

Discussion. The unit cell of the *A* lattice contains eight crystallographically equivalent BEDT-TTF cations, four HgBr₄ anions, and four disordered TCE molecules. The BEDT-TTF long molecular axis is parallel to the *ac* plane, while the molecular plane is tilted out of the *ac* plane by about 25°. The molecules are stacked along the short 4.202 Å axis. The stacks are interlinked by short S...S interactions to form sheets parallel to the *bc* plane (Fig. 2). The shortness of the *b* axis repeat [shorter than any repeat listed by Williams *et al.* (1987)] limits the tilting of the molecules, and thereby the occurrence of S...S distances much shorter than the translation period. In terms of the classification of Williams *et al.* (1987) the stacking is type *a* with a negligible offset, while the interstack arrangement is described by *L* and *W* for center of symmetry and screw-axis related molecules respectively. In terms of the same classification the unit cell can be described as (1,4,2).

HgBr₄ anions form ordered columns along the *b* axis, with a repeat period twice that of the BEDT-TTF lattice. This leads to half occupancy for Hg, Br1 and Br2. The separation of the two Br3 atoms of the HgBr₄ anion is almost exactly equal to *y*_A, giving full occupancy for this atom (Fig. 3).

The occurrence of diffuse reciprocal-lattice lines at $b_B^* = 0.5b_A^*$ indicates the existence of ordered domains of limited size. From the length of the segments along *a*^{*}, the correlation length is estimated to be about two unit cells, *i.e.* approximately eight HgBr₄ columns. The solvent molecules are interspersed between the anions in a highly disordered arrangement. The inclusion of disordered TCE solvent molecules has also been reported for (BEDT-TTF)₂-ClO₄.0.5TCE (Kobayashi, Kobayashi, Sasaki, Saito, Enoki & Inokuchi, 1983).

A number of other bromomercurate salts of BEDT-TTF have been described in the literature. Lyubovskaya *et al.* (1987) describe the low-

temperature superconductor (BEDT-TTF)₄Hg_{2.89}Br₈ with an apparently composite structure, while Mori, Wang, Imaeda, Enoki & Inokuchi (1987) report a semiconductor and a conductor, (BEDT-TTF)HgBr₃ and (BEDT-TTF)₅Hg₃Br₁₁. In the latter compound, BEDT-TTF ions with several different charges coexist, as shown by the analyses of the bond lengths (Mori *et al.*, 1987; Umland, Allie, Kuhlmann & Coppens, 1988). The bond lengths in the present structure are not sufficiently accurate for a reliable prediction, but we note that the BEDT-TTF molecules carry a formal charge of +1.

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Structure and Molecular Mechanics of Ferrirhodin

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Abstract. C₄₁H₆₄FeN₉O_{17.7}·¹/₂H₂O, *M*_r = 1146.0, orthorhombic, *P*2₁2₁2₁, *a* = 9.740 (7), *b* = 16.764 (10), *c* = 32.632 (17) Å, *V* = 5328 (6) Å³, *Z* = 4, *D*_x = 1.43 g cm⁻³, *Mo Kα*, λ = 0.71069 Å, μ =

3.26 cm⁻¹, *F*(000) = 2428, *T* = 138 (2) K, *R* = 0.0986 for 3543 observed reflections. Ferrirhodin, a ferrichrome siderophore (iron transport agent) was isolated from low-iron cultures of *Aspergillus*

