aux autres atomes d'indium présents; ainsi dans In_6Se_7 (Hogg, 1971) pour In(1), dans In_4Se_3 (Likforman & Etienne, 1972) pour In(5) et dans $In_6La_{10}O_6S_{17}$ (Gastaldi, Carré & Pardo, 1982) pour In(3).

L'étain divalent est à l'intérieur d'un prisme à base triangulaire dont les six sommets sont occupés par les atomes de soufre; un septième atome de soufre se situe en avant de l'une des faces latérales du prisme (prisme monocapé), à une distance plus grande. Le fait que son site ne soit occupé qu'une fois sur deux, en désordre statistique dans le cristal, fait que les atomes de soufre qui l'entourent [S(2), S(6), S(7)] ont des facteurs d'agitation thermique plus élevés que les autres atomes de soufre. Leur image moyenne est, en effet, un peu plus floue puisqu'ils entourent tantôt une lacune et tantôt un atome d'étain et que leur position n'est pas la même dans les deux cas. Cela confirme le désordre statistique du site de l'étain.

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Tribarium Strontium Diruthenate(V), $Ba_3SrRu_2O_9$, a Rietveld Refinement of Neutron Powder Diffraction Data

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Abstract. $M_r = 845{\cdot}83$, monoclinic, $C2/c$, $Z = 4$. At room temperature: $a = 5{\cdot}9614\ (2)$, $b = 10{\cdot}3054\ (3)$, $c = 15{\cdot}0763\ (7)$ Å, $\beta = 91{\cdot}181\ (2)°$, $V = 926{\cdot}02\ (7)$ Å^3, $D_x = 6{\cdot}067\ (1)$ Mg m^{-3}. At 4·2 K: $a = 5{\cdot}9548\ (2)$, $b = 10{\cdot}2740\ (3)$, $c = 15{\cdot}0129\ (6)$ Å, $\beta = 91{\cdot}687\ (2)°$, $V = 918{\cdot}09\ (6)$ Å^3, $D_x = 6{\cdot}119\ (1)$ Mg m^{-3}. The structure has been refined by Rietveld analysis of powder neutron diffraction data recorded at room temperature [$\lambda = 2{\cdot}5930\ (3)$ Å, $R_I = 2{\cdot}08$, $R_P = 4{\cdot}78$, $R_{wP} = 5{\cdot}67\%$] and at 4·2 K [$\lambda = 2{\cdot}5904\ (3)$ Å, $R_I = 1{\cdot}68$, $R_P = 4{\cdot}95$, $R_{wP} = 5{\cdot}65\%$], both for 217 reflections. The structure at both temperatures is of a modified hexagonal $BaTiO_3$ type. BaO_3 layers are stacked $(hcc)_2$ resulting in pairs of face-sharing octahedra, which share corners with single octahedra. The Sr atoms are located in the single octahedra and the Ru atoms in the face-sharing ones. All octahedra are tilted about an axis parallel to **b**.

Introduction. The preparation, crystal structure determination and solubility test in water at elevated temperatures and pressures form part of a research programme to investigate compounds with perovskite or related structures for their properties as a host lattice for nuclear waste. $Ba_3SrRu_2O_9$ is reported to adopt a monoclinically distorted 6*L* $BaTiO_3$ structure (Darriet, Drillon, Villeneuve & Hagenmuller, 1976), which was deduced from X-ray diffraction. Recently Treiber, Kemmler-Sack & Ehmann (1982) reported that the pure compound could not be prepared.

Experimental. AR starting materials $BaCO_3$, $SrCO_3$ and Ru thoroughly mixed in an agate mortar in the appropriate ratio; mixture heated at 1073 K for 1 d and at 1273 K for 3 d, both in air; after grinding, product was sealed in a platinum capsule and heated at 1473 K for one week. X-ray powder diffraction pattern obtained with a Philips PW 1050 diffractometer; all lines could be indexed with a monoclinic unit cell; systematically absent reflections suggest space groups $C2/c$ and Cc, in accordance with electron diffraction data (Siemens Elmiskop 102 electron microscope, double tilt, lift cartridge, 100 kV). Since no single crystals were available Rietveld's (1969) method was used for refinement of neutron powder diffraction data; $5° < 2\theta < 163°$ in steps of 0·1°; neutrons at room

