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Mo₄P₆Si₂O₂₅, an Mo^{III} Phosphosilicate Closely Related to V₃P₅SiO₁₉: Oxygen Non-stoichiometry in Silicophosphates

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Abstract. Mo₄P₆Si₂O₂₅, $M_r = 1025.76$, trigonal, $P\bar{3}$, $a = 14.705$ (4), $c = 7.3986$ (5) Å, $V = 1385.5$ (8) Å³, $Z = 3$, $D_x = 3.69$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 3.38$ mm⁻¹, $T = 294$ K, $F(000) = 1458$, $R = 0.065$ for 4016 observed reflections. The Mo has the valence III rarely observed in its oxides. The three-dimensional framework is built up from P₆Si₂O₂₅ units and Mo₂O₉ face-sharing clusters. The framework is very similar to that of V₃P₅SiO₁₉; both correspond to the general formulation $M_{12}P_{18+x}Si_{6-x}O_{75+x/2}$ ($0 \leq x \leq 6$). The structure shows also 'M₂P₆Si₂O₂₅' layers similar to those observed in other silicophosphates, but the stacking of these layers is different.

Introduction. Recent studies of oxides characterized by a mixed framework built up from octahedra and PO₄ and SiO₄ tetrahedra have shown the great ability of Mo to participate in the construction of such structures. Moreover, Mo offers a great diversity of oxidation states in those oxides, ranging from Mo^{VI} for MoP₂O₈ (Kierkegaard, 1962*a*), (MoO₂)₂P₂O₇ (Kierkegaard, 1962*b*), via Mo^V for K₄Mo₈P₁₂O₅₂ (Leclaire, Monier & Raveau, 1983) and Mo^{IV} for AMo₂P₃O₁₂ ($A = \text{K, Rb, Tl}$) (Leclaire, Monier & Raveau, 1985*a*; Leclaire & Raveau, 1988), to mixed-valence Mo^{IV-III} for AMo₃P₆Si₂O₂₅ ($A = \text{K, Rb, Tl, Cs}$) (Leclaire, Borel, Grandin & Raveau, 1985; Leclaire, Monier & Raveau, 1984; Leclaire, Monier & Raveau, 1985*b*) and finally to Mo^{III} for MoP₃SiO₁₁ (Leclaire & Raveau, 1987). Moreover, it appears that Mo^{III}, which is rather rarely observed in oxides, seems to be stabilized in those compounds, in the form of isolated MoO₆ octahedra. For this reason the investigation of the system Mo₂O₃-P₂O₅-SiO₂ was carried on further. The present work deals with the crystal structure of a new Mo^{III} oxide, Mo₄P₆Si₂O₂₅.

Experimental. The synthesis of the molybdenosilicophosphate Mo₄P₆Si₂O₂₅ in the form of a microcrystalline powder was carried out in two steps: First the oxides MoO₃, SiO₂ and the phosphate (NH₄)₂HPO₄ were mixed in adequate proportions for P, Si and O ($\rightarrow \text{Mo}_2\text{P}_6\text{Si}_2\text{O}_{25}$) and heated at 870 K in air in order to eliminate ammonia and water. Then, in the second step, metallic molybdenum was added to the resulting products to obtain adequate proportions. The mixture was homogenized by crushing, introduced into an evacuated silica ampoule and heated at 1470 K for several days. The samples were quenched at room temperature. Single crystals were grown in the following way: mixtures of MoO₃ and (NH₄)₂HPO₄ were first heated at 870 K in air as above, and the resulting mixture was then mixed with metallic molybdenum and heated directly in an evacuated silica ampoule without adding SiO₂, at about 1470 K. The crystals grew on the walls of the silica tube in the form of yellowish plates.

