)–O(3)	2·326 (5)	C(2)–H(2)	1·06
Cd(2)–O(5)	2·298 (5)	O(5)–H(3)	1·06
Cd(2)–O(6)	2·243 (5)	O(5)–H(4)	1·09
C(1)–O(1)	1·231 (8)	O(6)–H(5)	0·95
C(1)—O(2)	1·230 (7)	O(6)–H(6)	1·03
O(2)—Cd(1)–O(4)	92·9 (2)	Cd(1)–O(4)–C(2)	128·5 (4)
O(2)—Cd(1)–O(1^{i})	90·5 (2)	O(3)—C(2)–O(4)	127·0 (7)
O(4)—Cd(1)–O(1^{i})	87·7 (2)	Cd(2)–O(3)–C(2)	130·0 (5)
O(3)—Cd(2)–O(5)	87·5 (2)	O(1)—C(1)–H(1)	115
O(3)—Cd(2)–O(6)	89·6 (2)	O(2)—C(1)–H(1)	118
O(5)—Cd(2)–O(6)	90·1 (2)	O(3)—C(2)–H(2)	120
Cd(1^{i})–O(1^{i})–Cd(1)	125·4 (4)	O(4)–C(2)–H(2)	113
O(1)—C(1)—O(2)	127·6 (6)	H(3)–O(5)–H(4)	81
C(1)—O(2)–Cd(1)	122·2 (4)	H(5)–O(6)–H(6)	106

Table 4. *Hydrogen-bond distances* (Å) *and angles* (°)

O(5)–H(3)–O(2^{ii})	128	O(5)···O(2^{ii})	2·769 (7)
O(5)–H(4)–O(4)	118	O(5)···O(4)	2·748 (7)
O(6)–H(5)–O(1^{ii})	157	O(6)···O(1^{ii})	2·773 (8)
O(6)–H(6)–O(3^{iii})	175	O(6)···O(3^{iii})	2·721 (7)

Superscripts refer to the following symmetry-related positions:

(i)	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$
(ii)	x	$1+y$	z
(iii)	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$

Each coordination polyhedron is very close to regular octahedral (Table 3) and the variation in Cd–O distance [2·243(5)–2·326(5) Å] is within the range found with other cadmium carboxylates (Harrison & Trotter, 1972; Post & Trotter, 1974*a*, *b*, *c*). The longer distances Cd(1)–O(4) and Cd(2)–O(3) probably reflect the more sterically restrictive requirements imposed upon ligand *B* in bridging between Cd(1) and Cd(2) layers, although residual charge upon the metal atoms [Cd(1) is coordinated by six formate oxygen atoms and Cd(2) by only two] could be a contributing factor (Post & Trotter, 1974*b*). The residual charge effect could also produce the longer C(2)–O(4) bond (1·251 Å). Cd(2) may be expected to possess slight positive charge and, therefore, necessitate greater electron donation from O(3) than would be the case of donation from O(4) to Cd(1). In ligand *B*, a withdrawal of electrons into the bond C(2)–O(3), to facilitate such a trend toward neutralization of charge, would have a weakening effect upon the bond C(2)–O(4).

We thank the National Research Council of Canada for financial support.

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Acta Cryst. (1974). B**30**, 1882

Refinement of the Crystal Structure of $NaInSi_2O_6$

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(*Received* 26 *February* 1974; *accepted* 28 *February* 1974)

Abstract. $NaInSi_2O_6$, $C2/c$. Cell constants at 20 °C with Mo $K\alpha$ ($\lambda=0·71069$ Å): $a=9·9023$ (4), $b=9·1307$ (4), $c=5·3589$ (2) Å, $\beta=107·200$ (1)°. The variation in cell dimensions across the Na pyroxene series is linear with

the exception of $NaInSi_2O_6$ due to constraints applied by the M2 cation and elements of the tetrahedral chain on the rate of increase in the $a \sin \beta$ and c dimensions.

Introduction. The variation in cell volume of the Na pyroxenes is linear with the cube of the M1 cation radius (Prewitt & Shannon, 1969), except for $NaInSi_2O_6$, the cell volume of which is smaller than expected (Christiansen & Hazell, 1967). This refinement was made in order to allow a detailed comparison with the other isomorphous Na pyroxenes.

