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The Crystal and Molecular Structure of Bis(amidoxalato-*O*,*O*)-zinc Dihydrate

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The crystals of bis(amidoxalato-*O*,*O*)-zinc dihydrate, $Zn(OOC–CO–NH_2)_2.2H_2O$ are triclinic, space group $P\bar{1}$ with unit-cell constants: $a=6·309$, $b=7·777$, $c=4·970$ Å; $\alpha=74·67$, $\beta=76·16$, $\gamma=81·56°$. The structure determined by diffractometric three-dimensional data ($R=3·8$ %) is formed by *trans*-octahedral complexes. The coordination positions around zinc are all occupied by oxygen atoms; the ligand is chelated through one carboxylic oxygen O(3), and through the amidic oxygen O(1); the apical positions are occupied by water molecules $O(4)_w$ [$Zn–O(1)=2·152$, $Zn–O(3)=2·043$, $Zn–O(4)_w=2·088$ Å]. The water molecule forms strong hydrogen bonds [$O(4)_w\cdots O(2)=2·674$, $O(4)_w\cdots O(3)=2·678$ Å] with adjacent complexes thus forming layers parallel to (010). The angle in the water molecule is $H(3)–O(4)_w–H(4)=114·3°$. In the ligand molecule the carboxylic and amidic groups are each planar and rotated 1·3° from each other. The bond $C–C=1·546$ Å is longer than as expected for the $C_{sp2}–C_{sp2}$ bond but is in close agreement with several accurate studies in oxalates and amidoxalates, both by X-ray and neutron diffraction. The bonds $C(2)–O(2)=1·228$ and $C(2)–O(3)=1·258$ Å show that the single-double bond character is lowered in comparison with α-oxalic acid and increased in comparison with purely ionic compounds. The distances between oxygen, or nitrogen, and the hydrogen atoms are shorter than the distances found in analogous molecules by neutron diffraction.

Introduction

Amidoxalic acid, $H_2N–CO–COOH$, might form pentatomic chelate rings with metals, similar to those formed by α-aminoacids (Freeman, 1967), by hydrazinecarboxylic acid (Braibanti, Manotti Lanfredi, Tiripicchio & Bigoli, 1970) and by thiocarbohydrazide (Braibanti, Tiripicchio & Tiripicchio Camellini, 1969; Bigoli, Braibanti, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, to be published; Braibanti, Dallavalle & Leporati, 1969).

Two alternative pentatomic rings can be formed by amidoxalic acid: one of type O,O, i.e. through a carboxylic oxygen and the amide oxygen, and another less probable, of type O,N through a carboxylic oxygen and the amidic nitrogen. To solve this ambiguity we have now determined the crystal structure of the zinc compound, $Zn(NH_2–CO–COO)_2.2H_2O$.

Experimental

Preparation

Crystals of the compound can be obtained by evaporation of an aqueous solution of zinc carbonate and amidoxalic acid in stoichiometric ratio. The crystals present a prismatic habit and are often twinned.

Crystal data

Compound: bis(amidoxalato-*O*,*O*)-zinc dihydrate,
$Zn(H_2N–CO–COO)_2.2H_2O$
Formula weight, 277·50
Crystal class: triclinic, pinacoidal
Unit cell: radiation Cu $K\alpha$, $\lambda=1·54178$ Å
$a=6·309(3)$, $b=7·777(2)$, $c=4.970(2)$ Å
$\alpha=74·67(20)$, $\beta=76·16(20)$, $\gamma=81·56(12)°$
$V=227·4$ Å^3; $Z=1$; $D_x=2·03$, $D_m=2·02$ g.cm^{-3}
μ(Cu $K\alpha$)$=21·07$ cm^{-1}
Space group $P\bar{1}$ (C_i^1, No. 2), from structure determination.

Intensity data

860 independent reflexions have been measured by an automatic Siemens diffractometer 'on-line' (Cu $K\alpha$, $2\theta_{max}=140°$). In this apparatus integral gross intensity and the integral background are each measured twice.

Calculation

The usual corrections for geometrical factors have been applied but corrections for absorption and extinction have not been considered. Atomic form factors following Cromer & Mann (1968) have been used except for hydrogen for which the values of Stewart, Davidson & Simpson (1965) have been employed.

The structure has been solved by Fourier methods and refined by the full-matrix least-squares method with anisotropic thermal parameters. The weighting scheme used is of the type: $1/w=A+BF_o+CF_o^2$ where $A=0·15643$, $B=0·00929$, $C=0·00013806$. The hydrogen atoms have been identified in the $(\varrho_o–\varrho_c)$ map.

The conventional agreement factor is $R=3·9$ % without hydrogens and $R=3·8$ % with hydrogens.

All calculations have been performed on the CDC-6600 computer of Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna.

