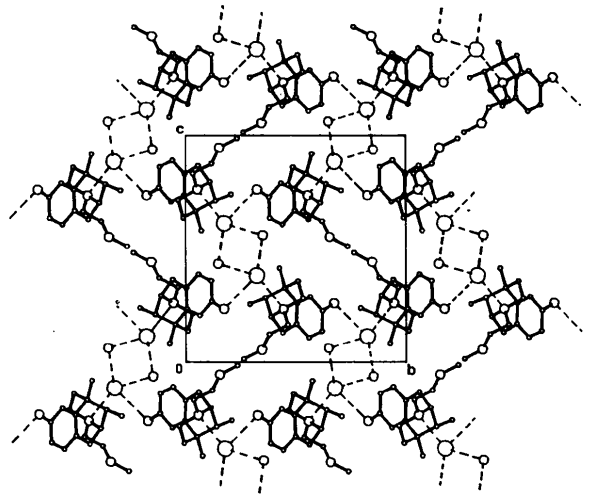

Fig. 3. A view of the crystal along a showing the packing. Hydrogen bonds are indicated by dashed lines.

171 (4)°; O(2′)···Br^{i} 3·254 (3), H(2′)···Br^{i} 2·41 (5) Å, O(2′)—H(2′)···Br^{i} 170 (4)°; O(16)···Br 3·385 (4), H(16*A*)···Br 2·85 (6) Å, O(16)—H(16*A*)···Br 131 (5)°; O(16)···Br^{ii} 3·485 (4), H(16*B*)···Br^{ii} 2·48 (7) Å, O(16)—H(16*B*)···Br^{ii} 152 (6)°; (i) $-x+1$, $y+\frac{1}{2}$, $-z+\frac{1}{2}$; (ii) $x+\frac{1}{2}$, $-y+\frac{1}{2}$, $-z+1$].

The authors thank Dr H. Merz, Boehringer Ingelheim, for providing the title compound.

References

Beurskens, G., Noordik, J. H. & Beurskens, P. T. (1980). *Cryst. Struct. Commun.* **9**, 23–28.
Beurskens, P. T., Bosman, W. P., Doesburg, H. M., Gould, R. O., van den Hark, Th. E. M., Prick, P. A. J., Noordik, J. H., Beurskens, G. & Parthasarathi, V. (1981). *DIRDIF*. Tech. Rep. 1981/2. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
De Ranter, C. J., Verlinde, C. L., Blaton, N. M. & Peeters, O. M. (1984). *Neuropeptides*, **5**, 209–212.
Giglio, E. (1969). *Nature (London)*, **222**, 339–341.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Merz, H. & Stockhaus, K. (1979). *J. Med. Chem.* **22**, 1475–1483.
Motherwell, S. (1974). *EENY*. Potential-energy calculation program, version of June 1974. Univ. Chemical Laboratory, Lensfield Road, Cambridge, England.
North, A. C. T., Phillips, D. C. & Mathews, F. (1968). *Acta Cryst.* A**24**, 351–359.
Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). The *XRAY76* system. Tech. Rep. TR446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **99**, 5063–5070.
Verlinde, C. L., Blaton, N. M., Peeters, O. M. & De Ranter, C. J. (1988). *Acta Cryst.* C**44**, 1789–1791.
Verlinde, C. L. & De Ranter, C. J. (1988). *Eur. J. Pharmacol.* **153**, 83–87.