The crystal used was provided by Dr Jun Ito of Harvard University. Precession photographs showed monoclinic symmetry and reflexions with $h+k=2n+1(hkl)$ and $l=2n+1(h0l,0kl)$ were absent, consistent with the space group $C2/c$ observed for other Na pyroxenes (Prewitt & Burnham, 1966; Clark, Appleman & Papike, 1969). Experimental procedure and data-reduction methods are given by Hawthorne & Grundy (1973). 969 intensities were collected, of which 902 were observed and used in the refinement.

After several cycles of least-squares refinement in which a scale factor and all symmetry-allowable positional parameters and temperature factors [of the form $\exp(-\sum_{i=1}^{3}\sum_{j=1}^{3} h_i k_j \beta_{ij})$] were included as variables, the structure converged with conventional and weighted (unit weights) R values of 2·4 %, 2·6 % for observed re-

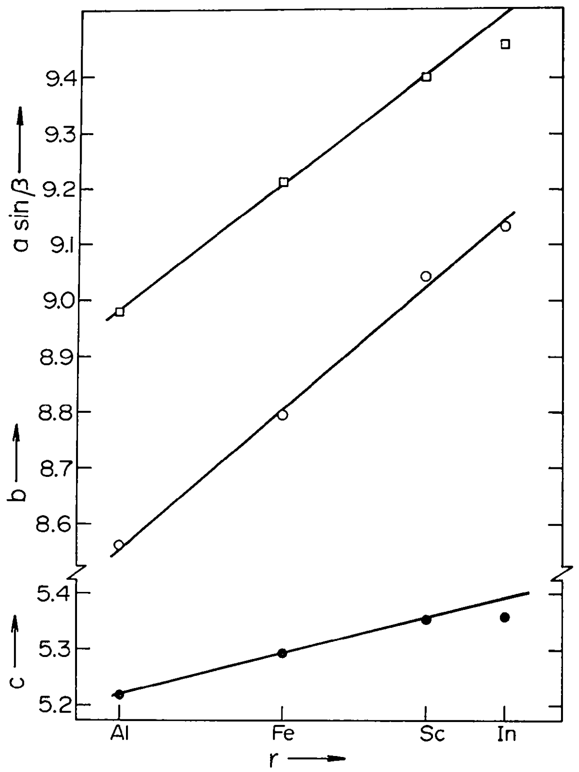

Fig. 1. Variation of cell dimension with M1 cation (X) radius for the Na pyroxenes ($NaXSi_2O_6$).

Table 1. Atomic parameters for $NaInSi_2O_6$

	x	y	z	Bequiv.	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O1A1	0·1193 (2)	0·0795 (2)	0·1519 (4)	0·41 (2)	0·00063 (16)	0·00134 (18)	0·00494 (65)	−0·00018 (13)	0·00024 (24)	0·00063 (25)
O2A1	0·3575 (2)	0·2456 (2)	0·3187 (5)	0·61 (2)	0·00210 (19)	0·00081 (18)	0·00800 (69)	−0·00066 (15)	0·00136 (28)	−0·00032 (27)
O3A1	0·3493 (2)	0·118 (2)	0·0180 (4)	0·52 (2)	0·00150 (18)	0·00209 (19)	0·00335 (66)	0·00001 (15)	0·00088 (25)	−0·00106 (27)
SiA1	0·29175 (8)	0·08640 (8)	0·2477 (1)	0·29 (1)	0·00084 (6)	0·00084 (7)	0·00278 (23)	−0·00017 (5)	0·00042 (9)	−0·00007 (9)
M1	0	0·89466 (3)	$\frac{1}{4}$	0·28 (1)	0·00091 (3)	0·00066 (3)	0·00261 (10)	0	0·00033 (3)	0
M2	0	0·3033 (2)	$\frac{1}{4}$	1·26 (2)	0·00456 (22)	0·00272 (20)	0·00787 (65)	0	−0·00142 (29)	0

Table 2. *Selected interatomic distances in* $NaInSi_2O_6$ (Å)