The results of the structure determination are summarized in Tables 1 & 2. A list of observed and calculated structure factors is available from the authors on request.

Table 1. *Final fractional atomic coordinates* (× 10^4) *with e.s.d.'s*

	x	*y*	*z*
Zn	0000 (0)	0000 (0)	0000 (0)
O(1)	0311 (4)	2687 (3)	−2579 (6)
O(2)	4276 (5)	3003 (4)	1075 (7)
O(3)	2430 (4)	0688 (3)	1487 (5)
O(4)$_w$	2325 (5)	−1043 (4)	−3060 (7)
N	2263 (7)	5012 (4)	−3047 (8)
C(1)	1713 (6)	3368 (5)	−1906 (8)
C(2)	2942 (6)	2267 (5)	0429 (8)
H(1)	1595 (83)	5664 (73)	−4331 (114)
H(2)	3182 (100)	5415 (79)	−2508 (131)
H(3)	3592 (89)	−1574 (71)	−2522 (114)
H(4)	2488 (86)	−0442 (74)	−4602 (120)

Discussion

The structure (Fig. 1) comprises *trans*-octahedral centrosymmetric complexes with all corners occupied by oxygen atoms. The complexes are joined to one another by strong hydrogen bonds to form layers parallel to (010); weaker hydrogen bonds operate between the layers. Four oxygen atoms of the coordination polyhedron (Fig. 2) belong to amidoxalato anions which chelate to zinc through amidic and carboxylic oxygen atoms; the remaining coordination positions are occupied by water. Distances between zinc and oxygen (Table 3) in the pentatomic ring are Zn–O(1) = 2·152 and Zn–O(3) = 2·043 Å; the former is longer than the latter because of the excess negative charge borne by O(3). This is in agreement with the anion function of the carboxylic group and the attractive power between positive and negative charges. The bond between zinc and water is Zn–O(4)$_w$ = 2·088 Å which is intermediate between the other two distances and can be explained as a bond with strong ion-dipole attraction. The long distance between zinc and O(1) is in agreement with the low coordinating power of the amidic oxygen. It is worth noting that the whole set of distances between zinc and surrounding oxygen atoms is perfectly in accordance with the chemical expectations based on the bonding power of donor atoms involved in the coordination. The angle O(1)–Zn–O(3) = 80·2° is conditioned by the 'biting' distance of the ligand, while O(4)$_w$–Zn–O(1) = 91·5 and O(4)$_w$–Zn–O(3) = 90·7° indicate a very small, or practically no, distortion in the direction normal to the plane of the chelate rings.

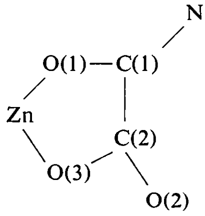

Table 3. *Bond distances and angles in the coordination polyhedron*

Zn–O(1)	2·152 (6) Å	O(1)–Zn–O(3)	80·2 (1)°
Zn–O(3)	2·043 (6)	O(1)–Zn–O(4)$_w$	91·5 (1)
Zn–O(4)$_w$	2·088 (5)	O(3)–Zn–O(4)$_w$	90·7 (1)
		Zn–O(1)–C(1)	109·4 (2)
		Zn–O(3)–C(2)	115·2 (2)

The hydrogen atoms of the water molecule (Fig. 3) form bonds O(4)$_w$–H(3) = 0·91 and O(4)$_w$–H(4) = 0·78 Å (Table 4). These values agree very well with values quoted by Coppens, Sabine, Delaplane & Ibers (1969) for α-oxalic acid dihydrate. It is remarkable that distances obtained by X-rays are shorter than those found by a neutron diffraction study of the same compound (Sabine, Cox & Craven, 1969). These authors explain the short bond lengths from X-ray analysis as being due to the actual diffracting electrons being withdrawn from the hydrogen atom into the O–H bond. Tomiie (1958) found short N–H bonds by X-rays in diformylhydrazine and gave the same explanation supported by theoretical calculations. The positions of the hydrogen atoms can therefore be treated with some confidence.

According to Chidambaram, Sequeira & Sikka (1964) water molecules can be bound to a metal *via* the bisector of the two lone pairs of the oxygen atom or *via* one lone pair. The first type of bonding can be interpreted as an ion–dipole interaction, with a covalent contribution due to a certain amount of sp^2 hybridization of oxygen. The second type of bonding, mainly covalent in character, should maintain sp^3 hybridization of oxygen. The angle H(3)–O(4)$_w$–H(4) = 114·3° indicates a relevant deviation from the value 104·5° found in water vapor (Darling & Dennison, 1940) and there-

Table 2. *Thermal parameters with e.s.d.'s* (Å^2)