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Table 1. *Fractional atomic coordinates and isotropic thermal parameters* (Å^2) *of* $Ba_3SrRu_2O_9$ *at room temperature and* 4·2 K

	x	*y*	*z*	*B*(Å^2)
$Ba_3SrRu_2O_9$, room temperature				
Ba(1)	0	−0·0033 (11)	0·25	1·2 (1)
Ba(2)	0·0042 (8)	0·3338 (8)	0·1035 (2)	1·3 (1)
Sr	0	0	0	1·0 (1)
Ru	−0·0129 (5)	0·3316 (6)	0·8385 (2)	1·2 (1)
O(1)	0	0·5168 (7)	0·25	0·7 (1)
O(2)	0·2272 (10)	0·7408 (6)	0·2575 (3)	0·7 (1)
O(3)	0·8019 (9)	0·5921 (5)	0·0827 (3)	1·7 (1)
O(4)	0·0334 (10)	0·8228 (5)	0·0979 (3)	1·8 (1)
O(5)	0·2621 (8)	0·5911 (5)	0·1065 (2)	1·2 (1)
$Ba_3SrRu_2O_9$, 4·2 K				
Ba(1)	0	−0·0052 (9)	0·25	0·0 (1)
Ba(2)	0·0080 (7)	0·3334 (7)	0·1021 (3)	0·7 (1)
Sr	0	0	0	0·4 (1)
Ru	−0·0212 (5)	0·3328 (5)	0·8382 (2)	1·1 (1)
O(1)	0	0·5145 (7)	0·25	−0·2 (2)
O(2)	0·2275 (8)	0·7399 (6)	0·2614 (2)	0·7 (1)
O(3)	0·8158 (6)	0·5943 (5)	0·0784 (2)	0·6 (1)
O(4)	0·0421 (7)	0·8244 (5)	0·1007 (2)	0·7 (1)
O(5)	0·2728 (7)	0·5932 (4)	0·1075 (2)	0·1 (1)
$Ba_3SrNb_2O_9$, room temperature				
Ba(1)	0	0	0·25	0·36 (8)
Ba(2)	$\frac{1}{3}$	$\frac{2}{3}$	0·1185 (2)	1·04 (7)
Sr	0	0	0	0·82 (8)
Nb	$\frac{1}{3}$	$\frac{2}{3}$	0·8465 (2)	0·28 (5)
O(1)	0·5645 (4)	0·0450 (4)	0·25	0·60 (5)
O(2)	0·7661 (3)	0·6446 (4)	0·0977 (1)	1·30 (4)

Table 2. *Atomic distances* (Å) *at room temperature*

a (about) equilateral distances. Atoms O(1) and O(2) of $Ba_3SrRu_2O_9$ correspond to O(1) of $Ba_3SrNb_2O_9$ and O(3), O(4) and O(5) to O(2).

$Ba_3SrRu_2O_9$ (this work)		$Ba_3SrNb_2O_9$ (Zandbergen & IJdo, 1983)	
Ba(1)–O(1) *a*	2·988 (1)	Ba(1)–O(1) *a*	2·781 (3)
–O(2) *a*	2·966 (12)	–O(1) *a*	3·306 (3)
–O(2) *a*	2·999 (11)		
–O(3)	3·279 (6)	–O(2)	3·015 (3)
–O(4)	2·920 (8)		
–O(5)	2·741 (6)		
Ba(2)–O(1)	2·905 (8)	Ba(2)–O(1)	2·839 (3)
–O(2)	2·781 (7)		
–O(2)	3·032 (7)		
–O(3) *a*	2·937 (9)	–O(2) *a*	2·716 (2)
–O(3) *a*	3·078 (9)	–O(2) *a*	3·393 (2)
–O(3)	3·152 (6)	–O(2)	3·721 (3)
–O(4) *a*	2·808 (8)		
–O(4) *a*	3·160 (8)		
–O(4)	3·442 (7)		
–O(5) *a*	2·889 (9)		
–O(5) *a*	3·065 (9)		
–O(5)	3·597 (5)		
Sr–O(3)	2·367 (5)	Sr–O(2)	2·422 (2)
–O(4)	2·354 (5)		
–O(5)	2·359 (4)		
Ru–O(1)	2·057 (8)	Nb–O(1)	2·147 (2)
–O(2)	2·042 (7)		
–O(2)	2·051 (6)		
–O(3)	1·884 (6)	–O(2)	1·879 (2)
–O(4)	1·863 (7)		
–O(5)	1·892 (6)		
Ru–Ru	2·676 (6)	Nb–Nb	2·968 (3)

