(Chidambaram & Sikka, 1968; Chidambaram, 1968). Preliminary calculations show the occurrence of an energy minimum at $O_2(13)$. If the O atom occurs at $O_2(13)$ with a probability x, the probability of forming the hydrogen bond $O_2(13)–H\cdots O_1(13)$ will be between x and $x(1-x)$ depending on the correlations between the occupances of $O_2(13)$ and $O_1(13)$ in neighbouring molecules.

We thank Dr M. S. Chadha for suggesting the problem and for his interest in the work. Crystals of the compound were kindly supplied by Dr G. Ramakrishnan. Useful discussions with Dr G. Ramakrishnan and Dr A. Banerji are also acknowledged.

References

BANERJI, A., RAMAKRISHNAN, G. & CHADHA, M. S. (1974). *Tetrahedron Lett.* pp. 1369–1370.
BOLTON, W. (1965). *Acta Cryst.* **18**, 5–10.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305 (with modifications by W. C. HAMILTON, J. A. IBERS, C. K. JOHNSON, S. SRIKANTA & S. K. SIKKA). The BESM-6 version is by H. RAJAGOPAL.
CHIDAMBARAM, R. (1968). *Nucl. Phys. Solid State Phys. (India)*, **11A**, 215–234.
CHIDAMBARAM, R. & SIKKA, S. K. (1968). *Chem. Phys. Lett.* **2**, 162–165.
CHRISTENSEN, A. T. & THOM, E. (1971). *Acta Cryst.* **B27**, 581–586.
COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.
EVANS, I. A. (1968). *Cancer Res.* **28**, 2252–2261.
FUKUOKA, M., KUROYANAGI, M., TOYAMA, M., YOSHIHIRA, K. & NATORI, S. (1972). *Chem. Pharm. Bull.* **20**, 2282–2285.
GROTH, P. (1969). *Acta Chem. Scand.* **23**, 1076–1078.
HASEGAWA, M. & AKABORI, Y. (1974). *Phytochemistry*, **13**, 509–511.
HAYASHI, Y., NISHIZAWA, M. & SAKAN, T. (1973). *Chem. Lett.* pp. 63–64.
HAYASHI, Y., NISHIZAWA, M. & SAKAN, T. (1974). *Chem. Lett.* pp. 945–946.
HIRONO, I., SHIBUYA, C., FUSHIMI, K. & HAGA, M. (1970). *J. Natl. Cancer Inst.* **45**, 179–188.
International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed. Birmingham: Kynoch Press.
PRICE, J. M. & PAMUKCU, A. M. (1968). *Cancer Res.* **28**, 2247–2250.
SIKKA, S. K. (1971). *SIGFMULA*. Report BARC 576, Bhabha Atomic Research Centre, Bombay.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
WADHAWAN, V. K. (1973). *CELPAR*. Program No. 193, *World List of Crystallographic Computer Programs*, 3rd ed., edited by G. C. BASSI. *J. Appl. Cryst.* (1973), **6**, 309.
WADHAWAN, V. K. (1976). Ph.D. thesis, Univ. of Bombay, Bombay.
YOSHIHIRA, K., FUKUOKA, M., KUROYANAGI, M. & NATORI, S. (1971). *Chem. Pharm. Bull.* **19**, 1491–1495.

Acta Cryst. (1977). B33, 433–437

The Crystal and Molecular Structure of Bis(L-asparaginato)zinc(II), $[Zn(OOC.CHNH_2.CH_2.CONH_2)_2]_n$

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The structure of bis(L-asparaginato)zinc(II) has been determined by counter methods and refined to R 0·045 for 1531 unique reflexions by least squares. The monoclinic unit cell, space group $P2_1$, has $a = 12·323$ (1), $b = 5·027$ (2), $c = 9·702$ (2) Å, $\beta = 99·12$ (4)°, $Z = 2$. The Zn atom is in a distorted octahedral environment. A carboxylic O atom and the α-amino N atom from each ligand coordinate to the Zn atom in a *trans* square-planar configuration (Zn–O 2·09, Zn–N 2·08 Å). The octahedral environment is completed by carbonyl O atoms from neighbouring molecules (Zn–O 2·28, 2·48 Å) creating infinite chains linked in the [011] direction.

