que le rendement de la réaction par rapport au chlorure de thionyle est faible (De Charentenay & Otton, 1971).

L'éther diméthoxy-1,2 éthane contribue au niveau de chaque atome de cobalt à compléter sous forme de chélate l'environnement octaédrique du métal. Chacun des deux atomes d'oxygène dans une hybridation à caractère sp^3 assure par l'intermédiaire d'un de ses doublets une liaison de coordination avec l'atome de cobalt central. Il est à noter l'absence de désordre au niveau des atomes de carbone C(4) et C(5) à la différence de ce qui est observé dans divers complexes et notamment dans le composé $[(Me_3Si)_2N]_2$ Eu(dme)$_2$ caractérisé par l'existence de deux conformations de ce ligand (Tilley, Zalkin, Andersen & Templeton, 1981). Les longueurs et angles de liaison observés (Tableau 3) avec un angle dièdre de 59° autour de la liaison C(4)—C(5) suggère l'absence de déformations notables au regard de la géométrie de l'éther à l'état libre du fait de la complexation. Il convient toutefois de noter un effet *trans* de l'atome de chlore sur l'atome d'oxygène O(3) qui se reflète par un écart significatif de 0,083 Å entre les deux liaisons Co—O(3) et Co—O(4).

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Références

Agambar, C. A. & Orell, K. G. (1969). *J. Chem. Soc. A*, pp. 897–904.

Brown, I. D. & Shannon, R. D. (1973). *Acta Cryst.* A**29**, 266–280.

Codet, G., Dawans, F., De Charentenay, F. X. & Teyssie, P. R. (1968). Brevet Français, No. 1.601.128.

Cotton, F. A. & Rice, G. W. (1978). *Inorg. Chim. Acta*, **27**, 75–79.

Cotton, F. A. & Webb, T. R. (1976). *Inorg. Chem.* **15**, 68–71.

Cromer, D. T. (1965). *Acta Cryst.* **18**, 17–23.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

De Charentenay, F. X. & Otton, J. (1971). Communication privée.

Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP–a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Determination.* Dans *Computing in Crystallography*, édité par H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi. Delft Univ. Press.

Johnson, C. K. (1965). *ORTEP.* Rapport ORNL-5138. Oak Ridge National Laboratory, Tennessee.

Levinson, J. J. & Robinson, S. D. (1967). *J. Chem. Soc. Chem. Commun.* **4**, 198–199.

Tilley, T. D., Zalkin, A., Andersen, R. A. & Templeton, D. H. (1981). *Inorg. Chem.* **20**, 551–554.

Valentine, J., Valentine, D. & Collman, J. P. (1971). *Inorg. Chem.* **10**, 219–225.

Acta Cryst. (1985). C**41**, 341–347

Ferrichrome Conformations: Ferrirubin, Two Crystal Forms: $C_{41}H_{64}FeN_9O_{17}.10\frac{1}{2}H_2O$ (I) and $C_{41}H_{64}FeN_9O_{17}.CH_3CN.H_2O$ (II)

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Abstract. (I) $M_r = 1200{\cdot}0$, triclinic, $P1$, $a = 13{\cdot}578\,(2)$, $b = 19{\cdot}519\,(2)$, $c = 11{\cdot}018\,(3)$ Å, $\alpha = 95{\cdot}81\,(1)$, $\beta = 91{\cdot}63\,(1)$, $\gamma = 82{\cdot}22\,(1)°$, $V = 2878\,(5)$ Å^3, $Z = 2$, $D_x = 1{\cdot}38$ g cm^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 3{\cdot}1$ cm^{-1}, $F(000) = 1280$, $T = 138\,(1)$ K, $R = 0{\cdot}067$ for 6790 observed reflections. (II) $M_r = 1069{\cdot}9$, monoclinic, $P2_1$, $a = 11{\cdot}170\,(3)$, $b = 12{\cdot}831\,(4)$, $c = 17{\cdot}852\,(6)$ Å, $\beta = 105{\cdot}34\,(2)°$, $V = 2467\,(13)$ Å^3, $Z = 2$, $D_x = 1{\cdot}44$ g cm^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 3{\cdot}4$ cm^{-1}, $F(000) = 1134$, $T = 138\,(1)$ K, $R = 0{\cdot}039$ for 4731 observed reflections. Ferrirubin was isolated from low-iron cultures of the fungus *Aspergillus ochraceous*. The material crystallized by evaporation from water and by diffusing acetonitrile into an ethanol solution. The solvent environments of the molecules in the two crystal forms are markedly different, but the conformations of the 18-membered cyclic hexapeptide rings, and of the molecules as a whole, are very similar. Observed ferrichrome conformations are compared with a calculated minimal-energy conformation.

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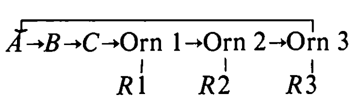
Introduction. The ferrichrome-type siderophores are iron(III)-binding cyclic hexapeptides, which are produced by a number of fungal species in response to low iron availability (Neilands, 1981; Emery, 1980). The general formula for these siderophore ligands (hereafter referred to collectively as ferrichrome) is:



$$\overline{A \rightarrow B \rightarrow C \rightarrow \underset{R1}{\mathrm{Orn}\ 1} \rightarrow \underset{R2}{\mathrm{Orn}\ 2} \rightarrow \underset{R3}{\mathrm{Orn}\ 3}}$$

where A and B are glycine, alanine or serine residues and C is a glycine residue, and Orn1, 2 and 3 are N^{δ}-acylated-N^{δ}-hydroxyornithine residues, with $R1$, $R2$ and $R3$, the acyl groups, derived from one or more of a number of carboxylic acids. The modifications to the ornithine residues result in three hydroxamic acid functional groups, which chelate the iron.

Ferrirubin in which $A = B =$ serine and $R1 \equiv R2 \equiv R3 \equiv$ $-C(O)-CH{=}C(CH_3)-CH_2-CH_2OH$ (*trans*), is produced by a number of *Ascomycetes*, especially members of the genus *Aspergillus*. We obtained ferrirubin from low-iron cultures of *A. ochraceous* strain gold. This organism produces more than a dozen siderochromes, with ferrirubin as the principal product (> 60%). This paper reports the structures of two crystal forms of this siderophore.

Experimental. The iron-free ligand of ferrirubin was produced in low-iron cultures of *Aspergillus ochraceous* strain gold. Culture conditions, preparation and extraction of the iron chelate were as described elsewhere (van der Helm, Baker, Eng-Wilmot, Hossain & Loghry, 1980; Garibaldi & Neilands, 1955). Ferrirubin was purified by silica-gel column chromatography, eluant $CHCl_3$:MeOH:H_2O (35:12:2 v/v).