Acta Cryst. (1988). C**44**, 1794–1797

X-ray Studies on Crystalline Complexes Involving Amino Acids and Peptides. XVI.* Structure of L-Ornithine D-Aspartate Monohydrate

By Jayashree Soman and M. Vijayan

Molecular Biophysics Unit, Indian Institute of Science, Bangalore – 560 012, India

(*Received* 16 *March* 1988; *accepted* 25 *May* 1988)

Abstract. $C_5H_{13}N_2O_2^+.C_4H_6NO_4^-.H_2O$, $M_r = 283$, monoclinic, $P2_1$, $a = 5{\cdot}118\,(1)$, $b = 7{\cdot}881\,(2)$, $c = 16{\cdot}025\,(2)$ Å, $\beta = 91{\cdot}78\,(2)°$, $V = 646{\cdot}1\,(4)$ Å^3, $Z = 2$, $D_m = 1{\cdot}46\,(2)$, $D_x = 1{\cdot}45$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}7107$ Å, $\mu = 1{\cdot}376$ cm^{-1}, $F(000) = 304$, final $R = 0{\cdot}055$ for 1370 observed reflections. The aggregation pattern in the present structure is entirely different from that in L-ornithine L-aspartate hemihydrate. It is similar to that in L-lysine D-aspartate monohydrate in that the unlike molecules aggregate into separate alternating layers, but is different from that in the other LD amino acid–amino acid complexes analysed so far. An interesting feature of the structure is an internal hydrogen bond between the α-amino group and one of the side-chain carboxyl O atoms in the aspartate ion. The structure contains a closed hydrogen-bonded loop made up of alternating amino and carboxylate groups.

Introduction. X-ray studies of crystalline complexes involving amino acids and peptides being carried out in

---

*Part XV: Soman, Suresh & Vijayan (1988).

0108-2701/88/101794-04$03.00 © 1988 International Union of Crystallography

Table 1. *Positional parameters* (× 10^4) *and equivalent isotropic temperature factors* (*Hamilton,* 1959) *of non*-H *atoms*

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

	x	y	z	B_{eq}(Å^2)
N1	5772 (6)	737	9264 (2)	1·59 (7)
O1	7639 (5)	2800 (5)	10522 (2)	2·33 (7)
O2	11606 (5)	2743 (5)	9996 (2)	2·22 (7)
C1	9199 (7)	2523 (5)	9956 (2)	1·46 (7)
C2	7964 (7)	1930 (5)	9119 (2)	1·39 (7)
C3	6881 (8)	3465 (6)	8642 (3)	1·94 (9)
C4	9002 (8)	4694 (6)	8405 (3)	2·07 (9)
C5	7854 (8)	6289 (6)	8023 (3)	2·10 (9)
N6	9919 (7)	7546 (5)	7887 (2)	2·01 (7)
N11	8909 (7)	7015 (5)	3657 (2)	1·99 (8)
O11	6763 (6)	5386 (5)	2331 (2)	2·50 (7)
O12	2848 (6)	5194 (5)	2867 (2)	2·81 (8)
C11	5240 (8)	5519 (6)	2902 (2)	1·81 (8)
C12	6317 (8)	6232 (6)	3748 (2)	1·70 (8)
C13	6504 (9)	4796 (6)	4396 (3)	2·59 (10)
C14	7693 (8)	5352 (6)	5245 (3)	2·28 (10)
O15	9456 (8)	6431 (6)	5264 (2)	4·00 (10)
O16	6854 (7)	4619 (6)	5870 (2)	3·34 (9)
*W*1	2441 (6)	5617 (5)	6635 (2)	2·92 (8)

this laboratory have provided useful information on biologically significant specific interactions and interaction patterns (Sudhakar & Vijayan, 1980; Sudhakar, Bhat & Vijayan, 1980; Salunke & Vijayan, 1981, 1983, 1984; Vijayan, 1983). They have also led to an approach to chemical evolution based on molecular interactions and interaction patterns (Vijayan, 1980; Suresh & Vijayan, 1983*a,b,c*; Suresh & Vijayan, 1985; Vijayan & Suresh, 1985). These studies have recently been expanded to include analysis of complexes containing D as well as L amino acids (Suresh, Ramaswamy & Vijayan, 1986; Soman, Suresh & Vijayan, 1988). The work on LD complexes has provided interesting insights into the effect of chirality on molecular aggregation and its possible implications. Here we report the crystal structure of another such complex, that between L-ornithine and D-aspartic acid.

