Abrahams, S. C., Sherwood, R. C., Bernstein, J. L. & Nassau, K. (1973*b*). *J. Solid State Chem.* **8**, 274–279.
Ammon, H. L. (1986). *CAD-4 PROFILE*. Unpublished.
Elemans, J. B. A. A. & Verschoor, G. C. (1973). *J. Inorg. Nucl. Chem.* **35**, 3183–3189.
Ghose, S. & Wan, C. (1974). *Acta Cryst.* B**30**, 965–974.
Ghose, S. & Wan, C. (1978). *Am. Mineral.* **63**, 172–179.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht).
Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* A**30**, 580–584.
Liminga, R. & Abrahams, S. C. (1976). *J. Appl. Cryst.* **9**, 243–244.
Liminga, R., Abrahams, S. C. & Bernstein, J. L. (1975). *J. Chem. Phys.* **62**, 4388–4399.
Liminga, R., Booles, S. R., Ghose, S. & Wan, C. (1978). *Acta Cryst.* B**34**, 2398–2402.
Nassau, K., Shiever, J. W. & Prescott, B. E. (1973). *J. Solid State Chem.* **7**, 186–204.
Nassau, K. Shiever, J. W., Prescott, B. E. & Cooper, A. S. (1974). *J. Solid State Chem.* **11**, 314–318.
Svensson, C., Albertsson, J., Liminga, R., Kvick, Å. & Abrahams, S. C. (1983). *J. Chem. Phys.* **78**, 7343–7352.
TEXSAN (1987). *Texray Structure Analysis System*. Version 2.0. Molecular Structure Corp., College Station, Texas.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.
Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.

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The Structure of Aluminium Iron Molybdate

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Abstract. Synthetic $AlFe(MoO_4)_3$, $M_r = 562{\cdot}64$, monoclinic, $P2_1/a$, $a = 15{\cdot}509\ (1)$, $b = 9{\cdot}1320\ (2)$, $c = 18{\cdot}021\ (1)$ Å, $\beta = 125{\cdot}306\ (5)°$, $V = 2082{\cdot}9\ (5)$ Å^3, $Z = 8$. The structure has been refined by Rietveld analysis of constant wavelength neutron powder diffraction data ($\lambda = 1{\cdot}909$ Å) recorded at $T = 4{\cdot}2$ K [$R_I = 3{\cdot}40$, $R_p = 6{\cdot}38$, $R_{wp} = 7{\cdot}12$, $R_{\rm exp} = 6{\cdot}63\%$]. It is isomorphous with the end member molybdates, $Fe_2(MoO_4)_3$ and $Al_2(MoO_4)_3$, without any detectable cation ordering. No magnetic ordering occurs at 4·2 K.

Introduction. The title compound was studied as part of our investigations into magnetic, structural and catalytic properties of $M_2(XO_4)_3$ type systems. Previous work has included $Fe_2(SO_4)_3$ (Long, Longworth, Battle, Cheetham, Thundathil & Beveridge, 1979), $Fe_2(MoO_4)_3$ (Battle, Cheetham, Long & Longworth, 1982), $Cr_2(MoO_4)_3$ (Battle, Cheetham, Harrison, Pollard & Faber, 1985), $Fe_2(WO_4)_3$ (Harrison, Chowdhry, Machiels, Sleight & Cheetham, 1986) and $Al_2(MoO_4)_3$ (Harrison, Cheetham & Faber, 1988). Pure, well characterized $M_2(MoO_4)_3$ type mixed molybdates of Fe, Cr and Al have been reported by Harrison (1986) and the catalytic properties of the aluminium-substituted iron molybdate, $Al_xFe_{2-x}(MoO_4)_3$ (Machiels, Chowdhry, Harrison & Sleight, 1985) have been discussed. The present work investigates the crystal structure of $AlFe(MoO_4)_3$.

Experimental. $AlFe(MoO_4)_3$ was synthesized from analytical grade reagents following the method of Machiels, Chowdhry, Harrison & Sleight (1985). X-ray powder diffraction patterns and analytical electron microscopy (Cheetham & Skarnulis, 1981) indicated that the product was single phase, homogeneous and crystalline. Neutron powder diffraction data were collected on the diffractometer D1a at ILL, Grenoble (Hewat & Bailey, 1976): mean neutron wavelength $\lambda = 1{\cdot}909$ Å; $6° \leq 2\theta \leq 145°$ in steps of 0·05°; vanadium tailed liquid helium 'orange' cryostat at 4·2 K; cylindrical vanadium sample can. Absorption was negligible and no correction was made. Data from the ten ^{3}He detectors were collated and normalized before refinement commenced (Hewat, 1978). A model was refined using the Rietveld profile method (Rietveld, 1969; Hewat, 1978) on a VAX 11-780 computer at Oxford University Computing Centre. A preliminary background subtraction was determined by extrapolation between those parts of the pattern containing no Bragg reflections at low angle and extended linearly to high angles. The structure of centrosymmetric monoclinic $Fe_2(MoO_4)_3$ (Chen, 1979) was used as a trial model. Coherent neutron scattering lengths were taken as: Fe/Al = 6·495 fm, Mo = 6·95 fm, O = 5·805 fm (Bacon, 1975). A total of 115 variable parameters including scale factor, four unit-cell constants, counter zero point error, empirical low-angle 'asymmetry correction', three Gaussian peak half-width variation parameters, 102 general atomic positional parameters and three atom-type isotropic thermal factors were included in the final full-matrix cycle of least-squares refinement. Refinement was terminated