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Molecular mechanics. All-atom model; force field given as a sum of strain energies for bond distances, bond angles and torsion angles, non-bonded interactions: Lennard-Jones and Coulomb-type contributions, corrections for hydrogen bonding. Calculations performed with molecular-mechanics program *AMBER* (Weiner & Kollman, 1981; Singh, Weiner, Caldwell & Kollman, 1986). Iron coordination: geometry reproduced with only the non-bonded interactions. The 1–4 van der Waals and 1–4 electrostatic interactions were scaled by a factor of 0.5, the well depth of the iron Lennard-Jones potential was set at 0.42 kJ mol⁻¹, while the iron van der Waals radius was adjusted to reproduce the mean X-ray Fe—O distance of 2.01 Å which gives the Fe radius of 0.80 Å. This compares to Fe³⁺ crystal and ionic radii of 0.785 and 0.645 Å, respectively (Shannon, 1976). Partial atomic charges were adopted from both the *ab initio* and the experimental electron density studies of model systems (Fidelis & van der Helm, 1990); steepest-descent/conjugate-gradient energy minimization performed *in vacuo*, $\epsilon = 4r$, to an energy gradient of 0.042 kJ mol⁻¹ Å⁻¹.

Discussion. The ferrirhodin numbering scheme, given with the structural formula of the molecule in Fig. 1, follows the convention of the IUPAC-IUB Commission on Biochemical Nomenclature (1970). Final atomic parameters and a stereo *ORTEP* plot of the molecule are given in Table 1* and Fig. 2.

Although the accuracy of the ferrirhodin structure is limited, the average peptide bond parameters, Table 2, compare very well with those observed in peptides (Karle, 1981). Similarly, the iron chelation geometry, Fig. 3 and Table 2, does not deviate

* Lists of structure factors, anisotropic thermal parameters, bond distances and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52842 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

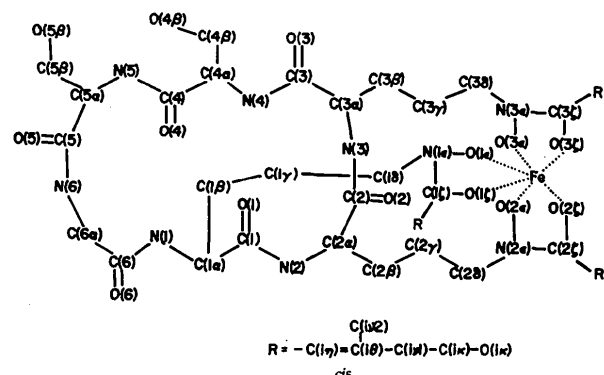


Fig. 1. Structural formula and atom-numbering scheme.

Table 1. Atomic coordinates and equivalent isotropic temperature factors with *e.s.d.*'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i U_{ii}$$