Experimental. Crystals of the complex were grown using the vapour diffusion technique from aqueous solutions of the amino acids in molar proportion, with acetone as the precipitant. Space group ($0k0$, k odd, systematically absent) and unit-cell dimensions were determined from preliminary X-ray diffraction photographs. The density was measured by flotation in a mixture of benzene and carbon tetrachloride. Crystal of dimensions 0·1 × 0·4 × 0·5 mm. Unit-cell dimensions and orientation matrix were refined on a CAD-4 diffractometer using 25 reflections in the range $14 < \theta < 25°$; monochromated Mo $K\alpha$ radiation; 2176 reflections measured with $\theta < 28°$; 2054 unique, 1370 with $I > 2\sigma(I)$; h 0 to 6, k 0 to 10, l −21 to 21. 348, 1,1,12, 446 used as standard reflections; maximum variation in intensity 2%; $R_{\rm int} = 0{\cdot}017$. Intensities were not corrected for absorption. The structure was solved by direct methods using the *MULTAN*80 system of programs (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The structure was refined against F, non-H atoms anisotropically and H atoms isotropically, using the block-diagonal least-squares method (9 × 9 and 4 × 4 matrices respectively for non-H and H atoms) employing the locally modified version of a program originally written by Dr R. Shiono. Refinement converged at $R = 0{\cdot}055$, $wR = 0{\cdot}070$, $S = 0{\cdot}6178$. Max. $\Delta/\sigma = 0{\cdot}146$. The weighting scheme used was of the form $1/(a + bF_o + cF_o^2)$ with $a = 2{\cdot}7800$, $b = -0{\cdot}3440$ and $c = 0{\cdot}0167$. Max. and min. values in the final difference Fourier map were 0·33 and −0·34 e Å^{-3}, respectively. Form factors for non-H atoms were taken from Cromer & Waber (1965) and those for H atoms from Stewart, Davidson & Simpson (1965). The final positional coordinates and equivalent isotropic temperature factors (Hamilton, 1959) of the non-H atoms are listed in Table 1.*

Discussion. *Molecular structure.* The bond lengths and angles in the positively charged ornithine molecule and the negatively charged aspartate ion are normal and do not merit any comment. The torsion angles that define the conformation of the two zwitterions (IUPAC–IUB Commission on Biochemical Nomenclature, 1970) are as follows:

Ornithine: $\psi' = -39{\cdot}0$ (4); $\psi'' = 143{\cdot}7$ (3); $\chi^1 = -175{\cdot}6$ (3); $\chi^2 = -173{\cdot}5$ (3); $\chi^3 = 173{\cdot}5$ (3)°;

aspartate: $\psi' = 13{\cdot}5$ (5); $\psi'' = -163{\cdot}9$ (4); $\chi^1 = 54{\cdot}5$ (5); $\chi^{21} = -35{\cdot}2$ (6); $\chi^{22} = 147{\cdot}4$ (4)°.

The energetically most favourable conformation with the side chain *trans* to the α-carboxylate group ($\chi^1 \sim -60°$) is found in L-ornithine L-aspartate hemihydrate (Salunke & Vijayan, 1983) and L-ornithine.HCl (Chiba, Ueki, Ashida, Sasada & Kakudo, 1967). The observed value of χ^1 in the present structure corresponds to the next most favourable conformation with the side chain *trans* to the α-amino group ($\chi^1 \sim 180°$). But, unlike L-ornithine aspartate hemihydrate where the side chain has a somewhat folded conformation, the side chain in the present structure has an all-*trans* fully extended conformation ($\chi^2 \sim 180°$, $\chi^3 \sim 180°$), as in L-ornithine.HCl.