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Table 1. *Final atomic coordinates and thermal factors for* $AlFe(MoO_4)_3$ *at* 4·2 K

	x	*y*	*z*
Fe/Al(1)	0·384 (1)	0·966 (1)	0·319 (1)
Fe/Al(2)	0·3673 (9)	0·460 (1)	0·0459 (8)
Fe/Al(3)	0·120 (1)	0·470 (1)	0·1839 (9)
Fe/Al(4)	0·1084 (9)	0·979 (1)	0·4176 (8)
Mo(1)	−0·0075 (9)	0·249 (1)	0·4855 (7)
Mo(2)	0·3591 (8)	0·122 (1)	0·1357 (7)
Mo(3)	0·1394 (9)	0·115 (1)	0·2499 (7)
Mo(4)	0·151 (1)	0·616 (1)	0·3828 (7)
Mo(5)	0·3523 (9)	0·629 (1)	0·2135 (6)
Mo(6)	−0·0023 (9)	0·740 (1)	0·0148 (7)
O(1)	0·5800 (9)	0·389 (1)	−0·0016 (8)
O(2)	0·990 (1)	0·409 (1)	0·1738 (9)
O(3)	0·825 (1)	0·186 (1)	0·0943 (8)
O(4)	0·774 (1)	0·499 (1)	0·0492 (9)
O(5)	0·5224 (9)	0·427 (1)	0·1456 (8)
O(6)	0·736 (1)	0·519 (1)	0·2743 (8)
O(7)	0·420 (1)	0·109 (1)	0·4128 (7)
O(8)	0·184 (1)	0·289 (1)	0·2487 (8)
O(9)	0·550 (1)	0·361 (1)	0·4450 (9)
O(10)	0·384 (1)	0·307 (1)	0·9744 (8)
O(11)	0·0670 (9)	0·378 (1)	0·0667 (8)
O(12)	0·410 (1)	0·357 (1)	0·5020 (8)
O(13)	0·855 (1)	0·385 (1)	0·2335 (8)
O(14)	0·2452 (9)	0·036 (1)	0·5106 (8)
O(15)	0·113 (1)	0·101 (1)	0·3359 (8)
O(16)	0·527 (1)	0·943 (1)	0·3571 (9)
O(17)	0·743 (1)	0·967 (1)	0·1931 (8)
O(18)	0·664 (1)	0·937 (1)	0·2978 (9)
O(19)	0·966 (1)	0·930 (1)	0·3172 (8)
O(20)	0·094 (1)	0·315 (1)	0·5940 (8)
O(21)	0·156 (1)	0·808 (1)	0·3885 (8)
O(22)	0·048 (1)	0·658 (1)	0·1218 (8)
O(23)	0·367 (1)	0·600 (1)	0·1273 (9)
O(24)	0·343 (1)	0·819 (1)	0·2285 (8)

All atoms on general Wyckoff positions 4(*e*).

Atom-type isotropic thermal factors (Å^2):

Fe/Al	1·01 (7)
Mo	1·25 (5)
O	0·99 (2)

Table 2. *Selected bond distances* (Å) *for* $AlFe(MoO_4)_3$ *at* 4·2 K

Fe/Al(1)–O(6)	1·95 (2)	Fe/Al(3)–O(2)	2·00 (2)
–O(7)	1·95 (2)	–O(8)	1·93 (1)
–O(13)	1·90 (2)	–O(11)	1·96 (2)
–O(16)	1·92 (2)	–O(17)	1·86 (2)
–O(20)	1·96 (2)	–O(18)	1·94 (2)
–O(24)	1·92 (2)	–O(22)	2·00 (1)
Average	1·93	Average	1·95
Fe/Al(2)–O(1)	1·98 (2)	Fe/Al(4)–O(9)	1·93 (2)
–O(3)	1·91 (2)	–O(12)	1·97 (2)
–O(4)	1·89 (1)	–O(14)	1·86 (1)
–O(5)	2·02 (1)	–O(15)	1·88 (2)
–O(10)	2·01 (2)	–O(19)	1·93 (1)
–O(23)	1·95 (2)	–O(21)	1·93 (2)
Average	1·96	Average	1·92

Average Fe/Al—O bond distance = 1·94 (2) Å; Shannon & Prewitt (1969). Average ionic radii sum for octahedral Fe^{3+}/Al^{3+} to O^{2-} = 1·94 Å.

