

Fig. 1. The molecular structure of  $Os_3(CO)_9Se_2$  showing the atom-numbering scheme.

 $Os_4(CO)_{12}H_2Se_2$  (Johnson *et al.*, 1979) where the Se atoms also bond to three Os atoms.

The three carbonyl groups bonded to each Os atom are staggered with respect to the metal-metal bonds. The carbonyls are all essentially linear, and the average Os-C and C-O bond lengths of 1.91(1) and 1.13(1)Å are similar to those found in Os<sub>3</sub>(CO)<sub>8</sub>(CS)S<sub>2</sub> (Broadhurst, Johnson, Lewis & Raithby, 1980).

In terms of electron counting, with the Se atoms acting as four-electron donors, the title compound is a

50 electron complex. This has two more electrons than the 'electron precise' 48 electron system, and the inclusion of an additional electron pair requires the cleavage of a metal-metal bond, in this case Os(2)-Os(3).

We thank the Science Research Council for financial support. Calculations were performed on the University of Cambridge IBM 370/165 computer with *SHELX* 76 (Sheldrick, 1976); the figure was drawn with *PLUTO* written by Dr W. D. S. Motherwell.

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## Structure of Arrojadite, KNa<sub>4</sub>CaMn<sub>4</sub>Fe<sub>10</sub>Al(PO<sub>4</sub>)<sub>12</sub>(OH,F)<sub>2</sub>

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Abstract. KNa<sub>4</sub>CaMn<sub>4</sub>Fe<sub>10</sub>Al(PO<sub>4</sub>)<sub>12</sub>(OH,F)<sub>2</sub>, monoclinic, C2/c, a = 16.526 (4), b = 10.057 (3), c = 24.730 (5) Å,  $\beta = 105.78$  (3)°. The structure was solved by direct and Fourier methods. An isotropic full-matrix least-squares refinement, followed by anisotropic block-diagonal least-squares cycles, led to a final R = 0.084 for 6910 reflections with  $I > 3\sigma(I)$ . The structure analysis indicated the ideal crystal chemical formula  $KNa_4CaMn_4Fe_{10}Al(PO_4)_{12}(OH,F)_2$ .

Introduction. The name arrojadite was first proposed by Guimaraes (1925) for a phosphate of Fe, Mn and Na from Sierra Branca pegmatite, Brazil. Lindberg (1950) identified arrojadite as the unnamed Na, Fe, Mn

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phosphate from Nickel Plate pegmatite, South Dakota, described by Headden (1891). Fisher (1955) showed arrojadite and dickinsonite to be isostructural and gave the correct cell parameters and space group for arrojadite.

Various crystal chemical studies were made on this mineral and various crystal chemical formulae were proposed. However, only a crystal-structure analysis could afford the correct solution to this interesting and important mineralogical problem. Thus a study was undertaken to determine the three-dimensional structure of the mineral and to unravel the intriguing crystal chemistry of the arrojadite-dickinsonite family, elucidating the positioning of the cations in the various sites.

When the study was complete and the paper already written, a paper on the crystal structure of arrojadite was published by Krutik, Puscharovskii, Pobedimskava & Belov (1979). Although the gross features of the two structural analyses are similar, there are important differences in some points of high crystal chemical relevance. Thus, whereas we defer to another paper (Moore, Araki, Merlino, Mellini & Zanazzi, 1981) a full discussion of the mineralogical and crystal chemical implications of our results and an extensive discussion of various phosphate phases structurally related to arrojadite, we think it useful to publish the results of our structural analysis and to compare them with those obtained by Krutik et al. (1979), stressing the more relevant discrepancies.

A sample of dark-green massive arrojadite from the Nickel Plate Mine, Keystone, South Dakota, was employed in the present study. A crystal fragment was ground into a sphere of diameter 0.6 mm. Preliminary precession photographs showed arrojadite to be monoclinic with lattice constants in agreement with those obtained by Fisher (1955). The crystal was mounted on a Philips PW 1100 diffractometer and the cell parameters were refined by least-squares fit to the angular coordinates of 25 reflections measured by graphite-monochromated Mo Ka radiation. Possible space groups from the systematic absences are Cc and C2/c; the latter was supported by intensity statistics and was later confirmed by the structure analysis.