Introduction

Both L-asparagine and L-glutamine are known to be essential growth factors (Williams, 1972) for a variety of tumours, particularly animal lymphomas. Recently it has been shown that the activity of L-asparaginase can be inhibited (Charlson, Coman, Karossi, Stephens, Vagg & Watton, 1976, unpublished) by a number of metal ions. In conjunction with this work a structural study of L-asparagine–metal complexes was undertaken. We have previously reported the structure of bis(L-asparaginato)copper(II) (Stephens, Vagg & Williams, 1975). Here we present the results of the analysis of bis(L-asparaginato)zinc(II), Zn(L-asn)$_2$.

Experimental

The complex was prepared by adding a stoichiometric amount of $ZnCl_2$ in aqueous solution to a dilute aqueous solution of L-asparagine. Slow evaporation yielded colourless plates of Zn(L-asn)$_2$.

Analysis calculated for $C_8H_{14}N_4O_6Zn$: $C = 29\cdot3$, $H = 4\cdot3$, $N = 17\cdot1\%$; found $C = 29\cdot4$, $H = 4\cdot2$, $N = 16\cdot8\%$.

Crystal data

$C_8H_{14}N_4O_6Zn$, $M_r = 327\cdot6$, monoclinic, $a = 12\cdot323$ (1), $b = 5\cdot027$ (2), $c = 9\cdot702$ (2) Å, $\beta = 99\cdot12$ (4)°, $U = 597\cdot5$ Å^3, $D_m = 1\cdot85$ (by flotation), $Z = 2$, $D_c = 1\cdot82$ g cm^{-3}; $F(000) = 336$, μ(Mo $K\alpha$) $= 21\cdot5$ cm^{-1}. Systematic absences $0k0$ if $k = 2n + 1$, space group $P2_1$ or $P2_1/m$. Unit-cell parameters were fitted to the θ values of a number of high-angle reflexions measured on an equi-inclination diffractometer.

Intensities were collected from two crystals $0\cdot5 \times 0\cdot4 \times 0\cdot2$ mm mounted about **a** and **b** on an automatic Buerger–Supper equi-inclination diffractometer (Freeman, Guss, Nockolds, Page & Webster, 1970) with Zr-filtered Mo K radiation. Each reflexion in the layers 0–$5kl$ and $h0$–$7l$ for $2\theta \leq 65°$ was recorded. 2238 reflexions gave counts for which $\sigma(I)/I < 0\cdot5$ and these were used for the structure analysis. Each reflexion was corrected for the Lorentz–polarization effect (Blount, 1970) but not for absorption or extinction.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1962), the Zn atom being corrected for anomalous dispersion. All calculations were carried out with the X-RAY package (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) on a Univac 1108 computer.

Structure determination

The centrosymmetric space group $P2_1/m$ with $Z = 2$ requires the molecule to possess either a centre of symmetry or a mirror plane. Neither is feasible for the molecule unless racemization of the L-amino acid has occurred. Thus the space group $P2_1$ was chosen, which imposes no symmetry constraints, and is confirmed by the successful refinement of the structure.

The positions of the Zn atom, the atoms forming the two five-membered coordination rings and the remaining O atoms of the carboxylic acid groups were readily obtained from a Patterson synthesis. The complete solution of the structure for the non-hydrogen atoms was obtained from a series of Fourier syntheses, each phased by an increasing number of atoms.

Refinement of the structure was carried out by full-matrix least squares in which the function minimized was $\Sigma\, w\Delta^2$. The weight for each reflexion, w, was taken as unity throughout since plots of $w\Delta^2$ as a function of $\sin\theta/\lambda$ and $|F_o|$ did not suggest any obvious weighting scheme. In the initial refinement, in which 2238 reflexions were used, individual layer scale factors together with positional and isotropic thermal parameters for each atom were refined. After four cycles of such refinement, at which stage the maximum shift in any parameter was of the order of its estimated standard deviation and R was 0·096, a difference synthesis was calculated. This map indicated the positions of all 14 H atoms which were included in subsequent calculations but not refined. Within each axial set of data the refined individual layer scale factors showed no significant variation from the mean value for that set; the maximum and average values for t [$=\Delta K/\sigma(\Delta K)$, where $\Delta K = |K_i - \bar{K}|$] (Jeffrey & Cruickshank, 1953) for the data sets were respectively 1·4 and 0·9 (nkl) and 1·1