(I) 0·25 × 0·35 × 0·50 mm, crystal highly unstable at room temperature, but stable at low temperature; $2\theta_{\max} = 46°$; $0 \le h \le 14$, $-21 \le k \le 21$, $-12 \le l \le 12$; data measured 7940, data observed 6790 [$I > 3\sigma(I)$]; $R = 0{\cdot}067$, R (all data) = 0·084, $S = 5{\cdot}15$, max. and av. Δ/σ (excluding solvent) = 0·60 and 0·20, max. and min. height in final difference Fourier map = 1·0 (around Fe) and $-0{\cdot}5$ e Å^{-3}. (II) 0·15 × 0·25 × 0·40 mm, crystals decay gradually at room temperature, stable at low temperature; $2\theta_{\max} = 53°$; $-14 \le h \le 14$, $0 \le k \le 16$, $0 \le l \le 22$; data measured 5282, data observed 4731 [$I \ge 3\sigma(I)$]; $R = 0{\cdot}039$, R (all data) = 0·048, $S = 2{\cdot}25$, max. and av. $\Delta/\sigma = 0{\cdot}60$ and 0·10, max. and min. height in final difference Fourier map = 0·3 and $-0{\cdot}4$ e Å^{-3}. Both structures: diffractometer Enraf–Nonius CAD-4, fitted with liquid-N_2 low-temperature device; $\pm 2\theta$ data at 138 K; 48 reflections from all octants of reciprocal space used for lattice constants; no absorption correction; structure solved by Patterson methods; $(|F_o| - |F_c|)^2$ minimized in least-squares refinements; hydrogens located on difference Fourier maps [except those of waters in (I) and some hydroxyls in both] and refined isotropically; non-hydrogen atoms refined anisotropically, except water O atoms of (I); scattering factors for C, N, O and Fe^{3+} atoms, including corrections for anomalous dispersion for Fe, taken from *International Tables for X-ray Crystallography* (1974); hydrogen scattering factors from Stewart, Davidson & Simpson (1965); structure factor, least-squares refinement and Fourier calculations performed using *SHELX76* (Sheldrick, 1976) first, followed by *NRC* programs (Ahmed, 1966) (block-diagonal least squares); absolute configuration determined by Bijvoet method using anomalous dispersion of Cu radiation by the Fe atom with crystal of (II), procedure for selecting best Friedel pairs described previously (Ealick, van der Helm & Weinheimer, 1975).*

Discussion. With this report, there are now six published crystal structures of iron complexes of ferrichrome-type siderophores, giving views of eight independent molecules: ferrichrome, $A = B =$ glycine, $R1 = R2 = R3 = -C(O)-CH_3$ (van der Helm *et al.*, 1980); ferrichrome A, $A = B =$ serine, $R1 = R2 = R3$ $= -C(O)-CH{=}C(CH_3)-CH_2COOH$ (Zalkin, Forrester & Templeton, 1966), ferrichrysin, $A = B =$ serine, $R1 = R2 = R3 = -C(O)-CH_3$ (Norrestam, Stensland & Brändén, 1975); ferricrocin, A = glycine, B = serine, $R1 = R2 = R3 = -C(O)-CH_3$, two independent molecules (Barnes, Eng-Wilmot & van der Helm, 1984); and the three molecules of ferrirubin in the present report.

A schematic drawing of ferrirubin is given in Fig. 1. The numbering scheme follows the convention of the IUPAC–IUB Commission on Biochemical Nomenclature (1970). The absolute configurations of

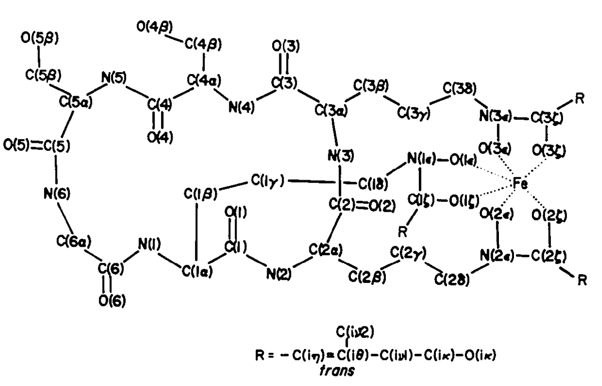


Fig. 1. Schematic drawing with atom numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters, bond distances, bond angles, H-atom coordinates and Friedel pair differences have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39739 (77 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\times 10^3$) *for non-hydrogen atoms*

$$U_{\rm eq} = \tfrac{1}{6}\pi^2 \textstyle\sum_i \sum_j \beta_{ij} \mathbf{a}_i . \mathbf{a}_j.$$

