O2^i—Re—O1	179.56 (14)	O4^i—Re—Cl1	91.50 (12)
O2^i—Re—O4^i	89.5 (2)	O3—Re—Cl1	88.95 (12)
O1—Re—O4^i	90.4 (2)		

Symmetry code: (i) $-x, 1-y, -z$.

The title structure was solved *via* direct methods and all non-H atoms were refined with anisotropic displacement parameters. A molecule of dichloromethane resides on a general position. H atoms were placed in idealized positions with C—H distances of 0.93 Å. The common orientation of the displacement ellipsoids of the core atoms of the molecule suggests the presence of systematic error, most probably associated with the effects of residual effects of uncorrected absorption. It is therefore to be anticipated that a small systematic error is associated with the atomic positions and necessarily with the bond lengths and angles involving these atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL93*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BS1024). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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6-L-Alanineferrirubin, a Ferrichrome-type Siderophore from the Fungus *Aspergillus ochraceous*

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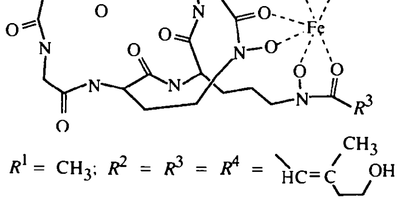
Abstract

The molecular structure of 6-L-alanineferrirubin tetradecahydrate, $[Fe(C_{41}H_{64}N_9O_{16})].14H_2O$, has been determined in order to confirm its chemical structure. The structural results show that the presence of an alanine in place of a serine or a glycine at position 6 in the cyclic hexapeptide has very little effect on the conformation of the 18-membered ring or on the geometry of the octahedral iron coordination.

Comment

The ferrichrome-type siderophores are a group of iron-chelating cyclic hexapeptides produced by a number of fungal species in response to low iron availability (Neilands, 1981). All the hexapeptides in this family have the general formula cyclo{Orn1–Orn2–Orn3–*A*–*B*–Gly}, where Orn1, Orn2 and Orn3 are *N*-acylated-*N*-hydroxyornithine residues, and *A* and *B* are either glycine or serine, and sometimes alanine, as in ferrichrome C (Tademura & Sato, 1967) and malinochrome (Emery, 1980). The *N*-acyl groups are derivatives of carboxylic acids.

Asperchromes are a group of new siderophores belonging to the ferrichrome family isolated from the fungus *Aspergillus ochraceous*. Most of them are characterized by having heterogeneous *N*-acyl groups, a feature which was not observed previously in ferrichromes. The isolation and description of their chemical structures



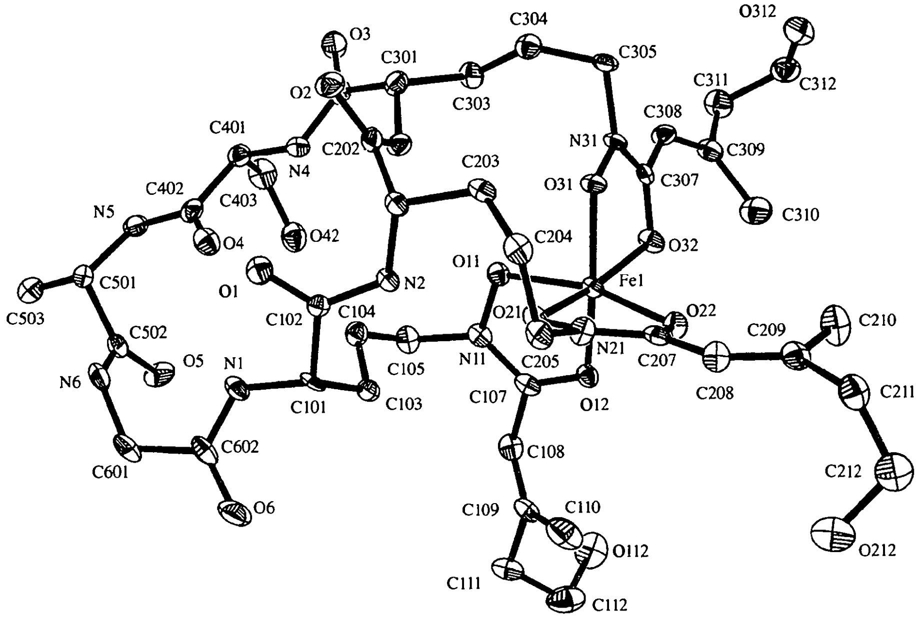


Fig. 1. Perspective drawing of the title molecule showing the atom-numbering scheme. The displacement ellipsoids correspond to 50% probability contours and H atoms have been omitted for clarity.

have been reported earlier (Jalal *et al.*, 1984). The crystal structures of two of the asperchromes (B1 and D1) have also been reported (Jalal, Hossain, van der Helm & Barnes, 1988). 6-L-Alanineferrirubin (asperchrome A) is different from the other asperchromes in that it has three homogeneous *N*-acyl groups, derived from *trans*-anhydromevalonic acid, as in ferrirubin (Barnes *et al.*, 1985), but differing from this compound in having the serine in position 6 replaced by alanine.