Table 1. *Final atomic coordinates (fractional) with estimated standard deviations in parentheses*

	x	y	z
Zn	0·4285 (1)	0·2500	0·2392 (1)
O(11)	0·5218 (3)	0·5045 (10)	0·0832 (4)
O(12)	0·6365 (4)	0·5299 (10)	−0·0749 (4)
O(13)	0·8780 (4)	−0·0217 (15)	0·2757 (5)
O(21)	0·4554 (3)	0·0121 (9)	0·4061 (4)
O(22)	0·3831 (3)	0·0239 (11)	0·6049 (4)
O(23)	0·1006 (4)	0·4939 (16)	0·2131 (5)
N(11)	0·6208 (4)	0·0574 (11)	0·1936 (5)
N(12)	0·9273 (5)	−0·1853 (18)	0·0766 (6)
N(21)	0·3595 (4)	0·4740 (12)	0·3098 (5)
N(22)	0·0712 (5)	0·5986 (15)	0·4298 (6)
C(11)	0·6094 (4)	0·4402 (12)	0·0372 (5)
C(12)	0·6889 (4)	0·2527 (18)	0·1307 (5)
C(13)	0·7755 (5)	0·1297 (16)	0·0550 (6)
C(14)	0·8623 (5)	−0·0275 (17)	0·1467 (6)
C(21)	0·3927 (4)	0·1097 (13)	0·4865 (5)
C(22)	0·3211 (4)	0·3483 (11)	0·4324 (5)
C(23)	0·2011 (4)	0·2436 (21)	0·3990 (6)
C(24)	0·1202 (4)	0·4541 (17)	0·3413 (6)
H(111)	0·667	−0·040	0·230
H(112)	0·575	−0·025	0·125
H(12)	0·725	0·350	0·200
H(131)	0·745	0·030	0·017
H(132)	0·797	0·250	−0·020
H(121)	0·905	−0·175	−0·030
H(122)	0·990	−0·099	0·086
H(211)	0·365	0·635	0·330
H(212)	0·320	0·440	0·257
H(22)	0·320	0·500	0·500
H(231)	0·177	0·155	0·495
H(232)	0·202	0·050	0·347
H(221)	0·010	0·595	0·402
H(222)	0·100	0·700	0·525

Table 2. *Final thermal parameters* ($\times 10^3$) *with estimated standard deviations in parentheses*

For all H atoms $U = 0{\cdot}051$ Å^2. The anisotropic thermal parameters are in the form:
$\exp[-(a^{*2}h^2U_{11} + b^{*2}k^2U_{22} + c^{*2}l^2U_{33} + 2a^*b^*hkU_{12} + 2a^*c^*hlU_{13} + 2b^*c^*klU_{23})]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn	45·3 (4)	31·1 (4)	36·6 (4)	17·8 (5)	30·6 (3)	17·7 (4)
O(11)	32 (2)	33 (3)	15 (2)	3 (2)	9 (2)	2 (2)
O(12)	36 (2)	28 (3)	25 (2)	1 (2)	16 (2)	8 (2)
O(13)	48 (3)	76 (5)	20 (2)	23 (3)	3 (2)	2 (3)
O(21)	34 (2)	13 (2)	23 (2)	7 (2)	14 (2)	4 (2)
O(22)	37 (2)	33 (3)	21 (2)	6 (2)	14 (2)	9 (2)
O(23)	47 (3)	91 (5)	23 (2)	34 (3)	10 (2)	13 (3)
N(11)	27 (2)	18 (3)	18 (2)	4 (2)	8 (2)	3 (2)
N(12)	60 (4)	82 (7)	26 (3)	38 (5)	11 (3)	0 (3)
N(21)	28 (2)	22 (3)	18 (2)	2 (2)	7 (7)	4 (2)
N(22)	39 (3)	50 (4)	29 (3)	7 (3)	9 (3)	−2 (3)
C(11)	25 (3)	14 (3)	16 (2)	−4 (2)	6 (2)	−2 (2)
C(12)	22 (2)	28 (3)	16 (2)	4 (4)	7 (2)	−6 (3)
C(13)	34 (3)	45 (4)	18 (2)	10 (3)	12 (2)	9 (3)
C(14)	24 (3)	49 (4)	22 (3)	7 (3)	6 (2)	3 (3)
C(21)	15 (2)	26 (3)	13 (2)	2 (2)	−1 (2)	3 (2)
C(22)	27 (3)	16 (2)	11 (2)	1 (2)	7 (2)	2 (2)
C(23)	20 (2)	33 (3)	44 (3)	1 (4)	2 (2)	13 (4)
C(24)	15 (2)	53 (4)	25 (3)	3 (3)	4 (2)	6 (3)