Crystals from water

Molecule *A*

	x	y	z	$U_{\rm eq}$(Å^2)
Fe	−11·7 (13)	−0·7 (9)	−3·7 (15)	17·5 (8)
N(1)	−3327 (7)	1556 (5)	−3965 (8)	23 (6)
C(1α)	−2950 (8)	1011 (6)	−3233 (10)	21 (7)
C(1)	−3403 (8)	1246 (5)	−1939 (11)	23 (7)
O(1)	−4089 (5)	1708 (4)	−1774 (7)	23 (5)
C(1β)	−1839 (9)	860 (6)	−3251 (10)	23 (7)
C(1γ)	−1324 (9)	1487 (6)	−2791 (10)	24 (7)
C(1δ)	−207 (8)	1351 (6)	−2731 (10)	23 (7)
N(1ε)	146 (6)	774 (4)	−1988 (8)	18 (5)
O(1ε)	−168 (6)	903 (4)	−784 (7)	26 (5)
C(1ζ)	611 (7)	162 (6)	−2350 (10)	19 (6)
O(1ζ)	768 (5)	−298 (4)	−1546 (7)	24 (5)
C(1η)	1011 (8)	26 (6)	−3595 (10)	23 (7)
C(1θ)	991 (8)	−562 (6)	−4315 (10)	24 (7)
C(1ν2)	556 (10)	−1192 (6)	−4001 (11)	31 (8)
C(1ν1)	1415 (9)	−606 (6)	−5587 (10)	28 (7)
C(1κ)	2379 (9)	−1073 (7)	−5722 (11)	33 (8)
O(1κ)	3173 (6)	−784 (4)	−5034 (8)	39 (6)
N(2)	−2997 (7)	884 (4)	−1008 (8)	19 (5)
C(2α)	−3442 (8)	1071 (5)	175 (10)	18 (6)
C(2)	−3178 (8)	1775 (5)	767 (9)	16 (6)
O(2)	−3806 (6)	2191 (4)	1329 (7)	26 (5)
C(2β)	−3068 (8)	526 (6)	1076 (10)	22 (7)
C(2γ)	−3377 (8)	−206 (5)	732 (10)	22 (7)
C(2δ)	−2798 (8)	−664 (6)	−316 (10)	24 (7)
N(2ε)	−1729 (7)	−680 (4)	−178 (8)	21 (5)
O(2ε)	−1378 (6)	−102 (4)	−610 (6)	20 (4)
C(2ζ)	−1044 (8)	−1112 (6)	359 (10)	22 (6)
O(2ζ)	−146 (5)	−971 (4)	383 (7)	19 (4)
C(2η)	−1340 (8)	−1748 (6)	748 (11)	27 (7)
C(2θ)	−748 (9)	−2190 (6)	1395 (10)	25 (7)
C(2ν2)	269 (10)	−2117 (7)	1907 (12)	41 (9)
C(2ν1)	−1151 (9)	−2862 (6)	1593 (12)	32 (8)
C(2κ)	−600 (9)	−3506 (6)	867 (12)	34 (8)
O(2κ)	−747 (6)	−3478 (4)	−412 (8)	38 (6)
N(3)	−2238 (7)	1881 (4)	667 (8)	20 (5)
C(3α)	−1845 (8)	2462 (5)	1428 (9)	20 (7)
C(3)	−1715 (9)	3065 (6)	717 (10)	27 (7)
O(3)	−1327 (7)	3568 (4)	1228 (7)	36 (5)
C(3β)	−907 (9)	2197 (6)	2078 (10)	22 (7)
C(3γ)	−1087 (9)	1711 (6)	3019 (11)	30 (7)
C(3δ)	−182 (8)	1203 (6)	3353 (10)	22 (7)
N(3ε)	198 (6)	771 (5)	2248 (8)	20 (5)
O(3ε)	−539 (5)	485 (4)	1578 (7)	24 (5)
C(3ζ)	1109 (8)	606 (5)	1903 (10)	17 (6)
O(3ζ)	1278 (5)	135 (4)	915 (6)	20 (4)
C(3η)	1930 (8)	915 (6)	2518 (10)	20 (7)
C(3θ)	2892 (8)	666 (6)	2597 (10)	23 (7)
C(3ν2)	3353 (8)	−33 (6)	2041 (11)	26 (7)
C(3ν1)	3596 (9)	1085 (6)	3266 (11)	27 (7)
C(3κ)	4019 (9)	762 (7)	4448 (11)	34 (8)
O(3κ)	3213 (6)	633 (4)	5184 (7)	32 (5)
N(4)	−2045 (7)	3053 (5)	−450 (8)	24 (6)
C(4α)	−2040 (9)	3621 (6)	−1228 (10)	24 (7)
C(4)	−2693 (8)	3443 (6)	−2342 (10)	20 (6)
O(4)	−3044 (5)	2887 (4)	−2468 (7)	24 (5)
C(4β)	−985 (9)	3713 (6)	−1560 (11)	26 (7)
O(4β)	−510 (6)	3138 (4)	−2320 (7)	31 (5)
N(5)	−2837 (7)	3910 (5)	−3161 (8)	23 (6)
C(5α)	−3558 (8)	3828 (6)	−4153 (10)	24 (7)
C(5)	−3295 (8)	3133 (6)	−4912 (10)	22 (7)
O(5)	−2492 (5)	2964 (4)	−5406 (7)	28 (5)
C(5β)	−3511 (8)	4392 (6)	−5011 (10)	24 (7)
O(5β)	−4232 (6)	4332 (4)	−5960 (7)	35 (5)
N(6)	−4039 (7)	2743 (5)	−5069 (8)	23 (6)
C(6α)	−3925 (9)	2072 (6)	−5819 (10)	25 (7)
C(6)	−3496 (8)	1449 (6)	−5174 (10)	19 (6)
O(6)	−3389 (7)	873 (4)	−5744 (7)	33 (5)