Si tetrahedron		M1 octahedron		M2 antiprism	
SiA1–O1A1	1·632 (3)	M1–O1A1, B1	2·211 (2)	M2–O1A1, O1B1	2·494 (3)
SiA1–O2A1	1·592 (2)	M1–O1A2, B2	2·141 (5)	M2–O2C2, O2D2	2·367 (6)
SiA1–O3A1	1·649 (3)	M1–O2C1, D1	2·071 (2)	M2–O3C1, O3D1	2·510 (4)
SiA1–O3A2	1·655 (3)	Mean	2·141	M2–O3C2, O3D2	2·899 (3)
Mean	1·632			Mean for 6	2·457
				Mean for 8	2·568
		O1A1–O1B1	2·857 (6)		
O1A1–O2A1	2·723 (4)	O2C1–O2D1	3·121 (5)	Cation–cation	
O1A1–O3A1	2·655 (4)	O1A1–O2C1	3·051 (3)	Si—SiA2	3·109 (1)
O1A1–O3A2	2·663 (7)	O1A1–O1A2	3·047 (2)	M1–M1(1)	3·290 (1)
O2A1–O3A1	2·661 (3)	O1A1–O2C1	3·058 (3)	M1–SiA1	3·381 (1)
O2A1–O3A2	2·593 (3)	O1A2–O2D1	3·118 (6)	M1–SiA2	3·307 (9)
O3A1–O3A2	2·688 (1)	O1A1–O1B2	2·840 (7)		
Mean	2·664		3·017		

Table 3. *Selected interatomic angles for* $NaInSi_2O_6$(°)

Si tetrahedron		M1 octahedron		Chain angles	
O1A1–Si–O2A1	115·2 (1)	O1A1–M1–O1B1	80·5 (1)	SiA1–O3A1–SiA2	140·5 (1)
O1A1–Si–O3A1	108·0 (2)	O1A1–M1–O2C1	91·1 (1) ×2	O3A2–O3A1–O3A2	170·8 (2)
O1A1–Si–O3A2	108·2 (2)	O1A1–M1–O1A2	88·9 (1) ×2	SiA1–O1A1–M1	122·5 (1)
O2A1–Si–O3A1	110·4 (1)	O1A1–M1–O1B2	81·5 (1) ×2	SiA2–O1A2–M1	121·8 (2)
O2A1–Si–O3A2	106·0 (1)	O1A2–M1–O2C1	92·8 (2) ×2	SiC1–O2C1–M1	144·1 (1)
O3A1–Si–O3A2	108·9 (1)	O1A2–M1–O2D1	95·5 (1) ×2	SiA1–O1A1–M2	114·7 (1)
Mean	109·5	O2C1–M1–O2D1	97·8 (1)	SiC2–O2C2–M2	98·3 (2)
		Mean	89·8		

flexions and 3·0%, 3·1% for all measured reflexions respectively. A correction for isotropic extinction was made during the final stages of the refinement by including the coefficient (Zachariasen, 1968) as a variable. Final parameters are given in Table 1. Selected interatomic distances and angles are presented in Tables 2 and 3 respectively.*

Discussion. The variation in cell dimensions with M1 cation radius for the Na pyroxenes is shown in Fig. 1. It is apparent that the relatively small $a \sin \beta$ and c dimensions in the In pyroxene contribute significantly to the anomalously small cell volume noted by Prewitt & Shannon (1969). The length of the octahedral chain increases as the radius of the M1 cation increases from Al to Sc; this is accompanied by an increase in the length of the tetrahedral chain through extension of the O(3)–O(3) edge and concomitant increase in the mean Si–O(3) distance. In the In pyroxene, the mean Si–O(3) distance is equal to that of the Sc pyroxene. Apparently the bonding requirements of the O(3) anion allow no further extension of the tetrahedral chain, resulting in the smaller than expected c dimension of the In pyroxene.

The M2–O(2) bond length is constant from Al to Sc, but decreases in the In pyroxene. This exerts a clamping effect on further increase in the **a*** direction leading to an anomalously low value for $a \sin \beta$ (Fig. 1). This can be compared to the situation in the Li pyroxenes where M2–O(2) decreases across the series from Al to Sc.

Interchain linkage is maintained during b axis expansion by a combination of rotation of the tetrahedra about an axis parallel to **c** and distortion of tetrahedral edge lengths, both of which produce an enlargement in the mirror component of the c-glide-related O(1)–O(1) separation. No obvious constraints occur on either of these processes, and the b axis increases normally throughout the whole series.

H.D.G. is grateful to the National Research Council of Canada for research grants awarded to assist this work.

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* A list of structure factors is available from the authors and has also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30389 (7 pp.). Copies may be obtained through: The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.