Two torsion angles, χ^1 and either χ^{21} or χ^{22}, are required to specify the conformation of the side chain in the aspartate ion. The torsion angle χ^1 in the present structure has a value close to 60°, corresponding to the sterically most favourable conformation in which the α- and the side-chain carboxyl groups are *trans* to each other. The molecule assumes this conformation in a majority of the crystal structures containing aspartic

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51072 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Hydrogen-bond parameters with e.s.d.'s in parentheses*

A—H$\cdots B$	$A\cdots B$(Å)	H—$A\cdots B$(°)	Symmetry of atom B
N1—H1(N1)$\cdots$O2	2·929 (4)	11 (3)	$x-1, y, z$
N1—H2(N1)$\cdots$O11	2·844 (4)	18 (4)	$-x+1, \frac{1}{2}+y-1, -z+1$
N1—H3(N1)$\cdots$O2	2·945 (4)	7 (3)	$-x+2, \frac{1}{2}+y-1, -z+2$
N6—H1(N6)$\cdots W$1	2·857 (5)	19 (3)	$x+1, y, z$
N6—H2(N6)$\cdots$O12	2·778 (5)	10 (4)	$-x+1, \frac{1}{2}+y, -z+1$
N6—H3(N6)$\cdots$O1	2·811 (4)	11 (5)	$-x+2, \frac{1}{2}+y, -z+2$
N11—H1(N11)$\cdots W$1	2·955 (6)	10 (3)	$-x+1, \frac{1}{2}+y, -z+1$
N11—H2(N11)$\cdots$O15	2·624 (5)	19 (5)	x, y, z
N11—H3(N11)$\cdots$O12	2·808 (5)	10 (3)	$x+1, y, z$
W1—H1(W1)$\cdots$O16	2·719 (5)	5 (3)	x, y, z
W1—H2(W1)$\cdots$O15	2·713 (5)	9 (8)	$x-1, y, z$

acid or the aspartate ion (Derissen, Endeman & Peerdeman, 1968; Rao, 1973; Bhat & Vijayan, 1976; Salunke & Vijayan, 1982*b*, 1983; Soman, Suresh & Vijayan, 1988). The side-chain carboxyl group does not appear to have a preferred orientation with respect to the rest of the molecule and χ^{21} (or χ^{22}) can assume all possible values (Bhat, Sasisekharan & Vijayan, 1979; Salunke & Vijayan, 1983). However, it is found that certain combinations of χ^1 and χ^{21} lead to the formation of an internal hydrogen bond between the α-amino group and the side-chain carboxyl group. This obviously cannot happen when the amino and the carboxyl groups are *trans* with respect to each other ($\chi^1 \sim 180°$). Simple calculations show that when $\chi^1 \sim 60°$ in a D isomer the internal hydrogen bond could occur for a wide range of values for χ^{21}, as indeed happens in the present structure (see Table 2). This range is more restricted when the side-chain carboxyl group is staggered between the α-amino and the α-carboxylate groups ($\chi^1 \sim -60°$ in the D isomer). An internal hydrogen bond in such a conformation has previously been found in the structure of L-arginine D-aspartate (Suresh, Ramaswamy & Vijayan, 1986).

Hydrogen bonding and molecular aggregation. The crystal structure of L-ornithine D-aspartate monohydrate, shown in Fig. 1, is stabilized by ionic interactions and hydrogen bonds. The parameters of the hydrogen bonds are given in Table 2. Each amino group is involved as donor in three N—H$\cdots$O hydrogen bonds. The α-carboxylate O2 and O12 atoms accept two hydrogen bonds each whereas O1 and O11 accept one hydrogen bond each. The protons of the water molecule in the structure are linked to each of the side-chain carboxyl O atoms of the aspartate ion and the O atom is linked to two protons in the side-chain amino group in ornithine and the α-amino group of the aspartate ion.