In the solid state, 6-L-alanineferrirubin displays all the common features of ferrichrome-type siderophores, the *Λ-cis* coordination for the iron and a hexapeptide ring conformation with two β-turns, *i.e.* a β(II) turn resulting in an N1—H···O4 hydrogen bond [3.021 (7) Å] and a β(I) turn without any N4—H···O1 [4.280 (8) Å] hydrogen bond. It also has the commonly observed intramolecular hydrogen bond [N2—H···O21 2.790 (7) Å] linking the peptide backbone with the iron coordination. The substitution of an alanine in place of a serine at residue 6 seems to have very little effect on the conformation of the 18-membered peptide ring. The r.m.s. difference of the 18 endocyclic torsion angles of 6-L-alanineferrirubin and ferrirubin is less than 3° (Barnes *et al.*, 1985). The iron coordination geometry in 6-L-alanineferrirubin also shows a remarkable similarity with that of the ferrirubin molecule.

Like most of the ferrichrome-type siderophores, the crystal structure of 6-L-alanineferrirubin is heavily hydrated. All the 14 water molecules are extensively hydrogen bonded among themselves and with the 6-L-alanineferrirubin molecules. There are no intermolecular hydrogen bonds.

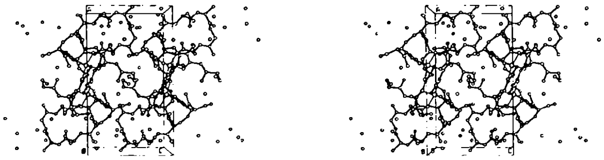


Fig. 2. A stereoview of the packing down the crystallographic *b* axis.

Experimental

6-L-Alanineferrirubin was crystallized from aqueous solution by slow evaporation. The small prismatic crystals were unstable at room temperature but were found to be suitable for data collection at low temperature.

Crystal data

$[\mathrm{Fe(C_{41}H_{64}N_9O_{16})}].14\mathrm{H_2O}$
$M_r = 1247.07$
Monoclinic
$P2_1$
$a = 19.903\ (6)$ Å
$b = 13.757\ (5)$ Å
$c = 10.966\ (4)$ Å
$\beta = 90.39\ (2)°$
$V = 3002.5\ (18)$ Å^3
$Z = 2$
$D_x = 1.379$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 44 reflections
$\theta = 10\text{–}14°$
$\mu = 0.345$ mm^{-1}
$T = 163\ (2)$ K
Prism
0.30 × 0.22 × 0.17 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none

$\theta_{\max} = 26.44°$
$h = -24 \rightarrow 24$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 13$

6423 measured reflections
6423 independent reflections
5471 reflections with $I > 2\sigma(I)$
3 standard reflections
frequency: 120 min
intensity decay: 4.5%

Refinement

Refinement on F^2
$R(F) = 0.0648$
$wR(F^2) = 0.1628$
$S = 1.079$
6416 reflections
730 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0864P)^2 + 6.0425P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.075$
$\Delta\rho_{\rm max} = 0.72$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.62$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.02 (3)

