

Fig. 2. Projection sur le plan ac mettant en évidence l'enchaînement dans une couche des polyèdres de césium.

entre elles selon a par des arêtes communes au niveau des polyèdres $Cs(1)O_8$.

La plus petite distance $Cs-Cs$ est de 4,712 (1) Å.

Environnement du lithium. Quatre atomes d'oxygène extérieurs aux chaînes $(PO_3)_\infty$ participent à la coordination de chaque site de lithium. Comme le montre le Tableau 2, les tétraèdres de lithium sont déformés. Les distances $Li-O$ varient de 1,88 à 2,02 Å et les angles $O-Li-O$ varient de 99,2 à 123,5°. Les tétraèdres LiO_4 sont tous isolés les uns des autres par l'intermédiaire des tétraèdres PO_4 et des polyèdres de coordination du césium.

Le tétraèdre $Li(1)O_4$ met en commun les deux arêtes $O(E22)-O(E12)$ et $O(E31)-O(E21)$ avec deux polyèdres $Cs(2)O_8$. Le tétraèdre $Li(2)O_4$ partage le sommet $O(E32)$ avec deux polyèdres $Cs(1)O_8$, l'arête $O(E11)-O(E41)$ avec un troisième polyèdre $Cs(1)O_8$ et le sommet $O(E11)$ avec un polyèdre $Cs(2)O_8$.

Les tétraèdres LiO_4 relient donc d'une part les différentes couches de polyèdres de césium entre elles et d'autre part les différentes chaînes $(PO_3)_\infty$ du polyphosphate. Ils assurent ainsi une cohésion tridimensionnelle à l'ensemble de la structure cristalline.

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Refinement of the Structure of Manganese Sodium Dimetasilicate

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Abstract. $MnNaSi_2O_6$, $M_r = 230.11$, monoclinic, $C2/c$, $a = 9.513$ (1), $b = 8.621$ (1), $c = 5.354$ (1) Å, $\beta = 105.14$ (1)°, $V = 423.9$ (1) Å³, $Z = 4$, $D_x = 3.61$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 38.6$ cm⁻¹, $F(000) = 448$, $T = 302$ K, $R = 0.034$ for 1522 independent reflections. The structure is isomorphous with other Na pyroxenes. Mn occupies a strongly distorted octahedral ($M1$) site. The distortion shows that there is Jahn-Teller stabilization of Mn^{3+} in this

pyroxene structure. The short $Mn-Mn$ distance of 3.131 (1) Å is correlated with the small $Mn-O1-Mn$ angle of 97.1 (1)° reflecting the repulsions between the O1 atoms and the non-bonding $3d$ electrons of the Mn ion.

Introduction. The $M1-M1$ distance of the Na pyroxenes increases smoothly with an increase of the $M1$ cation radius, except for $CrNaSi_2O_6$, the $Cr-Cr$

distance of which is shorter than expected (Hawthorne & Grundy, 1973). This refinement was made in order to allow a detailed comparison between the $M1-M1$ distance and the geometrical feature of the octahedral $M1$ site.

Experimental. The crystal used was synthesized at 1470 K under 6 GPa for 24 h. Rectangular prism crystal $0.05 \times 0.06 \times 0.08$ mm. Rigaku AFC5 four-circle diffractometer, graphite-monochromated $Mo K\alpha$ radiation. Lattice parameters from 18 reflections with $63 < 2\theta < 70^\circ$. Intensities measured up to $2\theta = 90^\circ$; $h = -18$ to 18 , $k = 0$ to 17 , $l = -10$ to 10 ; $\omega-2\theta$ scans. One standard reflection (221) every 100 reflections, variation less than 0.3% about mean. 3526 reflections in a hemisphere of reciprocal space, 2800 with $F_o > 1\sigma(F_o)$. If one of the symmetrically equivalent reflections is less than one standard deviation, the other equivalent reflection is rejected. These reflection data were averaged to produce 1522 symmetry-independent reflections with $R_{int} = 0.027$. Lorentz and polarization but no absorption or extinction correction. The structure refinement of F was made on a Facom-M380 computer by the least-squares method [*RADY* program supplied by Sasaki (1982)]. Initial positional parameters, with isotropic temperature factors, were taken from those of $FeNaSi_2O_6$ (Clark, Appleman & Papike, 1969). No anomalous-dispersion corrections were made. The atomic scattering factors for neutral atoms were taken from Cromer & Waber (1974). After