	x	y	z	U_{eq} (Å ²)
Fe	0.3666 (2)	0.11188 (9)	0.86950 (5)	0.0349 (5)
N(1)	0.3472 (13)	0.3084 (5)	0.6878 (3)	0.044 (2)
C(1 α)	0.2941 (14)	0.2925 (6)	0.7289 (4)	0.035 (2)
C(1 β)	0.3029 (13)	0.2014 (6)	0.7385 (4)	0.035 (2)
C(1 γ)	0.4510 (13)	0.1702 (6)	0.7361 (3)	0.031 (2)
C(1 δ)	0.4571 (13)	0.0797 (6)	0.7456 (3)	0.032 (2)
N(1 ϵ)	0.4045 (11)	0.0671 (5)	0.7880 (3)	0.036 (2)
O(1 ϵ)	0.4772 (10)	0.1050 (4)	0.8178 (2)	0.038 (2)
C(1 ζ)	0.2865 (15)	0.0305 (6)	0.7984 (4)	0.040 (2)
O(1 ζ)	0.2602 (11)	0.0320 (5)	0.8372 (3)	0.055 (2)
C(1 η)	0.201 (2)	-0.0064 (7)	0.7681 (4)	0.060 (2)
C(1 θ)	0.0595 (14)	-0.0098 (8)	0.7692 (5)	0.053 (2)
C(1 ν 1)	-0.027 (3)	0.037 (2)	0.8052 (9)	0.165 (3)
C(1 ν 2)	-0.017 (2)	-0.0429 (8)	0.7316 (4)	0.051 (2)
C(1 κ)	-0.036 (3)	-0.0367 (15)	0.8386 (13)	0.195 (3)
O(1 κ)	-0.169 (3)	0.011 (2)	0.8590 (7)	0.422 (3)
C(1)	0.3773 (13)	0.3468 (5)	0.7591 (3)	0.026 (2)
O(1)	0.4391 (11)	0.4061 (4)	0.7460 (2)	0.045 (2)
N(2)	0.3753 (10)	0.3305 (5)	0.7985 (3)	0.028 (2)
C(2 α)	0.4443 (11)	0.3841 (7)	0.8263 (3)	0.030 (2)
C(2 β)	0.4094 (11)	0.3704 (6)	0.8726 (3)	0.027 (2)
C(2 γ)	0.2607 (13)	0.3885 (8)	0.8859 (4)	0.042 (2)
C(2 δ)	0.1518 (12)	0.3254 (8)	0.8723 (4)	0.045 (2)
N(2 ϵ)	0.1941 (10)	0.2450 (6)	0.8829 (3)	0.035 (2)
O(2 ϵ)	0.2719 (8)	0.2100 (5)	0.8513 (2)	0.035 (2)
C(2 ζ)	0.1746 (14)	0.1989 (8)	0.9158 (4)	0.044 (2)
O(2 ζ)	0.2248 (9)	0.1282 (4)	0.9148 (2)	0.038 (2)
C(2 η)	0.0861 (13)	0.2295 (8)	0.9480 (4)	0.043 (2)
C(2 θ)	0.045 (2)	0.1902 (9)	0.9832 (4)	0.054 (2)
C(2 ν 1)	0.121 (2)	0.1167 (13)	0.9969 (6)	0.122 (2)
C(2 ν 2)	-0.040 (2)	0.2266 (10)	1.0131 (4)	0.062 (2)
C(2 κ)	0.031 (3)	0.0456 (14)	0.9863 (9)	0.129 (3)
O(2 κ)	0.032 (2)	0.0294 (12)	0.9421 (8)	0.110 (2)
O(2 κ) ^A	0.037 (4)	-0.043 (2)	0.994 (2)	0.214 (3)
C(2)	0.6017 (12)	0.3786 (6)	0.8236 (3)	0.030 (2)
O(2)	0.6729 (10)	0.4381 (5)	0.8262 (3)	0.045 (2)
N(3)	0.6552 (11)	0.3035 (5)	0.8210 (3)	0.035 (2)
C(3 α)	0.7988 (12)	0.2864 (7)	0.8274 (4)	0.032 (2)