The aggregation pattern in the present structure bears no resemblance to that observed in L-ornithine L-aspartate hemihydrate (Salunke & Vijayan, 1983). Among the four LD amino acid–amino acid complexes analysed so far (Suresh, Ramaswamy & Vijayan, 1986; Soman, Suresh & Vijayan, 1988), three have aggregation patterns based on double layers. The molecules in one of them, L-lysine D-aspartate monohydrate, however, aggregate into separate alternating layers of unlike molecules, a situation similar to that found in the present structure. The organization of molecules in the ornithine layer in the structure is similar to that in the lysine layer in L-lysine D-aspartate monohydrate. That in the aspartate layer, however, is very different in the two structures. In fact, the arrangement of the aspartate ions in the present structure appears to be very different from any observed so far in crystal structures containing aspartic acid or aspartate ions. The aspartate layer is made up of molecular ribbons parallel to the shortest axis, each containing an *S*2-type head-to-tail sequence (Suresh & Vijayan, 1983*b*). Adjacent ribbons in the layer are interconnected through water molecules and side-chain amino groups of ornithine molecules in the neighbouring layers.

It has been shown earlier that side-chain amino groups tend to form characteristic interaction patterns (Salunke & Vijayan, 1982*a*, 1983, 1984; Suresh & Vijayan, 1983*c*; Soman, Suresh & Vijayan, 1988). One such pattern involving a loop of alternating amino and carboxylate groups occurs in the present structure. This loop, as can be seen from Fig. 1, is made up of the side-chain amino group of an ornithine molecule, the α-amino group of an ornithine molecule related by a cell translation, the α-carboxylate group of another ornithine molecule related by a 2_1 screw axis and the α-carboxylate group of an aspartate ion. Similar loops have earlier been observed in the structure of L-ornithine L-aspartate hemihydrate (Salunke & Vijayan, 1983).

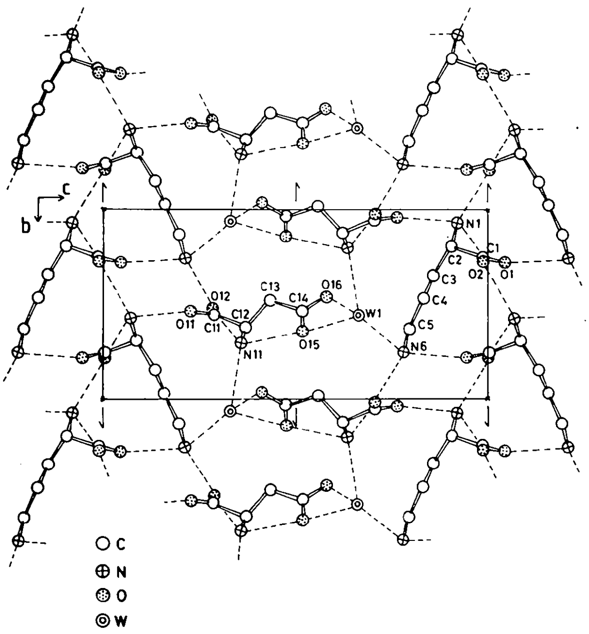

Fig. 1. The crystal structure as viewed along the *a* axis. The broken lines indicate hydrogen bonds.

The authors thank SERC, the Department of Science and Technology, Government of India, for support. Their thanks are also due to the Chairman and Professor H. Manohar of the Department of Inorganic and Physical Chemistry for making their diffractometer available and to Mr I. I. Mathews for assistance in data collection. The help of Mr G. Sridhar Prasad in the preparation of the crystals is gratefully acknowledged.

References

BHAT, T. N., SASISEKHARAN, V. & VIJAYAN, M. (1979). *Int. J. Pept. Protein Res.* **13**, 170–184.

BHAT, T. N. & VIJAYAN, M. (1976). *Acta Cryst.* B**32**, 891–895.

CHIBA, A., UEKI, T., ASHIDA, T., SASADA, Y. & KAKUDO, M. (1967). *Acta Cryst.* **22**, 863–870.

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

DERISSEN, J. L., ENDEMAN, H. J. & PEERDEMAN, A. F. (1968). *Acta Cryst.* B**34**, 1349–1354.

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

IUPAC–IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). *J. Mol. Biol.* **52**, 1–17.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

RAO, S. T. (1973). *Acta Cryst.* B**29**, 1718–1720.

SALUNKE, D. M. & VIJAYAN, M. (1981). *Int. J. Pept. Protein Res.* **18**, 348–351.