Molecule *B*

	x	y	z	$U_{\rm eq}$(Å^2)
Fe	−4581·2 (13)	−2167·2 (9)	−511·8 (15)	18·2 (9)
N(1)	−7274 (7)	−3651 (5)	3410 (8)	23 (6)
C(1α)	−7098 (8)	−3116 (5)	2629 (10)	22 (7)
C(1)	−7492 (8)	−3339 (5)	1365 (10)	19 (6)
O(1)	−8049 (5)	−3792 (4)	1201 (6)	20 (4)
C(1β)	−6030 (9)	−2991 (6)	2676 (10)	23 (7)
C(1γ)	−5328 (9)	−3644 (6)	2213 (11)	29 (7)
C(1δ)	−4212 (9)	−3511 (6)	2213 (11)	29 (7)
N(1ε)	−4086 (7)	−2951 (5)	1474 (8)	24 (5)
O(1ε)	−4371 (5)	−3067 (4)	276 (7)	21 (4)
C(1ζ)	−3830 (8)	−2327 (6)	1833 (10)	22 (7)
O(1ζ)	−3893 (5)	−1879 (4)	1097 (6)	22 (4)
C(1η)	−3482 (8)	−2190 (6)	3144 (10)	22 (7)
C(1θ)	−3783 (8)	−1602 (6)	3837 (11)	26 (7)
C(1ν2)	−4511 (10)	−1032 (7)	3470 (12)	41 (9)
C(1ν1)	−3386 (10)	−1523 (6)	5150 (11)	33 (8)
C(1κ)	−2681 (12)	−979 (8)	5348 (13)	54 (10)
O(1κ)	−1779 (8)	−1207 (6)	4688 (10)	64 (8)
N(2)	−7272 (7)	−2988 (5)	446 (8)	19 (5)
C(2α)	−7696 (8)	−3145 (6)	−756 (10)	22 (7)
C(2)	−7248 (8)	−3875 (6)	−1342 (9)	19 (6)
O(2)	−7765 (5)	−4245 (4)	−1948 (7)	23 (5)
C(2β)	−7553 (8)	−2613 (5)	−1642 (9)	18 (6)
C(2γ)	−8055 (9)	−1877 (6)	−1277 (11)	29 (7)
C(2δ)	−7599 (8)	−1453 (5)	−213 (11)	23 (7)
N(2ε)	−6552 (6)	−1450 (4)	−314 (8)	20 (5)
O(2ε)	−5973 (5)	−2033 (4)	76 (7)	22 (4)
C(2ζ)	−6011 (8)	−1012 (5)	−791 (10)	18 (6)
O(2ζ)	−5086 (5)	−1173 (4)	−879 (7)	22 (4)
C(2η)	−6556 (9)	−341 (6)	−1090 (10)	26 (7)
C(2θ)	−6190 (9)	139 (6)	−1683 (10)	24 (7)
C(2ν2)	−5161 (9)	33 (6)	−2259 (11)	28 (7)
C(2ν1)	−6789 (9)	812 (6)	−1806 (10)	27 (7)
C(2κ)	−6438 (9)	1426 (6)	−1022 (10)	25 (7)
O(2κ)	−6563 (6)	1366 (4)	257 (7)	28 (5)
N(3)	−6273 (6)	−4030 (4)	−1183 (8)	19 (5)
C(3α)	−5696 (8)	−4607 (5)	−1930 (10)	18 (6)
C(3)	−5401 (8)	−5270 (6)	−1224 (10)	22 (7)
O(3)	−4914 (6)	−5780 (4)	−1755 (7)	33 (5)
C(3β)	−4782 (8)	−4363 (5)	−2427 (10)	21 (7)
C(3γ)	−5085 (8)	−3896 (6)	−3457 (10)	22 (7)
C(3δ)	−4295 (9)	−3460 (6)	−3771 (10)	24 (7)
N(3ε)	−4088 (6)	−2972 (4)	−2707 (8)	17 (5)
O(3ε)	−4928 (5)	−2665 (4)	−2069 (7)	23 (5)
C(3ζ)	−3256 (8)	−2746 (6)	−2326 (10)	20 (7)
O(3ζ)	−3280 (5)	−2279 (4)	−1417 (7)	22 (5)
C(3η)	−2318 (8)	−3040 (6)	−2972 (10)	23 (7)
C(3θ)	−1468 (8)	−2742 (6)	−2985 (10)	24 (7)
C(3ν2)	−1324 (10)	−2024 (7)	−2393 (12)	40 (9)
C(3ν1)	−606 (9)	−3138 (7)	−3687 (11)	34 (8)
C(3κ)	−665 (14)	−2937 (8)	−5044 (15)	71 (12)
O(3κ)	187 (8)	−3265 (6)	−5685 (10)	75 (8)
N(4)	−5694 (7)	−5224 (5)	−70 (8)	24 (6)
C(4α)	−5543 (8)	−5806 (5)	673 (10)	22 (7)
C(4)	−6224 (8)	−5570 (6)	1789 (11)	25 (7)
O(4)	−4047 (6)	−5418 (4)	1706 (7)	32 (5)
C(4β)	−4458 (9)	−5982 (6)	1021 (11)	32 (8)
O(4β)	−6656 (6)	−4974 (4)	1947 (7)	25 (5)
N(5)	−6275 (7)	−6047 (5)	2587 (8)	24 (6)
C(5α)	−7041 (9)	−5898 (6)	3502 (11)	27 (7)
C(5)	−6880 (7)	−5209 (5)	4317 (10)	17 (6)
O(5)	−6039 (5)	−5118 (4)	4746 (7)	30 (5)
C(5β)	−6865 (10)	−6492 (7)	4358 (12)	39 (8)
O(5β)	−7630 (7)	−6375 (4)	5287 (8)	43 (6)
N(6)	−7700 (7)	−4770 (4)	4503 (8)	22 (6)
C(6α)	−7659 (9)	−4111 (6)	5288 (10)	25 (7)
C(6)	−7424 (8)	−3515 (5)	4613 (10)	19 (6)
O(6)	−7385 (6)	−2929 (4)	5174 (7)	34 (5)

Solvent

	x	y	z	$U_{\rm eq}$(Å^2)		x	y	z	$U_{\rm eq}$(Å^2)
W(1)	−1640 (7)	−60 (5)	−6535 (9)	54 (3)	*W*(12)	−424 (7)	−5301 (5)	−8123 (8)	46 (2)
W(2)	−725 (6)	−6529 (4)	−4653 (7)	30 (2)	*W*(13)	−8331 (7)	−8282 (5)	−4426 (8)	44 (2)
W(3)	−9776 (7)	−4703 (5)	−5968 (8)	44 (2)	*W*(14)	−8886 (7)	−5032 (5)	−9514 (8)	46 (2)
W(4)	1395 (7)	2483 (5)	7937 (9)	51 (3)	*W*(15)	−8369 (7)	−7305 (5)	−8005 (9)	55 (3)
W(5)	−2332 (6)	−4724 (4)	−2810 (8)	38 (2)	*W*(16)	−5267 (7)	2873 (5)	−2705 (9)	52 (3)
W(6)	−6125 (7)	−1961 (5)	−3901 (8)	45 (2)	*W*(17)	−2413 (7)	−4853 (5)	−8903 (9)	57 (3)
W(7)	−9013 (7)	−7179 (5)	−5728 (8)	42 (2)	*W*(18)	−465 (7)	−5130 (5)	−3859 (8)	41 (2)
W(8)	−2620 (6)	−3923 (4)	−543 (7)	29 (2)	*W*(19)	−7883 (9)	−6353 (6)	−9488 (11)	79 (4)
W(9)	1297 (6)	1750 (4)	8 (7)	30 (2)	*W*(20)	2815 (13)	3319 (9)	7998 (16)	132 (6)
W(10)	−5796 (6)	2513 (4)	1781 (8)	38 (2)	*W*(21)	2090 (15)	4364 (11)	7281 (19)	184 (8)
W(11)	−9645 (7)	−4568 (5)	−1699 (8)	45 (2)					

Table 1 (*cont.*)