A yellow crystal with dimensions 0.41 × 0.24 × 0.10 mm was selected for the structure determination. Cell parameters were initially measured on precession films and later refined by diffractometric techniques at 294 K with a least-squares refinement based upon 25 reflections. The structure refinement could only be performed in the space group $P\bar{3}$. The data were collected on an Enraf-Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The intensities were measured up to $\theta = 41^\circ$ with an $\omega - \frac{4}{3}\theta$ scan of $(1.0 + 0.35\tan\theta)^\circ$ and a counter-slit aperture of $(1.0 + \tan\theta)$ mm, all determined after a study of some reflections in the $\omega\theta$ plane ($h -27 \rightarrow 0$, $k 0 \rightarrow 27$, $l 0 \rightarrow 9$). The background intensity was measured on both sides of each reflection. A periodic control of three reflections verified the stability of the sample. Of the 8063

Table 1. Atomic parameters and equivalent isotropic thermal parameters

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

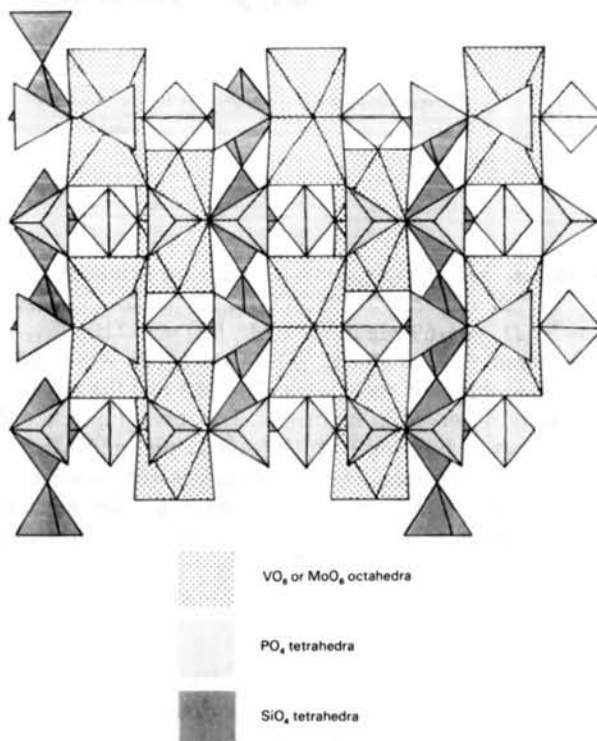
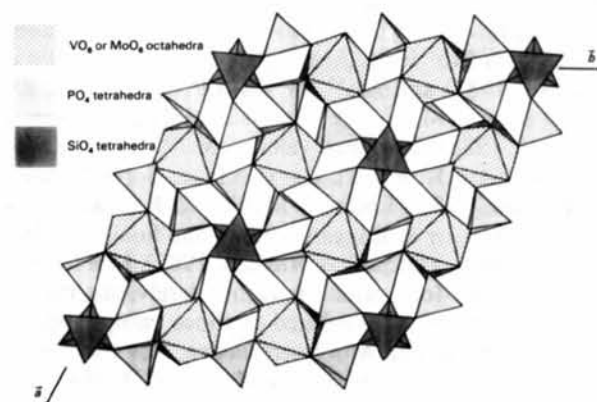
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Mo(1)	0.33924 (4)	0.34042 (4)	0.07322 (7)	0.39 (1)
Mo(2)	0.32866 (4)	0.32620 (4)	0.42460 (7)	0.39 (2)
P(1)	0.4368 (1)	0.1886 (1)	0.2501 (2)	0.43 (3)
P(2)	0.0856 (1)	0.2301 (1)	0.2470 (2)	0.42 (5)
P(3)	0.1036 (1)	-0.4776 (1)	0.2550 (2)	0.40 (5)
Si(1)	0.0	0.0	0.2895 (5)	0.19 (3)
Si(2)	↓	↓	0.2155 (6)	0.96 (9)
Si(3)	↓	↓	0.2163 (6)	1.10 (14)
O(1)	0.2063 (3)	0.3018 (4)	0.2422 (9)	0.75 (15)
O(2)	0.2521 (4)	0.2184 (4)	-0.0920 (8)	0.77 (6)
O(3)	0.3646 (4)	0.2369 (4)	0.2390 (8)	0.90 (16)
O(4)	0.4747 (4)	0.3786 (4)	-0.0710 (8)	0.95 (17)
O(5)	0.4303 (3)	0.4598 (3)	0.2674 (7)	0.48 (13)
O(6)	0.3026 (5)	0.4364 (5)	-0.0762 (9)	1.26 (19)
O(7)	0.2326 (4)	0.1891 (4)	-0.4313 (8)	0.61 (5)
O(8)	0.4545 (5)	0.3624 (4)	-0.4115 (9)	1.21 (19)
O(9)	0.2897 (5)	0.4122 (5)	-0.417 (1)	1.50 (21)
O(10)	0.0691 (3)	0.1177 (3)	0.2098 (7)	0.34 (5)
O(11)	0.0	0.0	0.50	0.70 (12)
O(12)	0.4057 (5)	-0.2155 (4)	0.282 (1)	1.41 (20)
O(13)	-0.2852 (4)	0.2638 (4)	0.285 (1)	1.32 (19)
O(14)	↓	↓	0.0007 (19)	1.30 (14)