C(3 β)	0.8150 (15)	0.2163 (8)	0.8588 (4)	0.049 (2)
C(3 γ)	0.7698 (14)	0.2444 (7)	0.9015 (4)	0.043 (2)
C(3 δ)	0.7336 (13)	0.1719 (8)	0.9294 (4)	0.040 (2)
N(3 ϵ)	0.6093 (11)	0.1292 (5)	0.9131 (3)	0.033 (2)
O(3 ϵ)	0.5152 (8)	0.1755 (4)	0.8936 (2)	0.029 (2)
C(3 ζ)	0.5750 (15)	0.0553 (6)	0.9193 (4)	0.038 (2)
O(3 ζ)	0.4661 (13)	0.0277 (4)	0.9043 (3)	0.057 (2)
C(3 η)	0.670 (2)	0.0001 (8)	0.9412 (4)	0.059 (2)
C(3 θ)	0.640 (2)	-0.0348 (7)	0.9772 (4)	0.062 (2)
C(3 ν 1)	0.492 (2)	-0.0120 (9)	0.9979 (4)	0.068 (2)
C(3 ν 2)	0.721 (2)	-0.0942 (10)	0.9961 (5)	0.097 (2)
C(3 κ)	0.539 (2)	0.0457 (9)	1.0358 (6)	0.068 (2)
O(3 κ)	0.426 (2)	0.0804 (8)	1.0554 (4)	0.103 (2)
C(3)	0.878 (2)	0.2695 (6)	0.7881 (4)	0.043 (2)
O(3)	1.0024 (8)	0.2558 (6)	0.7893 (3)	0.044 (2)
N(4)	0.8036 (11)	0.2730 (6)	0.7530 (3)	0.041 (2)
C(4 α)	0.866 (2)	0.2629 (8)	0.7137 (4)	0.054 (2)
C(4 β)	0.902 (2)	0.1731 (8)	0.7057 (4)	0.050 (2)
O(4 β)	0.7844 (11)	0.1264 (6)	0.7051 (3)	0.062 (2)
C(4)	0.764 (2)	0.2955 (7)	0.6824 (4)	0.046 (2)
O(4)	0.6503 (10)	0.3158 (5)	0.6929 (2)	0.039 (2)
N(5)	0.8119 (13)	0.3044 (6)	0.6444 (3)	0.050 (2)
C(5 α)	0.728 (2)	0.3442 (10)	0.6150 (5)	0.064 (2)
C(5 β)	0.787 (2)	0.3363 (12)	0.5709 (5)	0.076 (2)
O(5 β)	0.928 (2)	0.3643 (11)	0.5711 (6)	0.140 (2)
C(5)	0.583 (2)	0.3027 (8)	0.6124 (4)	0.057 (2)
O(5)	0.5772 (14)	0.2274 (6)	0.6098 (3)	0.076 (2)
N(6)	0.4731 (13)	0.3484 (6)	0.6144 (3)	0.042 (2)
C(6 α)	0.3342 (15)	0.3173 (8)	0.6143 (4)	0.049 (2)
C(6)	0.2685 (15)	0.2976 (7)	0.6545 (4)	0.043 (2)
O(6)	0.1479 (11)	0.2745 (6)	0.6559 (3)	0.056 (2)
W(1)	0.2654 (15)	0.3939 (8)	0.3819 (4)	0.099 (3)
W(2)	-0.366 (2)	-0.0176 (8)	0.8310 (4)	0.091 (3)
W(3)	0.062 (2)	0.1559 (8)	0.6015 (4)	0.099 (3)
W(4)	0.233 (2)	0.0228 (9)	0.6053 (5)	0.115 (3)
W(5)	0.137 (2)	0.2133 (14)	0.5243 (7)	0.184 (4)
W(6)	0.427 (2)	0.1934 (13)	0.5206 (7)	0.166 (4)
W(7) [†]	0.483 (2)	0.0588 (13)	0.5712 (7)	0.068 (4)
W(8) [†]	0.205 (4)	0.074 (3)	0.659 (2)	0.298 (4)
W(9) [†]	0.389 (4)	0.083 (3)	0.600 (2)	0.300 (4)