several cycles of least-squares refinement in which a scale factor and all symmetry-allowable positional parameters and temperature factors were included as variables, the structure converged with unweighted and weighted $[1/\sigma(F)]^2 R$ values of 5.3 and 3.4% respectively. $(\Delta/\sigma)_{max} = 0.001$. Max. and min. heights in final difference Fourier map 1.19 and $-1.23 e \text{ \AA}^{-3}$. Final parameters are given in Table 1. Selected interatomic distances and angles are presented in Table 2.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43446 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. $M1-M1$ and mean $M1-O1$ distances (\AA) and $M1-O1-M1$ angles ($^\circ$) in $NaM^{3+}Si_2O_6$ pyroxenes

M^{3+}	$M1-M1$	Mean $M1-O1$	$M1-O1-M1$	$M1-M1$ (calc.)*	Reference
Al	3.066 (1)	1.965	102.6 (1)	3.067	(a)
Cr	3.089 (4)	2.024	99.4 (1)	3.087	(a)
Ga	3.134 (1)	2.018	101.9 (2)	3.134	(b)
V	3.120 (1)	2.055	98.8 (1)	3.121	(c)
Fe	3.189 (1)	2.069	100.8 (1)	3.188	(a)
Mn	3.131 (1)	2.087	97.1 (1)	3.129	(d)
Ti	3.172 (1)	2.084	99.1 (1)	3.172	(e)
Sc	3.269 (1)	2.144	99.3 (1)	3.268	(f)
In	3.290 (1)	2.176	98.5 (1)	3.297	(g)

References: (a) Clark, Appleman & Papike (1969); (b) Ohashi, Fujita & Osawa (1983); (c) Fujita & Ohashi (1986); (d) present study; (e) Ohashi, Fujita & Osawa (1982); (f) Hawthorne & Grundy (1973); (g) Hawthorne & Grundy (1974).

$$* M1-M1(\text{calc.}) = 2(\text{mean } M1-O1) \sin[(M1-O1-M1)/2].$$

Table 1. Atomic coordinates and equivalent isotropic thermal parameters for $MnNaSi_2O_6$ with e.s.d.'s in parentheses

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
O1	0.1172 (2)	0.0761 (2)	0.1612 (3)	0.47 (4)
O2	0.3609 (2)	0.2597 (2)	0.3038 (3)	0.65 (4)
O3	0.3563 (2)	0.0080 (2)	0.0191 (3)	0.53 (4)
T(Si)	0.29402 (6)	0.08865 (8)	0.2463 (1)	0.31 (2)
M1(Mn)	0	0.90578 (6)	0.25	0.25 (1)
M2(Na)	0	0.2982 (2)	0.25	0.75 (4)

Table 2. Selected interatomic distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

Si tetrahedron		M1 octahedron	
Si-O1	1.628 (2)	$M1-O1A1, B1$	2.198 (2)
Si-O2	1.604 (2)	$M1-O1A2, B2$	1.975 (2)
Si-O3A1	1.641 (2)	$M1-O2C1, D1$	1.902 (2)
Si-O3A2	1.651 (2)	Mean	2.025
Mean	1.631		
Si-Si	3.083 (1)	$M1-M1$	3.131 (1)
M2 antiprism			
$M2-O1A1, O1B1$	2.326 (2)	Si-O3-Si	139.0 (1)
$M2-O2C2, O2D2$	2.461 (2)	$M1-O1-M1$	97.1 (1)
$M2-O3C1, O3D1$	2.405 (2)	$O1A1-M1-O1B2$	82.9 (1)
$M2-O3C2, O3D2$	2.786 (2)	$O3-O3-O3$	174.1 (2)
Mean	2.495		

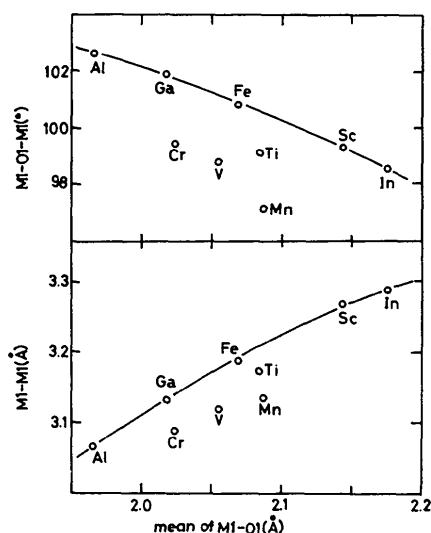


Fig. 1. Lower curve is the variation of the $M1-M1$ distance (\AA) with the mean $M1-O1$ distance for the $NaM^{3+}Si_2O_6$ pyroxenes. The upper curve is the variation of the $M1-O1-M1$ angle with the mean $M1-O1$ distance.