Mo(1)–O(7)	1·72 (1)	Mo(4)–O(14)	1·80 (1)
–O(9)	1·76 (2)	–O(16)	1·78 (2)
–O(12)	1·76 (2)	–O(18)	1·73 (2)
–O(20)	1·76 (1)	–O(21)	1·76 (1)
Average	1·75	Average	1·77
Mo(2)–O(2)	1·75 (2)	Mo(5)–O(17)	1·78 (2)
–O(3)	1·86 (1)	–O(19)	1·76 (1)
–O(4)	1·74 (1)	–O(23)	1·72 (2)
–O(13)	1·80 (2)	–O(24)	1·77 (1)
Average	1·79	Average	1·75
Mo(3)–O(5)	1·74 (1)	Mo(6)–O(1)	1·74 (2)
–O(6)	1·78 (2)	–O(10)	1·83 (2)
–O(8)	1·74 (2)	–O(11)	1·62 (1)
–O(15)	1·82 (2)	–O(22)	1·77 (2)
Average	1·77	Average	1·74

Average Mo—O bond distance = 1·76 (2) Å; ionic radii sum = 1·76 Å.

when $\Delta/\sigma < 0{\cdot}1$. Standard calculated agreement factors (Rietveld, 1969) are listed in the *Abstract*. The final goodness-of-fit, $\chi^2 = 1{\cdot}15$ for 2387 reflections distributed over 2573 contributing profile points. Attempts to model the structure as that of the related $Al_2(WO_4)_3$ (Craig & Stephenson, 1968) or $Fe_2(SO_4)_3$ (Long, Longworth, Battle, Cheetham, Thundathil & Beveridge, 1979) resulted in substantially poorer profile fits.

Discussion. Atomic and selected profile parameters are given in Table 1 and selected bond distance data in Table 2. These were calculated using the program *ORFFE* (Busing, Martin & Levy, 1984). The final observed, calculated and difference profiles are illustrated in Fig. 1.* The structure consists of an open three-dimensional network of discrete corner-linked MO_6 (M = Fe, Al) octahedra (linking to six different MoO_4 units) and MoO_4 tetrahedra (linking to four different MO_6 units), as discussed earlier (Battle, Cheetham, Long & Longworth, 1982). No evidence for octahedral cation ordering was found, either by allowing Fe/Al site occupancies to vary or by a Nord type analysis (Nord, 1984) using fixed cation configurations and comparing the various profile fits. The final octahedral bond distances (Table 2) are also in agreement with a random mixture of Fe^{3+} and Al^{3+} on each site. Magnetic susceptibility measurements indicate that no magnetic ordering occurs at 4·2 K. Powder X-ray studies (Harrison, 1986) indicate that Vegard's Law is obeyed for the $Al_xFe_{2-x}(MoO_4)_3$ solid solution. The precision of the bond distances extracted is similar to that for $Al_2(MoO_4)_3$ (Harrison, Cheetham & Faber, 1988), but at least one of the contacts is chemically unreasonable: the Mo(6)—O(11) bond distance of 1·62 Å. The refinement of complex structures by the Rietveld method is discussed elsewhere (Fischer, Zolliker, Meier, Ernst, Hewat, Jorgensen & Rotella, 1986; Battle, Cheetham, Harrison, Pollard & Faber, 1985). In the present case, we suspect that strain associated with the disordered distribution of cations leads to peak broadening, thus limiting the quality of the data. Nevertheless, the present study has established the structure and cation distribution in $AlFe(MoO_4)_3$, and confirmed the absence of magnetic ordering at 4·2 K.

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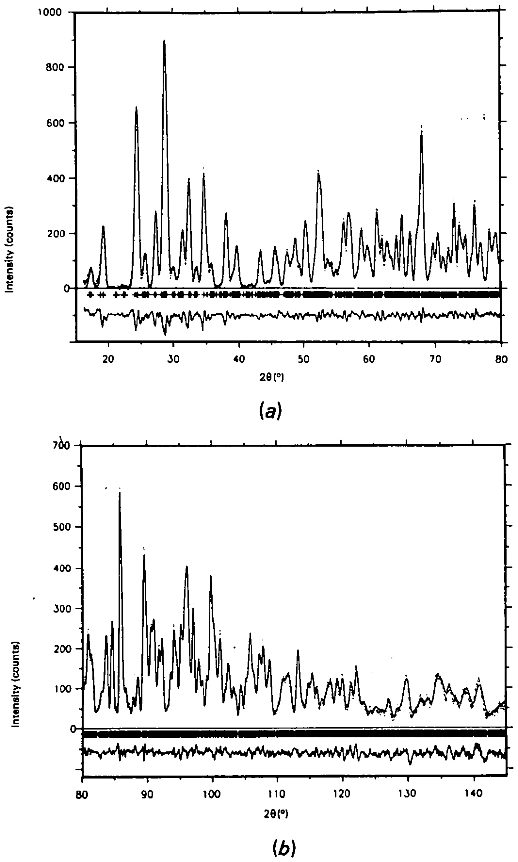
* A list of numerical values corresponding to the data in Fig. 1 has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51383 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