The intensity data collection was carried out with an  $\omega/2\theta$  scan technique. The scan rate was  $0.04^{\circ}$  s<sup>-1</sup>; the scan width 1.4°. As a check on the mechanical and electronic stability, three reflections were monitored every 3 h. A total of 8069 independent reflections were measured in the range  $3^{\circ} \leq \theta \leq 34^{\circ}$ . 1159 of these having  $I \leq 3\sigma(I)$  were considered as unobserved. The data were corrected for Lorentz and polarization effects. A spherical absorption correction was applied.

Several attempts to solve the structure by Patterson methods were unsuccessful because the special coordinates of the heaviest atoms gave rise to a large number accidental superpositions of vectors. The of

approximate atomic arrangement was determined by direct methods. A Fourier synthesis, computed with the best set of signs assigned by MULTAN (Main, Woolfson, Lessinger, Germain & Declercq, 1974) to the 499 highest E's ( $E \ge 1.86$ ), revealed the positions of 13 heavy atoms in the asymmetric unit.

The structure was completed by means of Fourier and difference syntheses and refined by full-matrix least-squares cycles with isotropic temperature factors. The refinement was then completed by means of block-diagonal least-squares cycles with anisotropic temperature factors for all the atoms, and unit weights. Atomic scattering factors for neutral atoms taken from International Tables for X-ray Crystallography (1974) were used throughout. The final R value for 6910 observed reflections was 0.084.

Table 1. Final positional parameters and isotropic thermal parameters  $(Å^2)$  with e.s.d.'s in parentheses

	x	y	Ζ	В
Al	0	0.5000	0	0.38 (5)
M(1)	0.2202(1)	0.8957(2)	0.4738(1)	2.52 (4)
M(2)	0.2123(1)	0.0078(1)	0.2674(1)	0.88 (2)
M(3)	0.1066(1)	0.0142(1)	0.1394(1)	$1 \cdot 14(2)$
M(4)	0.0222(1)	0.2496(1)	0.4036(1)	0.66(2)
M(5)	0.0334(1)	0.7434(1)	0.4004 (1)	0.58 (2)
M(6)	0.2044(1)	0.6992(1)	0.3517(1)	0.73(2)
M(7)	0.2193(1)	0.2945(1)	0.3432 (1)	0.90 (2)
X(1)	0.2322(2)	0.2223(3)	0.4848(1)	1.03 (5)
X(2)	0.1289 (4)	0.5150 (4)	0.1202 (2)	2.99 (11)
X(3)	0	0	0	1.95 (11)
X(4)	0	0.5043 (5)	0.2500	2.87 (8)
X(5)	0	0.1460 (18)	0.2500	6.40 (32)
P(1)	0.1130 (2)	0.0085 (3)	0.3662(1)	1.78 (4)
O(1)	0.0250 (3)	0.0614 (5)	0.3675 (3)	1.10 (10)
O(2)	0.1120 (4)	0.8584 (5)	0.3635 (3)	1.10 (10)
O(3)	0.1426 (5)	0.0770 (7)	0.3220 (4)	2.17 (16)
O(4)	0.1807 (6)	0.0462 (10)	0.4222 (5)	3.15 (18)
P(2)	0.1303(1)	0.4670(1)	0.4246(1)	0.48(3)
O(5)	0.0501(3)	0.4448(5)	0.4450(2)	0.53(8)
O(6)	0.1213(3)	0.5879(5)	0.3924(3)	0.96(9)
0(7)	0.1301(4)	0.3445(5)	0.38/1(3)	0.92(9)
O(8)	0.2103(4)	0.4637(7)	0.4733(3)	1.44(11)
P(3)	0.1259(1)	0.2518(2)	0.0383(1)	0.43(3)
0(9)	0.0842(3)	0.1004(3)	0.0751(2)	0.03(3)
O(10)	0.0941(3)	0.3931(3)	0.0300(2) 0.4794(2)	0.96 (10)
O(11)	0.1078(4) 0.2224(3)	0.2533(6)	0.4794(2) 0.0623(2)	1.07(10)
D(12) D(4)	0.1023(1)	0.7673(2)	0.0474(1)	0.47(3)
O(13)	0.0467(3)	0.6428(5)	0.0482(2)	0.66(8)
O(13)	0.0407(3)	0.8719(5)	0.0794(2)	0.82(9)
O(15)	0.0961(4)	0.1861(6)	0.4874(2)	$1 \cdot 16(10)$
O(16)	0.1939(3)	0.7357(6)	0.0770(3)	1.17 (10)
P(5)	0.1304(1)	0.7241(2)	0.2115(1)	0.57 (3)
O(17)	0.0484(4)	0.6785 (6)	0.1703(3)	1.21 (10)
O(18)	0.1315(4)	0.6781 (6)	0.2703 (2)	1.38 (11)
O(19)	0.1395 (5)	0.8773 (6)	0.2088 (3)	1.70 (12)
O(20)	0.2044 (4)	0.6604 (6)	0.1938 (3)	1.21 (10)
P(6)	0.1425(1)	0.2972 (2)	0.2045(1)	0.77 (3)
O(21)	0.0583 (4)	0.3402 (6)	0.1653 (2)	1.21 (10)
O(22)	0.1516 (6)	0.3509 (8)	0.2632 (3)	2.39 (16)
O(23)	0.1489 (4)	0.1447 (5)	0.2052 (2)	1.15 (10)
O(24)	0.2156 (4)	0.3541 (6)	0.1824 (3)	1.70 (12)
O(25)	0.2315 (3)	0.0013 (5)	0.1383 (3)	1.13 (10)