Crystals from acetonitrile/ethanol
Molecule *C*

	x	*y*	*z*	U_{eq}(Å^2)
Fe	759·2 (4)	2499·7 (5)	1348·5 (3)	14·5 (2)
N(1)	−2703 (3)	−824 (3)	2963 (2)	19 (1)
C(1α)	−2159 (3)	−477 (3)	2348 (2)	17 (2)
C(1)	−853 (3)	−949 (3)	2513 (2)	17 (2)
O(1)	−531 (2)	−1657 (2)	2981 (2)	23 (1)
C(1*β*)	−2207 (3)	707 (3)	2255 (2)	18 (2)
C(1*γ*)	−1496 (3)	1264 (3)	2991 (2)	20 (2)
C(1*δ*)	−1428 (3)	2440 (4)	2895 (2)	22 (2)
N(1*ε*)	−906 (3)	2710 (2)	2256 (2)	18 (1)
O(1*ε*)	311 (2)	2418 (2)	2356 (1)	20 (1)
C(1*ζ*)	−1482 (3)	3149 (3)	1587 (2)	19 (2)
O(1*ζ*)	−867 (2)	3282 (2)	1075 (1)	18 (1)
C(1*η*)	−2782 (4)	3469 (3)	1442 (2)	23 (2)
C(1*θ*)	−3666 (4)	3295 (4)	794 (3)	26 (2)
C(1*ν*2)	−3486 (4)	2674 (4)	125 (3)	36 (2)
C(1*ν*1)	−4962 (4)	3692 (4)	722 (3)	33 (2)
C(1*κ*)	−5362 (4)	4522 (4)	114 (3)	39 (2)
O(1*κ*)	−4594 (3)	5416 (3)	301 (2)	42 (2)
N(2)	−90 (3)	−567 (2)	2108 (2)	16 (1)
C(2α)	1153 (3)	−1019 (3)	2235 (2)	17 (2)
C(2)	2006 (3)	−703 (3)	3025 (2)	16 (2)
O(2)	2761 (3)	−1316 (2)	3401 (2)	27 (1)
C(2*β*)	1803 (3)	−689 (3)	1611 (2)	18 (2)
C(2*γ*)	1198 (4)	−1024 (3)	776 (2)	23 (2)
C(2*δ*)	30 (4)	−425 (3)	337 (2)	22 (2)
N(2*ε*)	177 (3)	698 (3)	415 (2)	19 (1)
O(2*ε*)	12 (2)	1088 (2)	1102 (1)	17 (1)
C(2*ζ*)	616 (3)	1375 (3)	−12 (2)	18 (2)
O(2*ζ*)	805 (2)	2308 (2)	232 (1)	19 (1)
C(2*η*)	808 (4)	1042 (3)	−765 (2)	23 (2)
C(2*θ*)	1590 (4)	1513 (3)	−1106 (2)	26 (2)
C(2*ν*2)	2446 (4)	2378 (4)	−754 (3)	37 (2)
C(2*ν*1)	1747 (4)	1132 (4)	−1880 (3)	32 (2)
C(2*κ*)	693 (5)	547 (4)	−2414 (3)	38 (2)
O(2*κ*)	−384 (3)	1151 (3)	−2719 (2)	43 (2)
N(3)	1911 (3)	295 (3)	3257 (2)	16 (1)
C(3α)	2820 (3)	773 (3)	3909 (2)	17 (2)
C(3)	2294 (3)	1019 (3)	4596 (2)	16 (2)
O(3)	2889 (2)	1569 (2)	5135 (2)	22 (1)
C(3*β*)	3371 (4)	1752 (3)	3640 (2)	20 (2)
C(3*γ*)	4238 (3)	1499 (3)	3129 (2)	18 (2)
C(3*δ*)	4445 (3)	2430 (4)	2645 (2)	21 (2)
N(3*ε*)	3257 (3)	2777 (2)	2132 (2)	16 (1)
O(3*ε*)	2461 (2)	1982 (2)	1819 (2)	19 (1)
C(3*ζ*)	2872 (3)	3735 (3)	1933 (2)	16 (2)
O(3*ζ*)	1762 (2)	3847 (2)	1492 (2)	18 (1)
C(3*η*)	3724 (3)	4614 (3)	2176 (2)	20 (2)
C(3*θ*)	3559 (4)	5603 (3)	1931 (2)	22 (2)
C(3*ν*2)	2408 (4)	6029 (4)	1370 (3)	40 (2)
C(3*ν*1)	4574 (4)	6407 (3)	2198 (3)	30 (2)
C(3*κ*)	5675 (4)	6130 (4)	2864 (3)	30 (2)
O(3*κ*)	5268 (3)	6013 (3)	3561 (2)	31 (1)
N(4)	1193 (3)	613 (3)	4582 (2)	19 (1)
C(4α)	587 (3)	788 (3)	5198 (2)	21 (2)
C(4)	−427 (3)	−38 (3)	5094 (2)	18 (2)
O(4)	−657 (2)	−640 (2)	4536 (2)	24 (1)
C(4*β*)	17 (5)	1896 (4)	5110 (3)	32 (2)
O(4*β*)	−435 (3)	2134 (3)	5757 (2)	41 (2)
N(5)	−1058 (3)	−29 (3)	5627 (2)	21 (2)
C(5α)	−2222 (4)	−619 (3)	5515 (2)	21 (2)
C(5)	−3045 (3)	−446 (3)	4693 (2)	19 (2)
O(5)	−3272 (3)	448 (2)	4434 (2)	28 (1)
C(5*β*)	−2863 (4)	−200 (4)	6110 (2)	28 (2)
O(5*β*)	−4063 (3)	−663 (3)	5966 (2)	31 (1)
N(6)	−3498 (3)	−1298 (3)	4288 (2)	19 (1)
C(6α)	−4413 (3)	−1213 (3)	3538 (2)	20 (2)
C(6)	−3941 (3)	−900 (3)	2845 (2)	19 (2)
O(6)	−4672 (2)	−760 (3)	2212 (2)	28 (1)
Solvent				
W(1)	−5894 (3)	788 (3)	1115 (2)	46 (2)
C(1*a*)	−3059 (4)	3507 (4)	4341 (3)	44 (3)
N(*a*)	−2775 (5)	4004 (4)	3890 (3)	64 (3)
C(2*a*)	−3451 (5)	2874 (4)	4901 (3)	47 (3)

Table 2. *Comparison of the average peptide bond parameters for ferrirubin with those given by Karle* (1981) *and comparison of iron-coordination geometry*

The first number in parentheses is the estimated $\sigma = [\sum(\Delta)^2/N(N-1)]^{1/2}$. The second number in parentheses is the average of the individual e.s.d.'s Distances in Å, angles in °.

	Ferrirubin			
	A	*B*	*C*	Karle
C(*i*α)—C(*i*)	1·532 (9)(16)	1·550 (11)(16)	1·529 (2)(5)	1·522
C(*i*)—O(*i*)	1·229 (6)(14)	1·234 (6)(14)	1·228 (4)(5)	1·229
C(*i*)—N(*i*+1)	1·345 (5)(14)	1·336 (5)(14)	1·340 (5)(5)	1·335
N(*i*+1)—C(*i*+1α)	1·460 (8)(14)	1·463 (5)(14)	1·462 (3)(5)	1·449
C(*i*α)—C(*i*)—O(*i*)	120·8 (5)(10)	120·5 (4)(10)	120·6 (2)(3)	120·4
C(*i*α)—C(*i*)—N(*i*+1)	116·5 (5)(10)	115·9 (5)(10)	116·6 (3)(3)	116·6
O(*i*)—C(*i*)—N(*i*+1)	122·6 (3)(10)	123·6 (7)(10)	122·7 (2)(4)	122·9
C(*i*)—N(*i*+1)—C(*i*+1α)	121·1 (12)(10)	120·6 (10)(10)	121·2 (6)(3)	121·9

	Ferrirubin			Ferri-
	A	*B*	*C*	chromes*
Fe—O(*ε*)	2·002 (10)(8)	1·991 (17)(7)	1·989 (5)(3)	1·981
Fe—O(*ζ*)	2·023 (5)(7)	2·039 (5)(7)	2·027 (6)(3)	2·036
N—O(*ε*)	1·393 (11)(11)	1·383 (7)(11)	1·376 (3)(4)	1·382
C—O(*ζ*)	1·319 (20)(13)	1·261 (11)(13)	1·284 (6) (4)	1·277
N—C	1·310 (13)(14)	1·331 (12)(15)	1·325 (3)(5)	1·312
O(*ε*)···O(*ζ*)	2·561 (19)(11)	2·534 (8)(11)	2·543 (13)(5)	2·533
Ligand bite†	1·27	1·26	1·27	1·26
Twist angle‡	−44·2 (18)(5)	−42·6 (8)(5)	−44·1 (10)(2)	−41·6
O(*ε*)—Fe—O(*ζ*)	79·0 (4)(3)	77·9 (3)(3)	78·6 (5)(1)	

* Average of ferricrocin, ferrichrome and ferrichrome A values previously published (Barnes *et al.*, 1984).