Discussion. The structure is isomorphous with other Na pyroxenes (Clark *et al.*, 1969). Mn occupies a strongly distorted octahedral (*M1*) site. The distortion shows that there exists Jahn–Teller stabilization of Mn^{3+} in this pyroxene structure. Table 3 summarizes the *M1–M1* and the mean *M1–O1* distances and the *M1–O1–M1* angles in the series of Na pyroxenes. The *M1–M1* distance is nearly the same as twice the product of the mean *M1–O1* distance and the sine of one-half of the *M1–O1–M1* angle as listed in the second and fifth columns of Table 3. The variation of the *M1–M1* distance across the shared *O1–O1* edge with the mean *M1–O1* distance is shown in Fig. 1 (lower curve); a smooth curve can be drawn through those points representing the Al, Ga, Fe, Sc, and In members but the Ti, V, Cr and Mn members deviate from the trend. The *M1–M1* distances in the latter are shorter than those estimated from the mean *M1–O1* distances. The shorter *M1–M1* distances correlate with the smaller *M1–O1–M1* angles as shown in Fig. 1 (upper curve). Hawthorne & Grundy (1973) predicted that the short metal–metal distance in $CrNaSi_2O_6$ and the suspected anomalous metal–metal distances in $TiNaSi_2O_6$ and $VNaSi_2O_6$ should be due to metal–metal bonds. However, these metal–metal distances are much longer than the distances in Ti_2O_3 and V_2O_3 with metal–metal bonding (Prewitt, Shannon, Rogers & Sleight, 1969). The shorter *M1–M1* distances in

pyroxenes may be caused by the geometrical features of the *M1* sites. The sum of the *M1–O1–M1* and the *O1A1–M1–O1B2* angles is 180° . Therefore, the smaller *M1–O1–M1* angles correspond to the larger *O1A1–M1–O1B2* angles. The larger *O1A1–M1–O1B2* angles may be caused by the repulsions between the *O1* atoms and the non-bonding *3d* electrons of the Ti, V, Cr and Mn ions. That is, the shorter metal–metal approaches may be correlated with the geometry of the $M1O_6$ octahedron.

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Trichloroselenonium(IV) Tetrachloroaurate(III)

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Abstract. $[SeCl_3][AuCl_4]$, $M_r = 524.1$, monoclinic, $P2_1/c$, $a = 8.484$ (3), $b = 10.184$ (3), $c = 12.135$ (4) Å, $\beta = 108.37$ (3)°, $V = 995.1$ Å³, $Z = 4$, $D_x = 3.50$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 20.2$ mm⁻¹, $F(000) = 928$, $T = 293$ K, $R = 0.069$, $wR = 0.059$ for 1139 reflections. The structure consists of centrosymmetric $[SeCl_3, AuCl_4]_2$ dimers; the coordination geometry at selenium (including secondary interactions) is distorted octahedral with mean Se–Cl 2.121, Se...Cl 2.941 Å. The compound is not isostructural with its tellurium analogue.

Introduction. Salts that contain the pyramidal cations MX_3^+ ($X =$ halogen; $M =$ S, Se, Te) display charac-

teristic secondary interactions between the atom *M* and the accompanying anions; this generally leads to an extended coordination geometry with a distorted octahedron around *M* (Christian, Collins, Gillespie & Sawyer, 1986, and references cited therein). Only one such structure involving a square-planar anion had been reported until recently ($SCl_3^+ \cdot ICl_4^-$; Edwards, 1978) and we have therefore begun to investigate the structures of $MCl_3^+ \cdot AuCl_4^-$. The tellurium derivative (Jones, Jentsch & Schwarzmann, 1986) consists of centrosymmetric dimers in which the extended coordination at tellurium is distorted square pyramidal. Powder data (Novitskaya, Timoshchenko & Fokina, 1979) indicate that the compounds $MCl_3^+ \cdot AuCl_4^-$ are not isostructural.