Table 3. *Bond lengths* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

Zn–O(11)	2·102 (4)	Zn–O(21)	2·086 (4)
Zn–N(11)	2·071 (5)	Zn–N(21)	2·092 (5)
Zn–O(12$^{\rm I}$)	2·278 (4)	Zn–O(22$^{\rm II}$)	2·481 (5)
C(11)–O(11)	1·275 (7)	C(21)–O(21)	1·280 (7)
C(11)–O(12)	1·270 (7)	C(21)–O(22)	1·252 (7)
C(12)–N(11)	1·488 (9)	C(22)–N(21)	1·491 (7)
C(11)–C(12)	1·549 (8)	C(21)–C(22)	1·537 (8)
C(12)–C(13)	1·524 (9)	C(22)–C(23)	1·556 (8)
C(13)–C(14)	1·501 (9)	C(13)–C(24)	1·504 (10)
C(14)–O(13)	1·236 (7)	C(24)–O(23)	1·245 (7)
C(14)–N(12)	1·385 (10)	C(24)–N(22)	1·342 (9)

O(11)–Zn–N(11)	80·9 (2)	O(21)–Zn–N(21)	81·1 (2)
O(11)–Zn–O(12$^{\rm I}$)	89·5 (2)	O(21)–Zn–O(22$^{\rm II}$)	91·3 (2)
N(11)–Zn–O(12$^{\rm I}$)	94·6 (2)	N(21)–Zn–O(22$^{\rm II}$)	86·9 (2)
O(11)–Zn–O(21)	174·8 (2)	N(11)–Zn–N(21)	171·1 (2)
O(12$^{\rm I}$)–Zn–O(22$^{\rm II}$)	173·1 (2)		
O(11)–Zn–N(21)	99·5 (2)	O(21)–Zn–N(11)	97·6 (2)
O(12$^{\rm I}$)–Zn–N(21)	94·3 (2)	O(22$^{\rm II}$)–Zn–N(11)	84·3 (2)
O(12$^{\rm I}$)–Zn–O(21)	95·6 (2)	O(22$^{\rm II}$)–Zn–O(11)	83·6 (2)
Zn–O(11)–C(11)	113·6 (4)	Zn–O(21)–C(21)	115·9 (4)
Zn–N(11)–C(12)	108·2 (4)	Zn–N(21)–C(22)	111·6 (4)
O(11)–C(11)–O(12)	124·1 (5)	O(21)–C(21)–O(22)	125·4 (6)
O(11)–C(11)–C(12)	116·3 (4)	O(21)–C(21)–C(22)	117·6 (5)
O(12)–C(11)–C(12)	119·5 (5)	O(22)–C(21)–C(22)	116·9 (5)
C(11)–C(12)–C(13)	113·4 (4)	C(21)–C(22)–C(23)	106·2 (5)
C(11)–C(12)–N(11)	107·5 (4)	C(21)–C(22)–N(21)	111·7 (4)
C(13)–C(12)–N(11)	114·0 (7)	C(23)–C(22)–N(21)	112·9 (4)
C(12)–C(13)–C(14)	114·7 (5)	C(22)–C(23)–C(24)	112·9 (7)
C(13)–C(14)–O(13)	124·8 (7)	C(23)–C(24)–O(23)	119·9 (6)
C(13)–C(14)–N(12)	115·0 (5)	C(23)–C(24)–N(22)	119·1 (5)
O(13)–C(14)–N(12)	120·2 (6)	O(23)–C(24)–N(22)	121·0 (7)

Roman numeral superscripts refer to the following equivalent positions relative to the atoms at x,y,z:
(I) $1-x, y-\frac{1}{2}, -z$; (II) $1-x, \frac{1}{2}+y, 1-z$.

and 0·4 (*hnl*). The two mean scale factors were used to scale the data and thus produce a unique set of 1531 reflexions which was used in further refinement.