† 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 octahedron with respect to O(1*ζ*)—O(2*ζ*)—O(3*ζ*) face.

the serine and ornithine residues (all L) and of the iron center (Λ-*cis*) were confirmed by measurement of the effect of anomalous dispersion of Cu $K\bar{\alpha}$ radiation by the Fe atoms. Final parameters for the non-H atoms are given in Table 1. Average structure parameters of the peptide bonds and iron chelate geometry are given in Table 2. These values compare very well with those observed in peptides (Karle, 1981) and other ferrichrome structures (Zalkin *et al.*, 1966; van der Helm *et al.*, 1980; van der Helm, Baker, Loghry & Ekstrand, 1981; Barnes *et al.*, 1984).

Perspective views of the two independent molecules of structure (I) and the single molecule of structure (II) are shown in Fig. 2. The similarity of conformation is obvious, and oriented views of the other ferrichrome structures would also appear similar. Certain structural details are common to all the ferrichrome crystal structures. The iron coordination octahedron is always Λ-*cis*, and this isomer probably strongly predominates in solution (Leong & Raymond, 1974; Abu-Dari & Raymond, 1977). The 18-membered cyclic hexapeptide ring assumes roughly a rectangular shape, with two *β* turns linked by two extended chains. The *β*(II) turn with residues 5 and 6 at the corners results in a weak 4→1 hydrogen bond. The N(1)···O(4) distances are 2·997 (13), 2·936 (12) and 3·126 (4) Å in the present structures, molecules *A*, *B* and *C*, respectively. This distance ranges from 2·98 to 3·18 Å in the other crystal structures. This is always a *β*(II) turn, as a result of the fact that the glycine, residue 6, assumes the conformational angles of a D-amino acid (Venkatachalam,

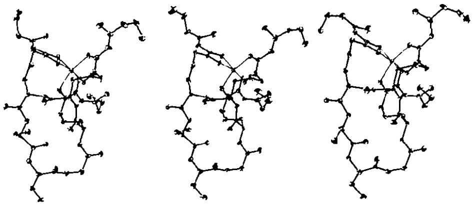

Fig. 2. Perspective views (Johnson, 1965) of (*a*) molecule *A* structure (I), (*b*) molecule *B* structure (I) and (*c*) molecule *C* structure (II). The thermal ellipsoids are drawn at the 50% probability level.

1968) and this is probably the reason that glycine as residue 6 is preserved in all known structures in the ferrichrome family.

The β(I) turn with ornithine residues 2 and 3 at the corners does not result in a hydrogen bond in any of the crystal structures. O(1) is rotated away from the mean plane of the peptide ring, and away from an interaction with N(4), apparently as a result of conformational constraints imposed on the molecule by metal chelation. The N(4)···O(1) distances are 4·21 (12), 4·13 (11), 4·24 (4) Å in molecules *A, B, C* and range from 3·9 to 4·5 Å in the other crystal structures.

A strong hydrogen bond linking the peptide backbone with the iron coordination octahedron is consistently observed in the crystal structures. The length of this bond, N(2)···O(2ε), is 2·776 (12), 2·799 (12) and 2·803 (4) Å, in molecules *A*, *B* and *C* of ferrirubin, respectively, and ranges from 2·73 to 2·81 Å in the other ferrichrome type structures.

Recently, Sheridan, Levy & Englander (1983) reported a study of the normal mode paths for exchange of the amide hydrogens of ferrichrome, in which an equilibrium conformation of ferrichrome was derived by applying energy-minimization calculation techniques to the X-ray structure coordinates. Given the presently available data base of crystal structures, it is worthwhile to compare the calculated conformational features and angles with those observed in the eight closely related molecules. All the observed and calculated (Sheridan *et al.*, 1983) conformational angles for the peptide ring are listed in Table 3. The largest deviation in equivalent peptide backbone torsion angles among the three ferrirubin molecules is at the ω angle of serine 4. This may well be related to the differing conformation of the serine side chains. The orientation of O(4β) with respect to N(4) is *gauche* in molecules *A* and *B*, and *trans* in molecule *C*. Among all the crystal structures, the most striking conformational variation is exhibited by ferricrocin molecule *A*, in which the Orn(3)—Gly(4) peptide bond is rotated well out of the mean plane of the hexapeptide ring, as indicated by the angles ψ_3 and φ_4. Such a rotation, which is hindered when residue 4 is a serine, tends to expose the N(4) hydrogen more to the solvent, and is a feature of the calculated minimum-energy ferrichrome conformation, as judged by the similar angles ψ_3 and φ_4. In the minimum-energy

Table 3. *Selected conformational angles* (°)

A molecule *A* of structure (I); *B* molecule *B* of structure (I); *C* molecule *C*, structure (II); *D* ferrichrome (van der Helm, Baker, Eng-Wilmot, Hossain & Loghry, 1980); *E* ferrichrome A (Zalkin, Forrester & Templeton, 1966); *F* ferrichrysin (Norrestam, Stensland & Brändén, 1975); *G, H* ferricrocin molecules *A* and *B* (Barnes, Eng-Wilmot & van der Helm, 1984); *I* 'energy-minimized conformation of ferrichrome' (Sheridan, Levy & Englander, 1983). E.s.d.'s are 1–2° for *A* and *B* and about 0·5° for *C*.