temperature and 4·2 K from (111) planes of a Cu crystal; pyrolytic graphite with a total thickness of 120 mm as a second-order filter; Soller slits, horizontal divergence 0·5°, placed between the reactor and the monochromator and in front of each of the four ^{3}He counters; sample holder (∅ = 29 mm) consisted of a V tube, closed with Cu plugs fitted with O-rings. No precautions against preferred orientations. Max. absorption correction 5%, $\mu R = 0{\cdot}455$ (Weber, 1967). Background determined from those parts in the diagram not containing any contribution from reflections or – for high values of 2θ – only a small contribution, and extrapolation between these points. Statistically expected values of R_{wP} 3·52 and 3·83% respectively. The stability in water at 573 K and 0·2 GPa for 1 h was tested; it was found that $Ba_3SrRu_2O_9$ decomposes completely. Similar results were obtained for $Ba_3MRu_2O_9$ compounds with M = Y, Nd or Ni. The hexagonal $BaTiO_3$ structure (Burbank & Evans, 1948) was used as a trial model, modified for space group *C*2/*c* with small shifts in the positional parameters from the ideal positions: Ba(1) on 4(*e*) (0,*y*,0); Ba(2) on 8(*f*) (*x*,*y*,*z*); Sr on 4(*a*) (0,0,0); Ru on 8(*f*); O(1) on 4(*c*) and O(2), O(3), O(4) and O(5) all on 8(*f*). 40 parameters in the refinement: a scale factor, three half-width parameters defining the Gaussian line shape of the reflections, the counter zero error, a preferred-orientation parameter (along [001]), an asymmetry parameter below $2\theta = 37°$, the unit-cell parameters, the atomic positional parameters and the isotropic thermal parameters. Coherent scattering lengths: Ba 5·25, Sr 7·02, Ru 7·21, O 5·805 fm (Koester, Rauch, Herkens & Schroeder, 1981). The Rietveld program minimizes the function $\chi^2 = \sum_i w_i[y_i(\text{obs.}) - (1/c)y_i(\text{calc.})]^2$, where y_i(obs.) and y_i(calc.) are the observed and calculated data points, w_i

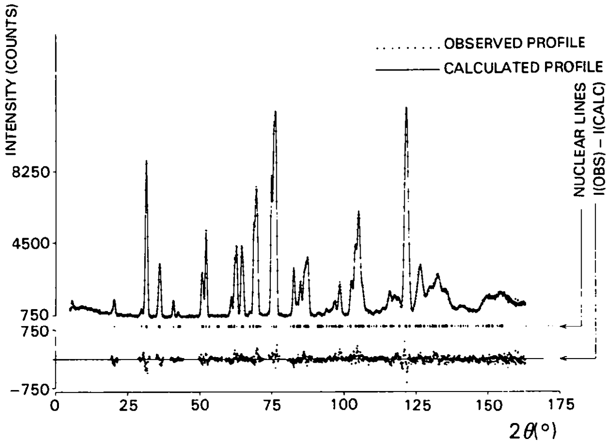

Fig. 1. Observed (dots) and calculated (full line) neutron diffraction profile of $Ba_3SrRu_2O_9$ at room temperature; a difference (observed – calculated) curve appears at the bottom of the figure. Tick marks below the profile indicate the positions of the Bragg reflections included in the calculation.

is the statistical weight $[1/y_i(\text{obs.})]$ allotted to each data point and c is the scale factor. The following R factors were calculated:

$$R_I = 100\sum|I_i(\text{obs.})-(1/c)I_i(\text{calc.})|/\sum I_i(\text{obs.}),$$
$$R_P = 100\sum|y_i(\text{obs.})-(1/c)y_i(\text{calc.})|/\sum y_i(\text{obs.}),$$
$$R_{wP} = 100[\sum w_i|y_i(\text{obs.})-(1/c)y_i(\text{calc.})|^2/\sum w_i|y_i(\text{obs.})|^2]^{1/2},$$

where I_i(obs.) and I_i(calc.) are the observed and calculated integrated intensities of each reflection. $\Delta/\sigma < 0.3$ in final cycle. To test whether or not a false minimum was obtained another refinement was performed using the atomic parameters of $SrIrO_3$ (Longo, Kafalas & Arnott, 1971), which also has a deformed $BaTiO_3$ structure; this lead to the same final parameters and R values. Refinement in space group *Cc* did not result in significantly lower R values.