* Disordered atom. Atom marked *A* has 30% occupancy.

[†] 50% occupancy.

Table 2. Comparison of the average geometrical parameters of the peptide bond (\AA , $^\circ$) with those given by Karle (1981) and comparison of the iron coordination geometry

	Ferrirhodin	Karle
$N(i)-C(ia)$	1.442 (17)	1.449
$C(ia)-C(i)$	1.540 (19)	1.522
$C(i)-O(i)$	1.233 (16)	1.229
$C(i)-N(i+1)$	1.338 (17)	1.335
$C(i-1)-N(i)-C(ia)$	121.0 (11)	121.9
$C(ia)-C(i)-O(i)$	120.2 (11)	120.4
$C(ia)-C(i)-N(i+1)$	116.7 (11)	116.6
$O(i)-C(i)-N(i+1)$	123.1 (12)	122.9

Average e.s.d.'s are given in parentheses.

	Ferrirhodin	Ferrichromes*
Fe—O(ϵ)	1.982 (8)	1.986
Fe—O(ζ)	2.030 (9)	2.030
N—O(ϵ)	1.375 (12)	1.382
C—O(ζ)	1.277 (16)	1.274
N—C	1.328 (16)	1.320
O(ϵ)-O(ζ)	2.532 (17)	2.540
Ligand bite†	1.26	1.26
Twist angle‡	42.6 (24)	42.2
O(ϵ)-Fe—O(ζ)	78.3 (4)	78.3

* Average of ferrichrome, ferrichrome *A*, ferricrocin, ferrirubin, asperchrome *D1* and *B1* values (see text).

† Ratio of O(ϵ)...O(ζ) distances to Fe—O distances.

‡ Angle of rotation of O(1 ϵ)—O(2 ϵ)—O(3 ϵ) face of coordination with respect to O(1 ζ)—O(2 ζ)—O(3 ζ) face.

significantly from other structures of the ferrichrome family (ferrichrome: van der Helm, Baker, Eng-Wilmot, Hossain & Loghry, 1980; ferrichrome *A*: Zalkin, Forrester & Templeton, 1966; van der Helm, Baker, Loghry & Ekstrand, 1981; ferrichrysin: Norrestam, Stensland & Branden, 1975; ferricrocin: Barnes, Eng-Wilmot & van der Helm, 1984; ferrirubin: Barnes, Hossain, Jalal, Eng-Wilmot, Grayson, Benson, Agarwal, Mocherla & van der Helm, 1985; asperchrome *B1* and *D1*: Jalal, Hossain, van der Helm & Barnes, 1988). In the present structure the absolute configuration of the molecule was not independently determined, but the assumed chirality of the serine and ornithine residues (all L), as well as of the iron center (*A*), is consistent with all other ferrichrome structures.

The 18-membered cyclic hexapeptide ring forms an antiparallel β structure with two chain reversals (β turns; Venkatachalam, 1968) linked by two extended residues and in general conforms with the Schwyzer model (Schwyzer, Sieber & Gorup, 1958). In case of the ferrichromes, however, only one relatively weak 4 \rightarrow 1 hydrogen bond, a part of the β turn with Ser5 and Gly6 in the corners, is present; the N(1)...O(4) distance in ferrirhodin is 2.960 (16) \AA and compares with 2.98–3.18 \AA in other ferrichromes. In all ferrichromes this is a β (II') turn (Hossain & van der Helm, 1978), in which glycine assumes the conformational angles of a D-amino acid. The other chain reversal, with Orn2 and Orn3 in the corners, is always a β (I) turn, but the conformation of the Orn1—Orn2 peptide bond, apparently a result of the

strain imposed on the molecule by the iron chelation, precludes the formation of a 4 \rightarrow 1 hydrogen bond. The N(4)...O(1) distance in ferrirhodin is 4.199 (14) \AA and compares with 3.90 to 4.68 \AA in other ferrichromes. A strong hydrogen bond links the peptide backbone with the coordination octahedron in all ferrichrome structures; N(2)...O(2 ϵ) distances range from 2.73–2.81 \AA . In ferrirhodin this bond distance is 2.838 (12) \AA . The overall conformation of ferrirhodin is therefore similar to the other structures in the ferrichrome family.

In order to investigate further the conformational properties of both ferrirhodin and ferrirubin, several energy-minimization calculations were carried out. First the ferrichrome backbone of the ferrirhodin and ferrirubin molecules was investigated. Minimizations using the two crystal structures as starting conformations (molecule *C* in the case of ferrirubin) gave similar energy values, with ferrirubin preferred by approximately 8.4 kJ mol⁻¹. Selected torsion angles of the two crystal structures and the two model calculations (for the molecular fragment common to all ferrichromes) are given in Table 3. The differences between the two sets of X-ray values and between the two calculations are smaller than the differences between the experimental and model

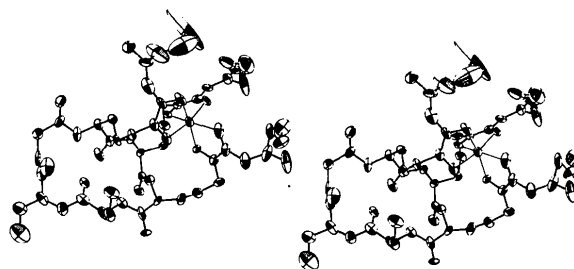


Fig. 2. Stereoview of the ferrirhodin structure. The thermal ellipsoids are drawn at the 50% probability level (Johnson, 1965).