		Orn *i*=1	Orn *i*=2	Orn *i*=3	Res *i*=4	Res *i*=5	Gly *i*=6
Endocyclic angles							
C(*i*−1)—N(*i*)—C(*i*α)—C(*i*)	*A*	−150	−73	−105	−167	−58	87
	B	−151	−69	−104	−166	−60	89
	C	−154	−72	−113	−164	−45	77
	D	−163	−67	−120	165	−63	77
	E	−146	−81	−102	−164	−58	81
	F	−155	−78	−124	−166	−58	90
	G	−136	−70	−118	103	−55	84
	H	−154	−77	−128	177	−55	75
	I	−124	−95	−110	133	−68	115
N(*i*)—C(*i*α)—C(*i*)—N(*i*+1)	*A*	−167	−43	6	177	127	5
	B	−170	−42	−1	175	134	−1
	C	−167	−40	12	178	130	6
	D	−176	−33	22	−163	130	11
	E	−158	−51	7	176	133	1
	F	−163	−29	19	177	137	−7
	G	−167	−38	82	180	125	−9
	H	−174	−23	22	−178	135	4
	I	−147	−40	76	160	107	−19
C(*i*α)—C(*i*)—N(*i*+1)—C(*i*+1α)	*A*	−177	−166	175	−171	177	178
	B	−175	−164	175	−168	178	176
	C	−178	−167	180	167	172	−177
	D	−173	−168	180	−174	177	−169
	E	−174	−169	175	−170	177	179
	F	−176	−170	170	170	179	−178
	G	180	−173	−177	−167	175	−175
	H	−171	−173	177	180	177	−173
	I	167	179	−175	−173	−173	−179
Exocyclic angles							
C(*i*−1)--N(*i*)—C(*i*α)—C(*i*β)	*A*	85	168	128	69	−175	
	B	83	168	131	71	−175	
	C	80	167	122	77	−165	
N(*i*)—C(*i*α)—C(*i*β)—C(*i*γ)	*A*	59	−65	−66	66*	−178*	
	B	62	−63	−74	60	−179	
	C	60	−63	−71	−172	173	
C(*i*α)—C(*i*β)—C(*i*γ)—C(*i*δ)	*A*	177	76	157			
	B	178	73	163			
	C	175	75	161			
C(*i*β)—C(*i*γ)—C(*i*δ)—N(*i*ε)	*A*	−55	48	−58			
	B	−57	50	−62			
	C	−55	47	−60			
C(*i*γ)—C(*i*δ)—N(*i*ε)—O(*i*ε)	*A*	−61	−83	−49			
	B	−59	−82	−41			
	C	−65	−81	−38			
C(*i*γ)—C(*i*δ)—N(*i*ε)—C(*i*ζ)	*A*	112	92	135			
	B	113	93	145			
	C	112	88	142			
C(*i*δ)—N(*i*ε)—C(*i*ζ)—C(*i*η)	*A*	12	10	−9			
	B	9	12	−5			
	C	3	12	6			
O(*i*ε)N(*i*ε)—C(*i*ζ)—O(*i*ζ)	*A*	−1	−3	−2			
	B	3	2	1			
	C	0	−2	3			

* For serines 5 and 6, this angle is N(*i*)—C(*i*α)—C(*i*β)—O(*i*β).

conformation, Sheridan *et al.* listed two strong hydrogen bonds, N(1)—H···O(4) (H···O = 1·94 Å, N—H···O = 169°, which gives N···O distance of 2·93 Å assuming N—H = 1·0 Å) and N(2)—H···O(2ε) (H···O = 1·90 Å, N—H···O angle = 157°, which gives N···O distance of 2·85 Å with N—H = 1·0 Å), which are consistent with all the crystal structures. The authors further suggest a weak hydrogen bond for the β(I) bend, N(4)—H···O(1), and the presence of yet another hydrogen bond, N(3)—H···O(1ε) but provide no hydrogen-bond parameters for these two bonds. The range of N(4)···O(1) distances observed in the crystal structures, 3·9–4·5 Å, excludes any possibility of hydrogen-bond interaction between these atoms in all observed structures. The N(3)···O(1ε) distances in the crystal structures range between 3·2 Å in ferrichrysin and ferricrocin to 3·8 Å in ferrichrome A. In ferrirubin, the distances are 3·51 (molecule *A*), 3·64 (molecule *B*), and 3·42 Å (molecule *C*). One can at best assume a very weak interaction between the ornithyl (3) amide group with the iron coordination.

It should be noted that in eleven of the eighteen conformational angles around the peptide ring the calculated geometry represents an extreme value. Also, while the root-mean-square deviation of the energy-minimized ferrichrome conformation relative to the starting coordinates is given as 0·63 Å, least-squares fits of the 49 equivalent non-H atoms of the other crystal structures to the ferrichrome structure give the following r.m.s. results: ferrichrome A, 0·38 Å; ferricrocin molecule *A*, 0·38 Å; ferricrocin molecule *B*, 0·22 Å; ferrirubin molecule *A*, 0·32 Å; ferrirubin molecule *B*, 0·38 Å; ferrirubin molecule *C*, 0·25 Å. Conformational angles for the ornithine side chains of the calculated ferrichrome structure were not provided. These angles for the ferrirubin structures are listed in Table 3, and the small variations are representative of those of the other ferrichrome structures, and indicate the rigidity imposed on the molecule by metal chelation.

The conformations of the siderophore molecules in the crystal structures represent low-energy states, presumably perturbed from minimal-energy states by packing forces. A minimum-energy conformation could be expected to fall within the range of the observed conformations, but the conformation calculated by Sheridan *et al.* does not. The root-mean-square deviations, calculated above, show this not to be the case in the fact that the r.m.s. deviation between the observed and calculated structure of ferrichrome is larger rather than smaller than those r.m.s. deviations calculated among the observed structures in the series. A comparison of the conformational angles also shows the calculated structure to be an extreme rather than to fall within the range of the observed conformations. Eight of the calculated ring torsion angles are 10° or more from the nearest observed conformer, and one, φ_6, is 25° away from the closest observed value. It appears therefore that improvements could be made in the calculated minimum-energy conformation, possibly by the use of different energy parameters.

Figs. 3 and 4 are stereoviews of the packing in structures (I) and (II), respectively. In structure (I), the two independent molecules of ferrirubin are heavily hydrated, and the network of hydrogen-bond interactions involving bridging water molecules is quite extensive. There are only three intermolecular peptide–peptide hydrogen bonds, O(1κ)*A*···O(3κ)*A* (*x*,*y*,*z*−1) = 2·759 (12) Å, O(5β)*A*···O(5)*B* (*x*,1+*y*,*z*−1) = 2·647 (13) Å, O(5β)*A*···O(4β)*B* (*x*,1+*y*,*z*−1) = 2·691 (13) Å. Water molecules form 31 hydrogen bonds with the peptide molecules. Of these only four (two for molecule *A* and two for molecule *B*) involve amide groups. For each molecule, only the amide groups of peptide units 5 and 6 are involved in solvent interaction [N(5)*A*···*W*(5) = 2·828 (13) Å, N(6)*A*···*W*(16) = 3·102 (13) Å, N(5)*B*···*W*(10) = 2·854 (15) Å, N(6)*B*···*W*(3) = 2·840 (15) Å]. The three ornithine amide groups and also the N(4)H are well shielded from solvent approach and this situation seems to be a common feature of all ferrichrome structures. The solvent structure consists of a primary

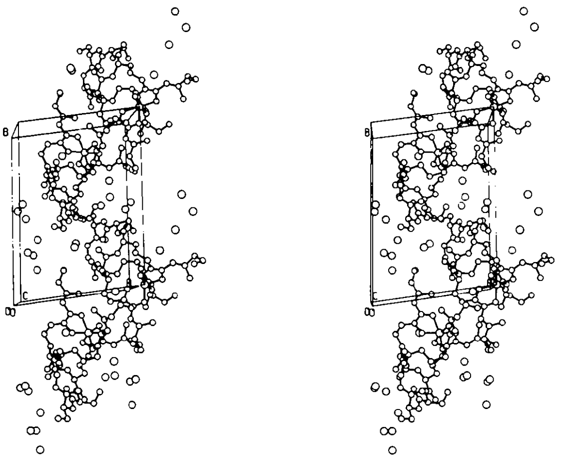

Fig. 3. Packing interactions, structure (I) (Motherwell, 1976).