The final positional coordinates and the temperature factors at the end of the isotropic refinement are given in Table 1.\*

**Discussion.** The cation populations in the various sites of the crystal structure were adjusted taking account of: (a) height of the peaks in the density map; (b) occupancy factors and thermal parameters; (c) average bond lengths and coordination numbers; (d) bondvalence balance; and (e) chemical data (Lindberg, 1950). The results are reported in Table 2 together with the coordination number and the mean bond length in the various cation polyhedra.

The bond-valence balance clearly indicated that O(1) to O(24), linked to P atoms, are O<sup>2-</sup>, whereas O(25), the common corner of the octahedra M(3), M(6) and M(7), corresponds to hydroxyl or fluorine anions. From Table 2, disregarding minor substitutions, the following ideal unit-cell content was derived for arrojadite:  $K_4Na_{16}Ca_4Mn_{16}^{2+}Fe_{40}^{2+}Al_4(PO_4)_{48}(OH,F)_8$ , which is in excellent agreement with the chemical data of Lindberg (1950).

X(1) and X(5) sites are partially occupied by Ca<sup>2+</sup> and Na<sup>+</sup> cations respectively: the partial occupancy as well as the high thermal parameter for site X(5) result from a disordered distribution of Na<sup>+</sup> cations around site X(5), whereas the half occupancy of the site X(1)is dependent on the random location of Ca<sup>2+</sup> cations in one of the two adjacent X(1) sites, 1 Å apart, symmetrically related by an inversion centre. Both sites were missed in the structure analysis by Krutik *et al.* (1979) which had two important consequences: (*a*) 'the contents of the unit cell display a deficit of Na atoms'; (*b*) a high charge imbalance was obtained for the atoms O(20) and O(24), corresponding to our atoms O(4) and O(15), which are strongly linked to the X(5) Ca<sup>2+</sup> cation: Krutik *et al.* (1979) restored the charge balance by assuming O-(OH,F) substitutions in those anionic sites.

On the other hand we think, in agreement with the Russian authors, that the relatively high thermal parameter of the P(1) atom, corresponding to the P(5) atom in their paper, is evidence for some deficit of P atoms in these sites, thus indicating a limited substitution of  $(PO_4)^{3-}$  anions by  $(O_4H_4)^{4-}$  or possibly  $(O_4H_5)^{3-}$  groups: similar substitutions were assumed in the structure of fillowite by Araki & Moore (1981).\*

The crystal structure of arrojadite is rather complex but can be conveniently described by Fig. 1, where two structural layers, seen along [010], are represented in terms of polyhedra around the cations Al, M(1) to M(7) and P(1) to P(6). All cations are disposed at levels with  $y \simeq 0, \frac{1}{4}, \frac{1}{2}, \ldots$  The octahedra M(4) to M(7)

Table 2. Coordination numbers, mean bond lengths (Å) and cation populations for the various coordinationpolyhedra in arrojadite