Refinement was continued with anisotropic thermal parameters for all non-hydrogen atoms and was terminated when the maximum shift in any parameter was less than 0·05σ. The values of R and R' [$=(\Sigma\, w\Delta^2/\Sigma\, w|F_o|^2)^{1/2}$] were 0·045 and 0·047 respectively. A final difference synthesis showed no peak of absolute density greater than 0·5 e Å^{-3}.

The final atomic parameters are given in Tables 1 and 2.*

Discussion

The bond lengths and angles are given in Table 3. Fig 1 shows a perspective drawing of the molecule and the labelling of the atoms (Johnson, 1965). Fig. 2 shows the packing in the crystal and the hydrogen-bond network. The proposed hydrogen bonds are N(21)–H(211)···O(21) at $x, 1+y, z$ [3·054 (7)] and N(12)–H(121)···O(23) at $1-x, y-\frac{1}{2}, -z$ [2·919 (8)] and a bifurcated bond from N(11)–H(112) to O(11) at $x, y-1, z$ [3·168 (7)] and at $1-x, y-\frac{1}{2}, -z$ [2·979 (5) Å].

The two L-asparagine ligands each coordinate to the Zn atom *via* a carboxylic O and the α-amino N atom forming a *trans* square-planar configuration; the Zn–O and Zn–N distances are respectively 2·09 and 2·08 Å and agree well with corresponding values observed in other zinc–L-α-amino acid complexes (Freeman, 1967). This arrangement is similar to that found in the corresponding copper(II) (Stephens *et al.*, 1975) and cadmium(II) (Flook, Freeman, Moore & Scudder, 1973) complexes. A distorted octahedral coordination about the Zn atom is completed *via* carbonyl O atoms from neighbouring molecules linked in the [011] direction; this arrangement is similar to that found in the Cd complex (Flook *et al.*, 1973) but different from that in the Cu complex (Stephens *et al.*, 1975) in which the amido O atoms from neighbouring molecules are used to complete the coordination sphere. The Zn–O distances completing the octahedron are not equivalent [2·278 (4) and 2·481 (5) Å] and are both significantly longer than the in-plane Zn–O distances. The directions of these axial Zn–O bonds are almost collinear with the normal to the mean plane defined by the square-plane ligand atoms (plane 1, Table 4), the maximum deviation being 3·9°. The Zn atom lies 0·13 Å out from the ligand-atom square plane towards the closer of the two carbonyl O atoms.

The two L-asparagine ligands exhibit variance in the five-membered coordination rings, one of which (plane 3, Table 4) may be considered as planar whereas the other (plane 2, Table 4) shows significant distortion from planarity. A similar distortion is apparent in the corresponding copper(II) complex (Stephens *et al.*, 1975) and it has been suggested that the distortion in this latter complex arises from strain imposed by the *trans* configuration of the ligands and the amido groups acting as bridging groups. In the present structure this form of bridging is absent and hence the cause of the

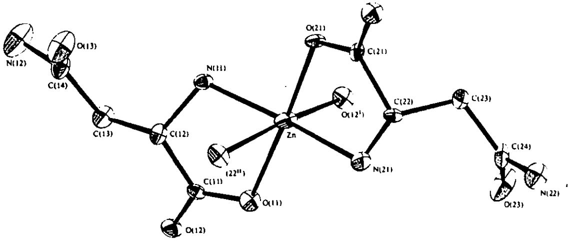

Fig. 1. Molecular environment about the Zn atom and the labelling of the atoms. Thermal ellipsoids are scaled to include 35% probability.