(a)

(b)

Fig. 1. Final profile plots for $AlFe(MoO_4)_3$. Observed data plotted as points, calculated as line. Difference profile and reflection positions included.

References

BACON, G. E. (1975). *Neutron Diffraction*. Oxford: Clarendon Press.

BATTLE, P. D., CHEETHAM, A. K., HARRISON, W. T. A., POLLARD, N. J. & FABER, J. JR (1985). *J. Solid State Chem.* **58**, 221.

BATTLE, P. D., CHEETHAM, A. K., LONG, G. J. & LONGWORTH, G. (1982). *Inorg. Chem.* **21**, 4223.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1984). *ORFFE*. Oak Ridge National Laboratory, Tennessee, USA.

CHEETHAM, A. K. & SKARNULIS, A. J. (1981). *Anal. Chem.* **53**, 1060.

CHEN, H. (1979). *Mater. Res. Bull.* **14**, 1583.

CRAIG, D. C. & STEPHENSON, N. C. (1968). *Acta Cryst.* B**24**, 1250–1255.

FISCHER, P., ZOLLIKER, P., MEIER, B. H., ERNST, R. R., HEWAT, A. W., JORGENSEN, J. D. & ROTELLA, F. J. (1986). *J. Solid State Chem.* **61**, 109–125.

HARRISON, W. T. A. (1986). PhD Thesis, Oxford Univ., England.

HARRISON, W. T. A., CHEETHAM, A. K. & FABER, J. JR (1988). *J. Solid State Chem.* **76**, 328–333.

HARRISON, W. T. A., CHOWDHRY, U., MACHIELS, C. J., SLEIGHT, A. W. & CHEETHAM, A. K. (1986). *J. Solid State Chem.* **60**, 101.

HEWAT, A. W. (1978). *Powder Rietveld Refinement System*. ILL, Grenoble.

HEWAT, A. W. & BAILEY, I. (1976). *Nucl. Instrum. Methods*, **137**, 462.

LONG, G. J., LONGWORTH, G., BATTLE, P., CHEETHAM, A. K., THUNDATHIL, R. V. & BEVERIDGE, D. (1979). *Inorg. Chem.* **18**, 624.

MACHIELS, C. J., CHOWDHRY, U., HARRISON, W. T. A. & SLEIGHT, A. W. (1985). In *Solid State Chemistry in Catalysis*, edited by R. K. GRASSELLI & J. F. BRAZDIL. ACS Symposium Series, Washington DC, USA.

NORD, A. G. (1984). *J. Appl. Cryst.* **17**, 55–60.

RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.

SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* B**25**, 925–946.

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Tetraamminbis[tetraiodothallat(III)]kupfer(II)

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Abstract. $[Cu(TlI_4)_2(NH_3)_4]$, $M_r = 1555{\cdot}671$, monoclinic, $P2_1/n$, $a = 7{\cdot}699\ (2)$, $b = 13{\cdot}997\ (4)$, $c = 11{\cdot}174\ (2)$ Å, $\beta = 95{\cdot}39\ (2)°$, $V = 1197{\cdot}9$ Å^3, $Z = 2$, $D_x = 4{\cdot}313$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 24{\cdot}639$ mm^{-1}, $F(000) = 2620$, $T = 299$ K, $R = 0{\cdot}035$ for 1658 reflections $[|F_o| \geq 3\sigma(F_o)]$. The structure consists of planar $Cu(NH_3)_4^{2+}$ complexes further coordinated by I atoms of slightly distorted TlI_4^- tetrahedra making a stretched octahedron. Bond lengths and angles are in the expected range.

Einleitung. Das Tetraamminbis[tetraiodothallat(III)]-kupfer(II) weicht in seinem Aussehen und Verhalten von dem anderer Tetraiodothallate ab (Cotton, Johnson & Wing, 1964). Die Farbe der stark glänzenden Kristalle ist dunkelrot-braun. Im offenen Gefäß oder beim Erhitzen erfolgt unter Abgabe von Ammoniak und Iod die Zersetzung zu einem Gemisch aus CuI and TlI. Darstellung und chemisches Verhalten weisen aber sonst auf einen üblichen Tetraiodo-Komplex des dreiwertigen Thalliums hin (Jörgensen, 1873). Zur

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