Discussion. Atomic parameters are given in Table 1, atomic distances in Table 2.[*] The agreement between the observed and calculated profiles of the room-temperature data is shown in Fig. 1.

The present refinement confirms the conclusion of Darriet, Drillon, Villeneuve & Hagenmuller (1976) that $Ba_3SrRu_2O_9$ adopts a monoclinically distorted $BaTiO_3$ structure. As in hexagonal $BaTiO_3$, in the title compound BaO_3 layers are stacked $(hcc)_2$ resulting in pairs of face-sharing octahedra, which share corners with single octahedra. The Sr atoms are located in the single octahedra and the Ru atoms in the face-sharing one.

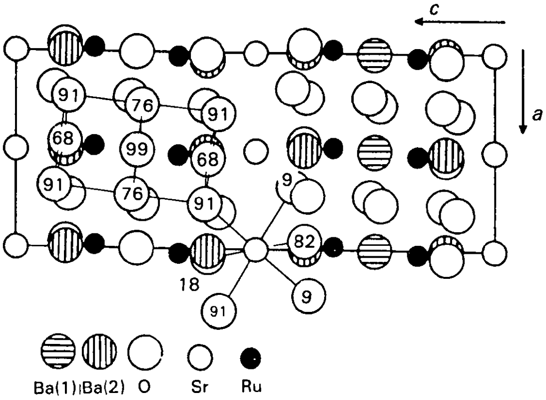

Fig. 2. $Ba_3SrRu_2O_9$ at 4·2 K. Projection on (010) showing the close-packed layers of the structure parallel to (001). One Ru_2O_9 bioctahedron (Ru on $y = 0.83$) and one SrO_6 octahedron (Sr on $y = 0$) are indicated, with the fractional y coordinates ($\times 10^2$) of their O^{2-} ions.

Unlike hexagonal $BaTiO_3$, in $Ba_3SrRu_2O_9$ all octahedra are tilted about an axis parallel to the b axis leading to a monoclinic distortion of the unit cell as can be seen from Fig. 2. If the angle between the Ru—Ru axis and $\mathbf{c}^*$ is taken as the tilting angle, the tilting angles for the Ru bioctahedra are 4·5 (1) and 7·1 (1)° at room temperature and 4·2 K respectively. For Sr at 0,0,0, if the angle between $\mathbf{c}^*$ and the axis between the centre of mass of the three O atoms at $z > 0$ and that of the three O atoms at $z < 0$ is taken as the tilting angle, these angles for the SrO_6 octahedra are 6·5 (1) and 8·4 (1)° respectively.

The deviation from the hexagonal $BaTiO_3$ structure can be explained as follows. In the parent structure the octahedra have about the same size, occupied by Ti^{4+} ions (radius 0·61 Å). In the compound investigated the radius of Sr^{2+} (1·18 Å) differs markedly from the radius of Ru^{5+} [0·57 Å, all radii for six coordination (Shannon, 1976)]. Consequently, octahedra of different sizes are expected and are indeed found. Stacking of SrO_6 and RuO_6 octahedra of different sizes results in too much space for Ba. This is decreased by a tilt of the octahedra. The SrO_6 octahedron and the Ru_2O_9 bioctahedron behave almost as rigid bodies and are consequently only slightly distorted by the rotation (see Table 2 and Fig. 2).

In $Ba_3SrNb_2O_9$ (Table 1) and $Ba_3SrTa_2O_9$, which adopt the same parent structure (radii 0·64 Å for Nb^{5+} and Ta^{5+}), it was found recently (Zandbergen & IJdo, 1983) that the octahedra are tilted around their threefold axis parallel to the c axis, leading to the space group $P6_3/m$. In this case larger differences in the Ba—O distances occur (Table 2).