independent reflections measured, 4016 reflections with $I > 3\sigma(I)$ were corrected for Lorentz and polarization effects; absorption corrections were performed with the program *AGNOST* (Coppens, Leiserowitz & Rabinovich, 1965; de Meulenaer & Tompa, 1965).

Atomic coordinates of the Mo ions and of the corresponding coordinated O atoms were fixed by the Patterson function and the other atoms were located by subsequent Fourier series. Anisotropic refinement on *F* of the atomic coordinates and their thermal motion by full-matrix least squares and a linear weighting scheme $w = f[(\sin \theta)/\lambda]$ adjusted using the program *POND* of Leclaire (unpublished) led to $R = 0.065$ and $wR = 0.074$, and to the atomic parameters* of Table 1. Scattering factors for Mo, P, Si and O were taken from *International Tables for X-ray Crystallography* (1974) and corrected for anomalous dispersion. $(\Delta/\sigma)_{\max} = 0.10$; $\Delta\rho < 2.00 \text{ e } \text{Å}^{-3}$.

Discussion. The three-dimensional view of the structure (Fig. 1) shows that the framework of Mo₄P₆Si₂O₂₅ is very similar to that of V₃P₅SiO₁₉ (Leclaire, Chahboun, Groult & Raveau, 1986) in spite of its different composition. One can recognize Mo₂O₉ units formed of two face-sharing octahedra, which are similar to the V₂O₉ clusters. In both structures the SiO₄ and PO₄ tetrahedra form P₆Si₂O₂₅ units which are built up from disilicate groups sharing their corners with six PO₄ tetrahedra (Fig. 2). The rows of Mo₂O₉ (or V₂O₉) clusters and of P₆Si₂O₂₅

running along *c* have exactly the same positions in the two structures: the Mo₂O₉ clusters share the corners of their octahedra with those of the PO₄ tetrahedra belonging to the P₆Si₂O₂₅ groups. The main difference between the two structures deals with the number of P₆Si₂O₂₅ columns running along *c*: in Mo₄P₆Si₂O₂₅ all the Mo₂O₉ clusters are linked through P₆Si₂O₂₅ units whereas in V₃P₅SiO₁₉ one P₆Si₂O₂₅ column out of three is replaced by columns built up from two P₄O₁₃ units. The configuration of two adjacent P₄O₁₃ units is in fact very close to that of a Si₂P₆O₂₅ unit: six PO₄ tetrahedra adopt the same configuration, and two P atoms take the

Fig. 1. Idealized projection along [120] on to (010) of Mo₄P₆Si₂O₂₅.Fig. 2. Projection of Mo₄P₆Si₂O₂₅ on (001).

*Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44889 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Distances (Å) and angles (°) in the polyhedra: the X—O distances are on the diagonal; above it are the O...O distances and below it are the O—X—O angles