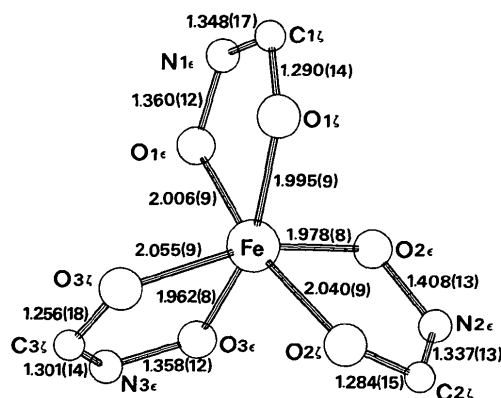


Fig. 3. Bond distances in the iron coordination octahedron (\AA). E.s.d.'s are given in parentheses.

Table 3. Selected conformational angles (°)

A: ferrirhodin crystal structure; B: model ferrirhodin; C: average of three independent molecules of ferrirubin (crystal structures); D: model ferrirubin. Ferrirhodin e.s.d.'s are 1–2°.

		Orn1	Orn2	Orn3	Ser4	Ser5	Gly6
C(i-1)—N(i)—C(α)—C(i)	A	-154	-72	-105	-163	-55	90
	B	-155	-76	-80	-157	-55	85
	C	-152	-71	-107	-166	-54	84
	D	-158	-74	-87	-160	-60	71
N(i)—C(α)—C(i)—N(i+1)	A	-163	-43	0	169	131	-2
	B	-160	-60	-12	178	126	7
	C	-168	-42	6	177	130	3
	D	-163	-61	-1	-177	129	20
C(α)—C(i)—N(i+1)—C(i+1α)	A	-176	-166	176	-172	-176	179
	B	-178	-172	179	-179	-179	174
	C	-177	-166	177	-177	176	179
	D	-179	-171	180	180	-179	173
N(i)—C(α)—C(iβ)—C(iγ)	A	59	-67	-69			
	B	66	-57	-74			
	C	60	-64	-70			
	D	68	-57	-69			
C(α)—C(iβ)—C(iγ)—C(iδ)	A	180	74	159			
	B	-176	77	163			
	C	177	75	160			
	D	-177	78	161			
C(iβ)—C(iγ)—C(iδ)—N(iε)	A	-61	50	-66			
	B	-61	52	-67			
	C	-56	48	-60			
	D	-60	51	-65			
C(iγ)—C(iδ)—N(iε)—C(iζ)	A	111	90	156			
	B	95	89	153			
	C	112	91	141			
	D	95	88	151			
C(iδ)—N(iε)—C(iζ)—C(iη)	A	4	5	-7			
	B	2	-3	-2			
	C	8	11	-3			
	D	0	-4	4			

values for a given molecule. This reflects the imperfections of the AMBER force field; however, the r.m.s. positional deviations from the respective crystal structures, calculated for the 49-atom ferrichrome fragment (0.26 Å for ferrirubin and 0.27 Å for ferrirhodin) indicate that the present calculation reproduces the ferrichrome geometry rather well. In comparison, a normal-mode molecular-mechanics study of ferrichrome (Sheridan, Levy & Englander, 1983) reports an r.m.s. difference between the energy-minimized and X-ray structure of 0.68 Å. The r.m.s. deviations between the ferrichrome-type crystal structures and ferrichrome itself range from 0.22 to 0.38 Å (Barnes *et al.*, 1985).