SALUNKE, D. M. & VIJAYAN, M. (1982*a*). *Acta Cryst.* B**38**, 287–289.

SALUNKE, D. M. & VIJAYAN, M. (1982*b*). *Acta Cryst.* B**38**, 1328–1330.

SALUNKE, D. M. & VIJAYAN, M. (1983). *Int. J. Pept. Protein Res.* **22**, 154–160.

SALUNKE, D. M. & VIJAYAN, M. (1984). *Biochim. Biophys. Acta*, **798**, 175–179.

SOMAN, J., SURESH, C. G. & VIJAYAN, M. (1988). *Int. J. Pept. Protein Res.* In the press.

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

SUDHAKAR, V., BHAT, T. N. & VIJAYAN, M. (1980). *Acta Cryst.* B**36**, 125–128.

SUDHAKAR, V. & VIJAYAN, M. (1980). *Acta Cryst.* B**36**, 120–125.

SURESH, C. G., RAMASWAMY, J. & VIJAYAN, M. (1986). *Acta Cryst.* B**42**, 473–478.

SURESH, C. G. & VIJAYAN, M. (1983*a*). *Int. J. Pept. Protein Res.* **21**, 223–226.

SURESH, C. G. & VIJAYAN, M. (2983*b*). *Int. J. Pept. Protein Res.* **22**, 129–143.

SURESH, C. G. & VIJAYAN, M. (1983*c*). *Int. J. Pept. Protein Res.* **22**, 617–621.

SURESH, C. G. & VIJAYAN, M. (1985). *Int. J. Pept. Protein Res.* **26**, 311–328, 329–336.

VIJAYAN, M. (1980). *FEBS Lett.* **112**, 135–137.

VIJAYAN, M. (1983). *Conformation in Biology*, edited by R. SRINIVASAN & R. H. SARMA, pp. 175–181. New York: Adenine Press.

VIJAYAN, M. & SURESH, C. G. (1985). *Curr. Sci.* **54**, 771–780.

Acta Cryst. (1988). C**44**, 1797–1800

TCNQ–Méthoxy-9 Ellipticine, Un Complexe par Transfert de Charge: Structure du Tétracyano-7,7,8,8 *p*-Quinodiméthane–Méthoxy-9 Diméthyl-5,11 6*H*-Pyrido[4,3-*b*]carbazole–Acétonitrile (1:1:1)

PAR B. VIOSSAT

Laboratoire de Chimie Générale, UER de Médecine et Pharmacie, 34 *rue du Jardin des Plantes,*
86034 *Poitiers CEDEX, France*

NGUYEN-HUY DUNG

Laboratoire de Chimie Minérale Structurale, associé au CNRS UA 200 (*Laboratoire de Physique*),
Faculté des Sciences Pharmaceutiques et Biologiques de Paris V, 4 *Avenue de l'Observatoire,*
75270 *Paris CEDEX* 06, *France*

ET J. C. DARAN

Laboratoire de Chimie des Métaux de Transition UA 419, *Université Pierre et Marie Curie,* 4 *Place Jussieu,*
75005 *Paris, France*

(*Reçu le* 30 *novembre* 1987, *accepté le* 5 *avril* 1988)

Abstract. $[C_{18}H_{16}N_2O.C_{12}H_4N_4].C_2H_3N$, $M_r = 521\cdot6$, monoclinic, $P2_1/c$, $a = 12\cdot587\ (2)$, $b = 13\cdot324\ (2)$, $c = 16\cdot733\ (2)$ Å, $\beta = 105\cdot18\ (2)°$, $V = 2708\cdot4\ (7)$ Å^3, $Z = 4$, $D_x = 1\cdot28$, $D_m = 1\cdot30\ (2)$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0\cdot71069$ Å, $\mu = 0\cdot092$ mm^{-1}, $F(000) = 1088$, room temperature, final $R = 0\cdot037$, $wR = 0\cdot035$ for 1816

0108-2701/88/101797-04$03.00 © 1988 International Union of Crystallography