Mo(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	2.144 (6)	2.983 (9)	2.92 (1)	4.21 (1)	2.937 (6)	2.945 (8)
O(2)	91.6 (2)	2.014 (5)	2.891 (9)	2.929 (7)	4.15 (1)	2.91 (1)
O(3)	86.4 (2)	88.5 (2)	2.127 (7)	2.974 (8)	2.924 (8)	4.19 (1)
O(4)	175.3 (2)	91.5 (2)	90.1 (3)	2.074 (6)	2.982 (9)	3.05 (1)
O(5)	86.5 (2)	174.7 (2)	86.5 (2)	90.1 (2)	2.142 (5)	3.076 (9)
O(6)	88.8 (3)	90.9 (3)	171.1 (2)	94.8 (3)	94.0 (2)	2.065 (8)
Mo(2)	O(1)	O(3)	O(5)	O(7)	O(8)	O(9)
O(1)	2.131 (6)	2.92 (1)	2.937 (6)	3.061 (9)	4.17 (1)	2.919 (9)
O(3)	86.4 (2)	2.140 (7)	2.924 (8)	2.974 (8)	3.066 (9)	4.15 (1)
O(5)	87.3 (2)	86.6 (2)	2.123 (4)	4.21 (1)	2.886 (9)	2.963 (9)
O(7)	93.1 (2)	89.5 (2)	176.0 (2)	2.085 (5)	2.974 (7)	2.96 (1)
O(8)	174.8 (2)	94.1 (3)	87.5 (2)	92.1 (2)	2.047 (7)	2.86 (1)
O(9)	89.7 (3)	175.7 (3)	91.6 (2)	92.4 (3)	89.7 (3)	2.008 (9)
P(1)	O(3)	O(6 ⁱⁱ)	O(9 ⁱⁱⁱ)	O(13 ⁱⁱⁱ)		
O(3)	1.548 (8)	2.54 (1)	2.50 (1)	2.46 (1)		
O(6 ⁱⁱ)	112.2 (3)	1.517 (7)	2.54 (1)	2.53 (1)		
O(9 ⁱⁱⁱ)	110.1 (3)	114.7 (5)	1.497 (8)	2.43 (1)		
O(13 ⁱⁱⁱ)	104.2 (3)	110.1 (4)	104.8 (4)	1.569 (8)		
P(2)	O(1)	O(2 ⁱⁱⁱ)	O(7 ⁱⁱⁱ)	O(10)		
O(1)	1.547 (5)	2.522 (9)	2.507 (9)	2.448 (6)		
O(2 ⁱⁱⁱ)	111.7 (4)	1.499 (6)	2.539 (8)	2.442 (7)		
O(7 ⁱⁱⁱ)	110.5 (4)	115.4 (5)	1.505 (6)	2.513 (7)		
O(10)	103.5 (3)	105.4 (3)	109.6 (3)	1.571 (6)		
P(3)	O(4 ^{iv})	O(5 ⁱⁱⁱ)	O(8 ^{iv})	O(12 ^v)		
O(4 ^{iv})	1.510 (6)	2.528 (7)	2.534 (9)	2.53 (1)		
O(5 ⁱⁱⁱ)	110.8 (3)	1.561 (5)	2.532 (7)	2.449 (8)		
O(8 ^{iv})	115.7 (3)	112.6 (3)	1.483 (7)	2.40 (1)		
O(12 ^v)	110.2 (4)	102.8 (3)	103.6 (4)	1.572 (7)		
Si(1)	O(10)	O(10 ^{vi})	O(10 ⁱⁱⁱ)	O(11)		
O(10)	1.618 (4)	2.610 (6)	2.610 (6)	2.623 (5)		
O(10 ^{vi})	107.5 (3)	1.618 (4)	2.610 (6)	2.623 (5)		
O(10 ⁱⁱⁱ)	107.5 (3)	107.5 (3)	1.618 (4)	2.623 (5)		
O(11)	111.4 (2)	111.4 (2)	111.4 (2)	1.557 (4)		
Si(2)	O(12)	O(12 ^v)	O(12 ⁱⁱⁱ)	O(14 ⁱⁱⁱ)		
O(12)	1.592 (6)	2.620 (8)	2.620 (8)	2.59 (1)		
O(12 ^v)	110.8 (4)	1.592 (6)	2.620 (8)	2.59 (1)		
O(12 ⁱⁱⁱ)	110.8 (4)	110.8 (4)	1.592 (6)	2.59 (1)		
O(14 ⁱⁱⁱ)	108.1 (3)	108.1 (3)	108.1 (3)	1.60 (2)		
Si(3)	O(13)	O(13 ^{iv})	O(13 ^v)	O(14)		
O(13)	1.590 (8)	2.61 (1)	2.61 (1)	2.59 (1)		
O(13 ^{iv})	110.3 (3)	1.590 (8)	2.61 (1)	2.59 (1)		
O(13 ^v)	110.3 (3)	110.3 (3)	1.590 (8)	2.59 (1)		
O(14)	108.6 (3)	108.6 (3)	108.6 (3)	1.60 (2)		