	Multiplicity	Occupancy	Coordination number	Mean bond length	Cation population	Corresponding names in the paper by Krutik <i>et al.</i> (1979)
Al	4	1	6	1.88	Al <sup>3+</sup>	X(8)
M(1)	8	1	4	2.04	$0.06 \text{ Li}^+ + 0.25 \text{ Mg}^{2+} + 0.69 \text{ Fe}^{2+}$	X(7)
M(2)	8	1	5	2.11	Fe <sup>2+</sup>	X(5)
M(3)	8	1	6	2.11	Fe <sup>2+</sup>	X(6)
M(4)	8	1	6	2.14	Fe <sup>2+</sup>	X(2)
M(5)	8	1	6	2.15	Fe <sup>2+</sup>	X(1)
M(6)	8	1	6	2.22	Mn <sup>2+</sup>	X(3)
M(7)	8	1	6	2.22	Mn <sup>2+</sup>	X(4)
X(1)	8	0.5	6	2.35	Ca <sup>2+</sup>	
X(2)	8	1	7	2.49	Na <sup>+</sup>	A(3)
X(3)	4	1	8	2.56	Na <sup>+</sup>	A(2)
X(4)	4	1	8	2.89	0.75 K <sup>+</sup> + 0.25 Na <sup>+</sup>	A(1)
X(5)	4	0.86	6	2.85	Na <sup>+</sup>	_
P(1)	8	1	4	1.53	P <sup>5+</sup>	P(5)
P(2)	8	1	4	1.54	P <sup>5+</sup>	P(2)
P(3)	8	1	4	1.54	P <sup>5+</sup>	P(6)
P(4)	8	1	4	1.54	P <sup>5+</sup>	P(1)
P(5)	8	1	4	1.54	P <sup>5+</sup>	P(4)
P(6)	8	1	4	1.54	P <sup>5+</sup>	P(3)

<sup>\*</sup> Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35967 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

<sup>\*</sup> Note added in proof: A different description is developed in the paper by Moore, Araki, Merlino, Mellini & Zanazzi (1981): the deficiency of phosphorus in the P(1) site is coupled with occupancy of the site P(1x) at 0.0799, 0.9948, 0.3354 by phosphorus and the site O(3x) at 0.0234, 0.9678, 0.2720 by oxygen. O(3x) together with O(1), O(2) and O(3) completes the tetrahedral coordination around P(1x). Two more sites, X(6) at 0.2077, 0.9417, 0.4567 and X(7) at 0, 0.9192,  $\frac{1}{4}$ , appear partially occupied by sodium cations.

and the tetrahedra P(2) to P(5) are located at level  $y \simeq \frac{1}{4}$ (Fig. 1a). The interconnections of such polyhedra by edge and corner sharing build up a continuous sheet in which six-membered rings, made up by four octahedra and two tetrahedra, around inversion centres and twofold axes, as well as four-membered rings, made up by two octahedra and two tetrahedra, can be easily recognized. Screw axes generate an equivalent sheet at  $v \simeq \frac{3}{4}$ : sandwiched between these sheets is the one described in Fig. 1(b) made up of Al and M(3)octahedra, M(2) square pyramids and M(1), P(1) and P(6) tetrahedra. These polyhedra are linked to build chains which run in the [101] direction and in which six-membered rings, centred on twofold axes and similar to those found in the preceding sheet but rotated by 90°, may be recognized. The succession of these sheets in the [010] direction builds up a threedimensional framework, in the cavities of which X(1)to X(5), alkali and Ca<sup>2+</sup> cations are located.

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Fig. 1. Crystal structure of arrojadite seen along [010]. (a) Structural slab with cations at  $y \simeq \frac{1}{4}$ , showing the tetrahedra P(2) to P(5), the edge-sharing M(5) and M(6) octahedra and the corner-sharing M(4) and M(7) octahedra; triangles and squares correspond to Ca<sup>2+</sup> and Na<sup>+</sup> cations respectively. (b) Structural slab with cations at  $y \simeq \frac{1}{2}$ , showing the phosphate tetrahedra P(1) and P(4), both sharing a corner with the tetrahedron M(1), the Al octahedron in a special position and the edge-sharing M(3)octahedron and M(2) square pyramid. Circles and squares correspond to P<sup>5+</sup> and Na<sup>+</sup> cations respectively.