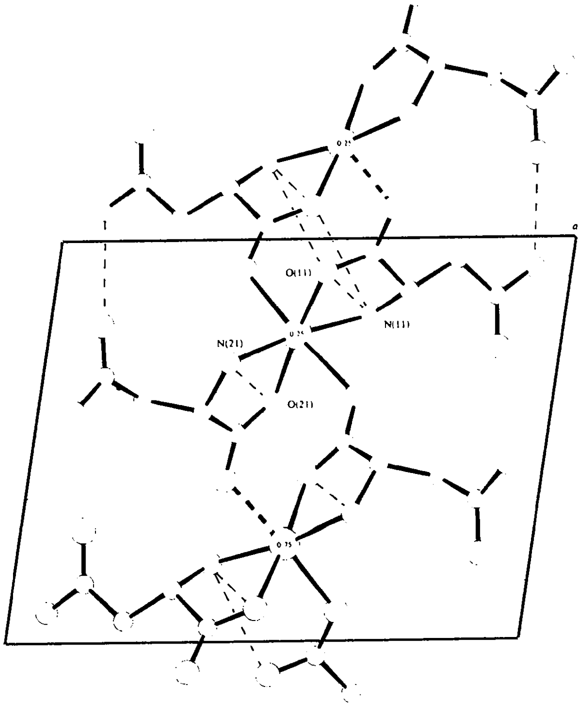

Fig. 2. Molecular packing in the crystal. The molecules represented are indicated by the y coordinate for the Zn atoms. Broken lines indicate that one of the atoms involved in the bond is from a molecule a cell away in **b**. Proposed hydrogen bonds are represented by thin lines.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32054 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Equations of the planes of best fit in the form* $lX' + mY' + nZ' - p = 0$ *where the orthogonalized coordinates* X', Y', Z' *are derived from the atomic coordinates* X,Y,Z *by:* $X' = X\sin\beta$, $Y' = Y$, $Z' = X\cos\beta + Z$

Deviations (Å) of the most relevant atoms from the planes are given in square brackets. For superscripts see Table 3.

	l	*m*	*n*	*p*
Plane 1				
O(11), O(21), N(11), N(21)	0·6385	0·5274	0·5605	5·3144
[O(11) –0·03, O(21) –0·03, N(11) 0·03, N(21) 0·03, Zn –0·13, O(12^{I}) –2·40, O(22^{II}) 2·35]				
Plane 2				
Zn, O(11), C(11), N(11)	0·5634	0·5387	0·6264	4·8390
[Zn 0·01, O(11) –0·02, C(11) 0·02, N(11) –0·01, C(12) 0·52, O(12) –0·27]				
Plane 3				
Zn, O(21), C(21), C(22), N(21)	0·7000	0·5361	0·4718	5·4181
[Zn 0·02, O(21) –0·07, C(21) 0·09, C(22) –0·06, N(21) 0·02, O(22) 0·33]				
Plane 4				
C(11), O(11), O(12), C(12)	0·4604	0·7808	0·4225	4·8189
[C(11) –0·018, O(11) 0·006, O(12) 0·007, C(12) 0·005, Zn –0·55, N(11) –0·83]				
Plane 5				
C(21), O(21), O(22), C(22)	0·7323	0·6145	0·2936	4·9930
[C(21) 0·007, O(21) –0·003, O(22) –0·003, C(22) –0·002, Zn 0·49, N(21) 0·36]				
Plane 6				
C(14), O(13), N(12), C(13)	0·6430	0·7566	–0·1185	6·6725
[C(14), O(13), N(12), C(13) $<\lvert 0·0001\rvert$]				
Plane 7				
C(24), O(23), N(22), C(23)	0·7436	0·6674	–0·0406	2·4995
[C(24) –0·004; O(23), N(22), C(23) 0·001]				

distortion is not readily evident; it may just be a result of crystal packing.

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References

BLOUNT, J. (1970). Programs *PTP* and *PTPEDIT*, Department of Chemistry, Univ. of Sydney.

FLOOK, R. J., FREEMAN, H. C., MOORE, C. J. & SCUDDER, M. C. (1973). *Chem. Commun.* pp. 753–754.

FREEMAN, H. C. (1967). *Advanc. Protein Chem.* **22**, 257–424.

FREEMAN, H. C., GUSS, J. M., NOCKOLDS, C. E., PAGE, R. & WEBSTER, A. (1970). *Acta Cryst.* A**26**, 149–152.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–204, 215. Birmingham: Kynoch Press.

JEFFREY, G. A. & CRUICKSHANK, D. W. J. (1953). *Quart. Rev.* **7**, 335–376.

JOHNSON, C. K. (1965). *ORTEP.* Oak Ridge National Laboratory Report ORNL-3794, revised 1971.

STEPHENS, F. S., VAGG, R. S. & WILLIAMS, P. A. (1975). *Acta Cryst.* B**31**, 841–845.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The X-RAY system – version of June 1972. Tech. Rep. 192, Computer Science Centre, Univ. of Maryland.

WILLIAMS, D. R. (1972). *Chem. Rev.* **72**, 203–213.