Symmetry code: (i) $x, y, 1+z$; (ii) $y, y-x, -z$; (iii) $y-x, -x, z$; (iv) $x-y, x-1, -z$; (v) $-y, x-y-1, z$; (vi) $-y, x-y, z$; (vii) $1+y-x, -x, z$; (viii) $-x, -y, -z$; (ix) $-y, 1+x-y, z$; (x) $y-x-1, -x, z$.

place of the Si atoms; but these latter PO₄ tetrahedra are not connected to each other contrary to the SiO₄ tetrahedra: they point their free vertex in the same direction along *c*. Consequently, the structure of Mo₄P₆Si₂O₂₅ (Mo₁₂P₁₈Si₆O₇₅) can be deduced from that of V₃P₅SiO₁₉ (V₁₂P₂₀Si₄O₇₆) by a simple replacement of V by Mo and a third of the P by Si, and by creation of anionic defects. Thus, these results show clearly, as previously foreseen by analysis of the structure of V₃P₅SiO₁₉, that this structure offers the possibility of a rather wide range of non-stoichiometry on oxygen corresponding to the general formulation M₁₂P_{18+x}Si_{6-x}O_{75+x/2} with 0 ≤ *x* ≤ 6; Mo₄P₆Si₂O₂₅ and V₃P₅SiO₁₉ correspond to the lower limit (*x* = 0) and the intermediate composition (*x* = 2), respectively, whereas the upper limit M₂P₄O₁₃ (*x* = 6) is hypothetical.

The PO₄ tetrahedra, characterized by O—O distances ranging from 2.40 to 2.54 Å (Table 2), appear as rather regular. However, examination of the P—O distances and O—P—O angles shows that the P atom is slightly off centre in its tetrahedron, namely 0.073–0.089 and 0.107 Å for P(1), P(2) and P(3) respectively. The distribution of the P—O distances in each tetrahedron is in agreement with the nature of the polyhedra linked to the PO₄ tetrahedra. The longest P—O distances (1.569–1.572 Å) are observed for O atoms common to the PO₄ and SiO₄ tetrahedra, the medium P—O distances (1.547–1.561 Å) correspond to the O atoms common to one PO₄ tetrahedron and two MoO₆ octahedra, and the two shortest ones (1.483–1.517 Å) to O atoms bridging a P and an Mo atom.

The SiO₄ tetrahedra are almost regular; O...O distances are close to 2.60 Å, and O—Si—O angles are close to the ideal value 109°.

The O—O distances, ranging from 2.86 to 3.06 Å, show that the MoO₆ octahedra are more regular than the VO₆ ones in V₃P₅SiO₁₉ (Leclaire *et al.*, 1986) in spite of their connection through one of their faces. The Mo ions exhibit three short distances (mean value 2.04 Å) and three longer ones (mean value 2.13 Å) as in MoP₃SiO₁₁ (Leclaire & Raveau, 1987) (2.084–2.104 Å), where the Mo^{III}O₆ octahedra are isolated from each other by PO₄ tetrahedra. The Mo atoms are less off-centre in their octahedra (about 0.08 Å) than the vanadium atoms in V₃P₅SiO₁₉ (about 0.22 Å) giving an Mo—Mo distance of 2.60 Å, shorter than the V—V distances of 2.90 Å.

The sum of the bond strengths for the two Mo atoms from the Zachariasen (1978) curves is about 3.2, confirming the low valency of the Mo.

It must also be pointed out that the oxide Mo₄P₆Si₂O₂₅ is also closely related to the oxides AMo₃P₆Si₂O₂₅ (Leclaire *et al.*, 1984, 1985*a,b*) and MoP₃SiO₁₁ (Leclaire & Raveau, 1987): all those frameworks exhibit similar Mo₂P₆Si₂O₂₅ layers parallel to the (001) plane in which P₆Si₂O₂₅ units are connected to MoO₆ octahedra. In those three structures the Si₂O₇ groups exhibit a staggered configuration, whereas a semi-eclipsed configuration is observed in V₃P₅SiO₁₉.

The three structures Mo₄P₆Si₂O₂₅, AMo₃P₆Si₂O₂₅ and MoP₃SiO₁₁ exhibit different stacking of identical Mo₂P₆Si₂O₂₅ layers. For MoP₃SiO₁₁ two adjacent layers are directly linked to each other, in such a way that the PO₄ tetrahedra of one layer share their corners with the PO₄ of the second layer. In AMo₃P₆Si₂O₂₅ two successive layers are connected to each other through a plane of octahedra which share their corners with those of the PO₄ of the layers. In Mo₄P₆Si₂O₂₅ two successive layers are also connected by octahedra but they share one of their faces with one octahedron of a layer and three corners with the PO₄ of the other layer.