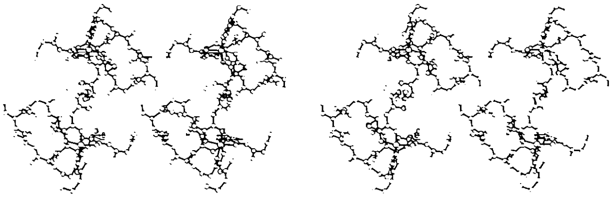

Fig. 4. Packing interactions, structure (II) (Motherwell, 1976).

and a secondary hydration sphere. Eighteen of the twenty-one water molecules are connected through a network of hydrogen bonds. $W(1)$, $W(6)$ and $W(10)$, which bridge peptide molecules, are not involved in any water–water interactions. Water molecules $W(15)$, $W(18)$, $W(19)$ and $W(20)$, on the other hand, do not form any hydrogen bond with the peptide molecules, and constitute the secondary hydration shell. Each of the water molecules, $W(2)$, $W(3)$, $W(8)$, $W(9)$, $W(11)$, $W(16)$ and $W(21)$ form two hydrogen bonds with the peptide molecules, while the rest of the water form only one hydrogen bond with the peptide molecules. Thirteen of the water molecules have a tetrahedral environment and the rest have trigonal arrangements of hydrogen bonds about them. The minimal solvent content of structure (II) allows for considerable direct intermolecular hydrogen bonding. There are five peptide–peptide and three peptide–water interactions. Only one of these involves an amide group, $O(3)C\cdots N(6)C$ $(-x, 0{\cdot}5+y, 1-z) = 2{\cdot}940\ (13)$ Å. The lone water molecule serves to bridge three siderophore molecules *via* hydrogen bonds, $W(1)\cdots O(6)$, $W(1)\cdots O(3\varepsilon)$ and $W(1)\cdots O(1\kappa)$. The acetonitrile does not hydrogen bond, but is involved in a number of close contacts. Despite the fact that the molecules *A*, *B* and *C* of ferrirubin have different modes of solvent interactions, the conformational differences in the three molecules are not very significant. It appears that, at least for ferrirubin, solvent interactions have very little effect on the conformation of the peptide backbone.

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References

ABU-DARI, K. & RAYMOND, K. N. (1977). *J. Am. Chem. Soc.* **99**, 2003–2005.

AHMED, F. R. (1966). SFLS program *NRC*-10. National Research Council, Canada.

BARNES, C. L., ENG-WILMOT, D. L. & VAN DER HELM, D. (1984). *Acta Cryst.* C**40**, 922–926.

EALICK, S. E., VAN DER HELM, D. & WEINHEIMER, A. J. (1975). *Acta Cryst.* B**31**, 1618–1626.

EMERY, T. (1980). *Biochem. Biophys. Acta*, **629**, 382–390.

GARIBALDI, J. A. & NEILANDS, J. B. (1955). *J. Am. Chem. Soc.* **77**, 2429–2430.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

IUPAC–IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). *Biochemistry*, **9**, 3471–3479.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KARLE, I. L. (1981). *The Peptides*, Vol. 4, edited by E. GROSS & J. MEINHOFER, p. 1. New York: Academic Press.

LEONG, J. & RAYMOND, K. N. (1974). *J. Am. Chem. Soc.* **96**, 6628–6630.

MOTHERWELL, W. D. S. (1976). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

NEILANDS, J. B. (1981). *Annu. Rev. Biochem.* **50**, 715–731.

NORRESTAM, R., STENSLAND, B. & BRÄNDÉN, C.-I. (1975). *J. Mol. Biol.* **99**, 501–506.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

SHERIDAN, R. P., LEVY, R. M. & ENGLANDER, S. W. (1983). *Proc. Natl Acad. Sci. USA*, **80**, 5569–5572.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

VAN DER HELM, D., BAKER, J. R., ENG-WILMOT, D. L., HOSSAIN, M. B. & LOGHRY, R. A. (1980). *J. Am. Chem. Soc.* **102**, 4224–4231.

VAN DER HELM, D., BAKER, J. R., LOGHRY, R. A. & EKSTRAND, J. D. (1981). *Acta Cryst.* B**37**, 323–330.

VENKATACHALAM, C. M. (1968). *Biopolymers*, **6**, 1425–1436.

ZALKIN, A., FORRESTER, J. D. & TEMPLETON, D. H. (1966). *J. Am. Chem. Soc.* **88**, 1810–1814.

Acta Cryst. (1985). C**41**, 347–350

Structure of Diaquaoxodiperoxomolybdenum(VI)–1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6) Monohydrate, $[MoO(O_2)_2(H_2O)_2].C_{12}H_{24}O_6.H_2O$

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Abstract. $M_r = 494{\cdot}30$, orthorhombic, $A2_1ma$, $a = 12{\cdot}882\ (2)$, $b = 13{\cdot}683\ (2)$, $c = 12{\cdot}020\ (2)$ Å, $V = 2118{\cdot}7\ (6)$ Å^3, $Z = 4$, $D_m = 1{\cdot}570\ (2)$, $D_x = 1{\cdot}550$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 6{\cdot}77$ cm^{-1}, $F(000) = 1024$, $T = 293\ (2)$ K. Final $R = 0{\cdot}028$ for 1252 observed reflections. The Mo atom has a distorted pentagonal bipyramidal seven-coordination with the two peroxo groups and one water in the equatorial plane, and the double-bonded O and another water at the apices. Two O atoms of the 18-crown-6 are on the mirror plane, but the symmetry of the crown is actually close to D_{3d} with the configurations at C—C *gauche*, at C—O *trans*. Five of the O atoms of the crown are hydrogen-bonded to water molecules; the sixth O does not participate in hydrogen bonding. The presence of the peroxo groups was unexpected, since no strong oxidizing agent was added in the preparation of the compound.

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