The 4·2 K diffraction pattern gave no indication of a three-dimensional (3D) spin ordering. This result is in agreement with Drillon (1977) and Darriet, Soubeyroux & Murani (1983) who found no 3D magnetic ordering at 4·2 K by Mössbauer measurements. The Ru—Ru distance is nearly the same at both temperatures: 2·676 (6) Å at 300 K and 2·668 (6) Å at 4·2 K. In the related compounds $Ba_3SrM_2O_9$, $M = $ Nb, Ta (Zandbergen & IJdo, 1983), the M—M distance in the M_2O_9 group is significantly longer, 2·968 (3) and 2·951 (3) Å respectively. The octahedral tilt in the probably isomorphous $SrIrO_3$ (Longo *et al.*, 1971) is currently under research.

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[*] The numerical intensity of each measured point, as a function of the angle, and the final parameters, which are not given in this paper, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39238 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Ferricrocin ($C_{29}H_{44}FeN_9O_{13}.7H_2O$), an Iron(III)-Binding Peptide from *Aspergillus versicolor*

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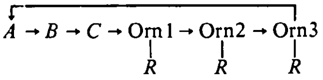
Abstract. $M_r = 908{\cdot}7$, $P2_1$, $a = 11{\cdot}178\,(5)$, $b = 17{\cdot}809\,(11)$, $c = 21{\cdot}805\,(13)$ Å, $\beta = 104{\cdot}14\,(3)°$, $V = 4209{\cdot}2$ Å^3, $Z = 4$, $D_x = 1{\cdot}43$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 4{\cdot}5$ cm^{-1}, $F(000) = 1924$, $T = 138\,(2)$ K, final $R = 0{\cdot}0991$ for 8973 unique reflections, $R = 0{\cdot}0716$ for 6879 observed data. Ferricrocin was isolated from low-iron cultures of *Aspergillus versicolor,* and purified by silica-gel chromatography. One of the two independent molecules is conformationally very similar to the crystal structure conformations of ferrichrome and ferrichrome A, but the other molecule assumes a somewhat different conformation of the cyclic hexapeptide ring.

Introduction. In response to low iron availability, microorganisms elaborate iron-binding compounds of low molecular mass ($\lesssim$1000 daltons), which are capable of solubilizing ferric iron and making it available to the cell. These compounds have been called siderochromes and siderophores. Emery and Neilands have suggested that the term siderophore be reserved for those compounds proven to transport iron across the cell membrane (Emery, 1980; Neilands, 1981*a,b*).

The ligand of the ferrichrome-type siderophores (hereafter referred to collectively as ferrichromes) are cyclic hexapeptides of the general formula

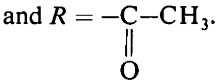


$$\overline{A \rightarrow B \rightarrow C \rightarrow \underset{R}{\underset{|}{\mathrm{Orn1}}} \rightarrow \underset{R}{\underset{|}{\mathrm{Orn2}}} \rightarrow \underset{R}{\underset{|}{\mathrm{Orn3}}}}$$

where A and B are glycine, alanine or serine residues and C is a glycine residue, and Orn1, 2 and 3 are N^{δ}-acyl-N^{δ}-hydroxyornithine residues, with R, the acyl group, derived from one or more of a number of carboxylic acids. Ferrichromes chelate iron with the six oxygens of the hydroxamate moieties of the modified ornithine residues. The dissociation constants of the ferric complexes are of the order of 10^{-30} (Anderegg, L'Eplattenier & Schwarzenbach, 1963).

Ferrichromes have been found to be produced by *Penicillia, Aspergilli, Neurospora* and *Ustilago* species (Neilands, 1981*a*) and by *Fusarium roseum* (Emery, 1980). It is not uncommon that a fungal culture will yield more than one of these siderochromes, though there is species specificity at least in the relative proportions produced.

We report here the crystal structure of ferricrocin, for which $A = C =$ glycine, $B =$ serine, and



$R = -\underset{\underset{\displaystyle O}{\|}}{C}-CH_3.$

Experimental. The iron-free ligand of ferricrocin was produced in low-iron cultures of *Aspergillus versicolor* (wild type). 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). Ferricrocin was purified by preparative thin-layer silica-gel chromatography, developing solvent $CHCl_3$: CH_3OH:

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