As a conclusion the close relationships between these different oxides show that the mixed frameworks built

up from PO₄ and SiO₄ tetrahedra and from MoO₆ or VO₆ octahedra offer new possibilities of non-stoichiometry owing to their great flexibility. Moreover the chemistry of Mo^{III} and of mixed-valence compounds Mo^{III}-Mo^{IV} should be carried on further in those oxides.

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Structure of Bis(2,2'-bipyridine)dicyanoiron(III) Perchlorate

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Abstract. [Fe(CN)₂(C₁₀H₈N₂)₂](ClO₄), $M_r = 519.71$, orthorhombic, $P2_12_12_1$, $a = 10.950$ (6), $b = 11.941$ (2), $c = 16.912$ (4) Å, $U = 2211.1$ Å³, $D_x = 1.561$, $D_m = 1.551$ Mg m⁻³, $Z = 4$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.843$ mm⁻¹, $F(000) = 1060$, $T = 297$ (5) K. Final $R = 0.044$, $wR = 0.034$ for 1853 significant reflections. The iron atom is six coordinate. Each N atom of the two bipyridines and each C atom of the two cyanides shares in the coordination. The two cyanides are in the *cis* configuration. Both five-membered chelate rings are close to an envelope conformation. The two least-squares planes of each bipyridine moiety intersect at an angle of 86.1 (1)°. The two cyanides subtend 85.6 (3)° with the Fe atom as the vertex.

Introduction. Spectral data of Fe(CN)₂(L-L)^{0,+1}, where L-L = 2,2'-bipyridine or 1,10-phenanthroline, give contradictory results with respect to the geometry of these metal complexes. For example, the IR spectrum of Fe(CN)₂(bipy)₂ shows a single ν_{CN} at 2080 cm⁻¹ favoring a *trans* structure, but its ¹³C NMR data are better interpreted in terms of a *cis* geometry (Agarwala, Ramanathan & Khetrpal, 1985). To present a correct description for the structure of this type of metal complex, a representative of these series was examined by single-crystal X-ray diffraction methods. In this paper, the results of the investigations are reported.

Experimental. A bright red crystal of size 0.95 × 0.25 × 0.25 mm for X-ray structural analysis was obtained from a slow addition of NaClO₄ solution (0.20 g in 5 mL water) to Fe(CN)₂(bipy)₂ ion in hydrochloric acid (1 M). The Fe cation was generated by passing Cl gas into a suspension of 0.50 g of Fe(CN)₂(bipy)₂ in 50 mL of 1 M hydrochloric acid (Schilt, 1960). D_m by flotation (CCl₄ + CHCl₃), CAD-4 diffractometer, setting angles of 25 reflections ($18.76 < 2\theta < 26.64^\circ$) used to determine unit-cell constants and crystal orientation. $[(\sin\theta)/\lambda]_{\text{max}} = 0.594$ Å⁻¹ ($0 \leq h \leq 12$, $0 \leq k \leq 14$, $0 \leq l \leq 20$), ω - 2θ scan, width = $2(0.8 + 0.35 \tan\theta)^\circ$, 2θ scan speed = 20/2 to 20/13° min⁻¹, graphite-monochromated Mo $K\alpha$ radiation. Three standard reflections (512, $\bar{5}12$, $5\bar{1}2$) monitored every 2 h, varied within $3\sigma(I)$. 2388 reflections collected, 1853 observed with $I > 2.5\sigma(I)$. Empirical absorption correction based on azimuthal rotation from three reflections: 20 $\bar{1}$, $\bar{5}12$, $\bar{6}03$ (North, Phillips & Mathews, 1968). The minimum, maximum and average normalized correction factors are 0.9235, 0.9998 and 0.9701 respectively. The position of the Fe atom was determined by Patterson synthesis. Other atoms were located by successive difference Fourier synthesis and full-matrix least-squares fit. The positions of the H atoms were located by calculation through the assumption that they were in the radial direction of the pyridines and at a CH bond length of