Table 1. *Selected geometric parameters (Å, °)*

Fe1—O31	1.974 (4)	C202—N3	1.349 (9)
Fe1—O21	1.989 (5)	C205—N21	1.481 (9)
Fe1—O22	2.010 (5)	N21—C207	1.319 (9)
Fe1—O11	2.012 (4)	N3—C301	1.462 (8)
Fe1—O12	2.026 (4)	C301—C302	1.524 (9)
Fe1—O32	2.031 (5)	C301—C303	1.543 (9)
O11—N11	1.380 (7)	C302—O3	1.241 (8)
O12—C107	1.271 (8)	C302—N4	1.325 (9)
O21—N21	1.368 (7)	C305—N31	1.468 (7)
O22—C207	1.296 (9)	N31—C307	1.323 (9)
O31—N31	1.377 (7)	N4—C401	1.460 (8)
O32—C307	1.282 (8)	C401—C403	1.511 (10)
N1—C602	1.307 (8)	C401—C402	1.531 (10)
N1—C101	1.449 (8)	C402—O4	1.252 (9)
C101—C103	1.538 (9)	C402—N5	1.330 (9)
C101—C102	1.543 (8)	C403—O42	1.409 (9)
C102—O1	1.233 (8)	N5—C501	1.481 (9)
C102—N2	1.332 (8)	C501—C502	1.504 (9)
C105—N11	1.456 (8)	C501—C503	1.535 (9)
N11—C107	1.316 (9)	C502—O5	1.249 (9)
N2—C201	1.476 (8)	C502—N6	1.323 (10)
C201—C202	1.534 (9)	N6—C601	1.464 (9)
C201—C203	1.529 (9)	C601—C602	1.517 (10)
C202—O2	1.231 (8)	C602—O6	1.254 (9)
O31—Fe1—O21	91.3 (2)	N3—C202—C201	116.1 (6)
O31—Fe1—O22	97.1 (2)	C207—N21—O21	116.6 (5)
O21—Fe1—O22	78.0 (2)	C207—N21—C205	129.5 (6)
O31—Fe1—O11	92.0 (2)	O21—N21—C205	113.8 (5)
O21—Fe1—O11	87.2 (2)	O22—C207—N21	116.7 (6)
O22—Fe1—O11	162.7 (2)	O22—C207—C208	122.4 (6)
O31—Fe1—O12	163.9 (2)	N21—C207—C208	120.8 (6)
O21—Fe1—O12	101.2 (2)	C202—N3—C301	122.4 (6)
O22—Fe1—O12	95.4 (2)	N3—C301—C302	113.7 (5)
O11—Fe1—O12	78.7 (2)	N3—C301—C303	108.5 (5)
O31—Fe1—O32	78.2 (2)	C302—C301—C303	112.1 (6)
O21—Fe1—O32	169.0 (2)	O3—C302—N4	123.2 (6)
O22—Fe1—O32	99.6 (2)	O3—C302—C301	119.0 (6)
O11—Fe1—O32	96.6 (2)	N4—C302—C301	117.8 (6)
O12—Fe1—O32	89.7 (2)	C307—N31—O31	116.1 (5)
N11—O11—Fe1	110.2 (3)	C307—N31—C305	129.6 (6)
C107—O12—Fe1	113.0 (4)	O31—N31—C305	114.1 (5)
N21—O21—Fe1	111.7 (4)	O32—C307—N31	117.7 (6)
C207—O22—Fe1	114.0 (4)	O32—C307—C308	123.2 (6)
N31—O31—Fe1	111.7 (3)	N31—C307—C308	119.0 (5)
C307—O32—Fe1	112.8 (4)	C302—N4—C401	123.7 (6)
C602—N1—C101	122.8 (6)	N4—C401—C403	112.9 (6)
N1—C101—C103	112.6 (5)	N4—C401—C402	106.0 (6)
N1—C101—C102	107.2 (5)	C403—C401—C402	112.5 (6)
C103—C101—C102	113.8 (5)	O4—C402—N5	122.2 (6)
O1—C102—N2	122.0 (6)	O4—C402—C401	120.8 (6)
O1—C102—C101	120.2 (5)	N5—C402—C401	117.0 (6)
N2—C102—C101	117.7 (5)	O42—C403—C401	113.1 (6)
C107—N11—O11	116.9 (5)	C402—N5—C501	119.6 (6)
C107—N11—C105	127.3 (5)	N5—C501—C502	110.8 (5)
O11—N11—C105	115.3 (5)	N5—C501—C503	109.9 (6)
O12—C107—N11	119.1 (6)	C502—C501—C503	107.2 (5)
O12—C107—C108	122.0 (6)	O5—C502—N6	121.4 (6)
N11—C107—C108	119.0 (6)	O5—C502—C501	122.5 (7)
C102—N2—C201	118.7 (5)	N6—C502—C501	116.0 (6)
N2—C201—C202	110.8 (5)	C502—N6—C601	122.0 (6)
N2—C201—C203	112.0 (5)	N6—C601—C602	115.9 (5)
C202—C201—C203	109.3 (5)	O6—C602—N1	124.0 (6)
O2—C202—N3	122.2 (6)	O6—C602—C601	119.3 (6)
O2—C202—C201	121.6 (6)	N1—C602—C601	116.7 (6)
C602—N1—C101—C102	−149.7 (6)		
N1—C101—C102—N2	−167.7 (5)		
C101—C102—N2—C201	−177.9 (5)		
C102—N2—C201—C202	−70.5 (7)		
N2—C201—C202—N3	−47.8 (7)		
C201—C202—N3—C301	−164.6 (5)		
C202—N3—C301—C302	−103.6 (8)		
N3—C301—C302—N4	2.6 (9)		
C301—C302—N4—C401	172.7 (6)		
C302—N4—C401—C402	−161.6 (6)		
N4—C401—C402—N5	179.2 (6)		
C401—C402—N5—C501	−175.0 (6)		
C402—N5—C501—C502	−55.3 (8)		
N5—C501—C502—N6	133.2 (6)		
C501—C502—N6—C601	176.7 (6)		
C502—N6—C601—C602	81.2 (8)		
C101—N1—C602—C601	179.6 (6)		
N6—C601—C602—N1	3.5 (10)		

All the H atoms were placed in calculated positions, riding on their attached atoms, with atomic displacement coefficients 1.2 times the $U_{\rm eq}$ values of the attached atom. No attempts were made to locate the H atoms of the water molecules.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: local program. Data reduction: local program. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXL*93 and *PLUTO* (Motherwell & Clegg, 1978).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BS1004). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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