Second, the conformation of the acyl groups derived from anhydromevalonic acid in ferrirhodin and ferrirubin was investigated. Electron-density delocalization gives C(ζ)—C(η) a partial double-bond character and consequently one can expect the torsion angle χ_6 , O(ζ)—C(ζ)—C(η)—C(θ) to assume values close to 0 or 180°. Owing to unfavorable steric interactions between δ and ν1 —CH₂— groups in ferrirhodin, and between δ —CH₂— and ν2 methyl groups in ferrirubin, the 180° configuration is very improbable. Indeed, for the two configurations, at 0 and 180°, the difference in minimized energy is 84 kJ mol⁻¹ for ferrirhodin and 59 kJ mol⁻¹ for ferrirubin. Therefore, with χ_6 in the vicinity of 0° and with either *cis* or *trans* configuration of the C(η)=C(θ) double bond, the overall

Table 4. Torsion angles $\chi_6(i)$, O(iζ)—C(iζ)—C(iη)—C(iθ), before and after energy minimization, *i* indexes the ornithine residues

Corresponding energy values for minimized structures are also given, E_{tot} is total minimized energy; E_{tor} , E_{nb} are torsion angle and non-bonded contributions

	Initial χ_6 (°)			Final χ_6 (°)			Energy values (kJ mol ⁻¹)		
	<i>i</i> =1	<i>i</i> =2	<i>i</i> =3	<i>i</i> =1	<i>i</i> =2	<i>i</i> =3	E_{tot}	E_{tor}	E_{nb}
Ferrirubin									
Crystal structure	44	17	-19	27	-3	20	-489.1	38.0	-52.7
Ferrirhodin									
Crystal structure	34	3	-68	44	5	-45	-481.1	58.1	-66.9
$\chi_6 = -90^\circ, i=3$	34	3	-90	42	8	-50	-479.9	60.6	-67.7
$\chi_6 = +90^\circ, i=3$	34	3	90	27	17	20	-484.0	40.5	-58.1
$\chi_6 = 0^\circ, i=1, 2, 3$	0	0	0	34	6	17	-486.6	41.0	-57.7

conformation of the *N*-acyl groups in both ferrirubin and ferrirhodin should be to a considerable extent predetermined. However, this is not exactly the case as the χ_6 torsion angles in both the crystal and the energy-minimized structures deviate considerably from the ideal value of 0°. In addition, the differences between crystal and energy-minimized structures are quite large, especially in the case of ferrirubin (Table 4). The latter effect may be due to the imperfections of the force field but most probably reflects the difference between crystal and vacuum environment of the molecule, with ferrirubin acyl groups being practically unhindered *in vacuo*. It may also indicate larger conformational freedom in the case of ferrirubin *trans* [C(η)=C(θ)] acyl groups. In the ferrirhodin crystal structure, the deviation of torsion angle χ_6 from 0°, in one of the acyl groups (*i* = 3), is quite considerable (-68°). Investigation of this unexpected observation reveals an alternative conformation of the acyl groups. This has been established by three additional energy minimizations with modified starting geometries. In the first one, the initial χ_6 (*i* = 3) value was set to -90°, in the second to +90°, and in the third all three χ_6 values were set to 0°. The first of these calculations converged to the same minimum as the crystal structure, while the second and the third to a separate one (Table 4). The first of the two minima is characterized by a larger strain in torsion angles (by ~16 kJ mol⁻¹). In the second one, on the other hand, for which there exists a roughly threefold symmetry of the acyl groups, the non-bonded interactions are less favorable (by ~8 kJ mol⁻¹). Overall the second minimum is only slightly lower in energy (~4 kJ mol⁻¹) suggesting that both conformations are plausible, and that small perturbations such as crystal packing could favor one over the other. The view down the coordination octahedron threefold axis of the ferrirhodin crystal structure (representative of the first energy minimum) is shown in Fig. 4(a). The same view for the conformation corresponding to the second energy

minimum is given in Fig. 4(b), while the crystal structure conformation of ferrirubin (molecule C) is in Fig. 4(c). It is quite apparent that the acyl environment of iron is different both in shape and location of functionality (OH groups) for ferrirubin when compared to either of the two possible conformations of ferrirhodin (Fig. 4). Also, in ferrirubin, the *N*-acyl groups stick outward while in ferrirhodin they are bent inward, giving overall a more compact structure. It is therefore plausible, in agreement with earlier suggestions (Huschka *et al.*, 1986), that the strength of binding with the receptor protein is different for the two molecules.

In the ferrirhodin crystal structure there are two intermolecular peptide-peptide hydrogen bonds, $O(2\kappa)\cdots O(5\beta)$ ($1-x, -\frac{1}{2}+y, 1\frac{1}{2}-z$) with distances of 2.83 (3) and 2.65 (5) Å for the sites occupied by $O(2\kappa)$ at 70 and 30% occupancy respectively, and $O(3\zeta)\cdots N(6)$ ($1-x, -\frac{1}{2}+y, 1\frac{1}{2}-z$) with a distance of 3.123 (12) Å. The water molecules form channels along the *a* axis; all but one, *W*(5), are hydrogen bonded to the siderophore molecule. *W*(1) forms hydrogen bonds with both $O(4\beta)$ and $O(5)$ of the same molecule, while *W*(4) and *W*(6) bridge to the

neighboring asymmetric units. The water-water hydrogen bonding is extensive and involves all water molecules with the exception of *W*(2), which is coordinated by $N(1\epsilon)$, $O(1\epsilon)$, $O(3\zeta)$ (x, y, z), $N(1)$, $O(1)$, $N(6)$ ($1-x, -\frac{1}{2}+y, 1\frac{1}{2}-z$), and $O(1\kappa)$ ($1+x, y, z$), all within hydrogen-bond distance.

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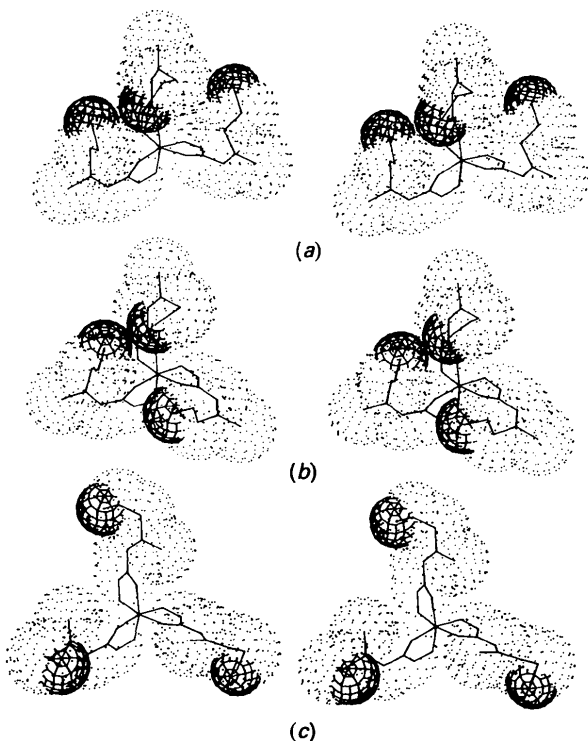


Fig. 4. Conformation of the *N*-acyl groups: (a) in ferrirhodin crystal structure; (b) in ferrirhodin energy-minimized structure (second minimum); (c) in ferrirubin crystal structure (molecule C). Only the iron coordination and *N*-acyl groups are shown. Filled and dotted van der Waals surfaces for O and C atoms, respectively. Van der Waals radii for CH_2 and CH_3 groups were adjusted appropriately.