	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zn	3·195 (0·027)	2·238 (0·024)	3·211 (0·027)	−0·901 (0·021)	−1·314 (0·022)	0·298 (0·020)
O(1)	2·893 (0·105)	1·758 (0·092)	2·941 (0·107)	−0·773 (0·079)	−1·293 (0·086)	0·595 (0·079)
O(2)	3·741 (0·132)	2·287 (0·110)	5·546 (0·163)	−0·921 (0·098)	−2·634 (0·122)	0·047 (0·105)
O(3)	2·870 (0·106)	1·949 (0·096)	2·893 (0·108)	−0·789 (0·080)	−1·471 (0·087)	0·410 (0·081)
O(4)$_w$	3·204 (0·125)	3·056 (0·121)	2·688 (0·120)	−0·306 (0·097)	−0·964 (0·097)	0·179 (0·098)
N	3·900 (0·162)	1·832 (0·124)	3·777 (0·162)	−0·956 (0·115)	−1·517 (0·134)	0·524 (0·114)
C(1)	2·522 (0·138)	1·660 (0·125)	2·520 (0·140)	−0·452 (0·105)	−0·541 (0·112)	0·001 (0·105)
C(2)	2·476 (0·139)	1·808 (0·129)	2·919 (0·149)	−0·459 (0·108)	−0·930 (0·117)	−0·040 (0·112)
H(1)	4·26 (1·15)					
H(2)	5·34 (1·39)					
H(3)	4·36 (1·13)					
H(4)	4·12 (1·19)					

fore should indicate a trend towards sp^2 hybridization of $O(4)_w$. Angles of 113·2 and 110·3° have been found by neutron diffraction (Agron & Busing, 1969) in $Mg(OH_2)_6Cl_2$; also, angles of 114, 111 and 109° have been found by neutron diffraction (Bacon & Curry, 1962) in $CuSO_4.5H_2O$. In all these cases the water molecules are bound to metal ions; smaller angles have been found whenever water is not coordinated, for instance in α-oxalic acid dihydrate (Delaplane & Ibers, 1969; Sabine, Cox & Craven, 1969) or in several cases cited by Chidambaram (1962). The angles $Zn–O(4)_w–H(3) = 115·8$ and $Zn–O(4)_w–H(4) = 115·4°$ also deviate from tetrahedral values. These results are confirmed by the angles $Zn–O(4)_w \cdots O(2) = 113·9$ and $Zn–O(4)_w \cdots O(3) = 116·3°$ formed with oxygen atoms bound through hydrogen bonds. Altogether the bond $Zn–O(4)_w$ can be considered as being intermediate between class 1 and class 2 of Chidambaram, Sequeira & Sikka (1964). It is likely that the orientation of the water molecule is conditioned not only by the metal–oxygen bond but also by the strong hydrogen bonds with O(2) and O(3).

The pentatomic chelate ring (Fig. 4) as a whole is not exactly planar. In the amidoxalato anion, however, the two groups of atoms $C(2)–C(1)<\genfrac{}{}{0pt}{}{O(1)}{N}$ and $\genfrac{}{}{0pt}{}{O(3)}{O(2)}>C(2)–C(1)$ are strictly planar (Table 5), the angle between the two planes being 1·26°. This corresponds in the present case to the rotation angle around C(1)–C(2). The bond C(1)–C(2) = 1·546 Å is longer than that generally accepted for two carbon atoms in sp^2 hybridization. Long bonds have been found in ammonium amidoxalate (C–C = 1·564 Å, Beagley & Small, 1963), in potassium oxalate monohydrate (C–C = 1·581 Å, Sequeira, Srikanta & Chidambaram, 1970), in α-oxalic acid dihydrate (by X-rays: C–C = 1·538 Å, Delaplane & Ibers, 1969; by neutrons: C–C = 1·536 Å, Sabine, Cox & Craven, 1969), in the completely deuterated analogue of α-oxalic acid dihydrate (by X-rays: C–C = 1·537 Å, Delaplane ;& Ibers, 1969; by neutrons: C–C = 1·539 Å, Coppens & Sabine, 1969), in potassium tetraoxalate (C–C = 1·553, 1·554, 1·551 Å, Haas 1964), in dimethyl oxalate (C–C = 1·53 Å, Dougill & Jeffrey, 1953), and in ammonium oxalate monohydrate (C–C = 1·569 Å, Robertson, 1965). This distance is longer than the experimental values 1·515 (Almenningen, Bastiansen & Skancke, 1958) and 1·499 Å (Bart, 1968) for unconjugated $C_{sp^2}–C_{sp^2}$ bonds. The difference-Fourier map for α-oxalic acid dihydrate with amplitudes $F_o–F_c$, where F_c has been calculated from the positional parameters obtained from the neutron determination (Coppens, Sabine, Delaplane & Ibers, 1969) shows a peak

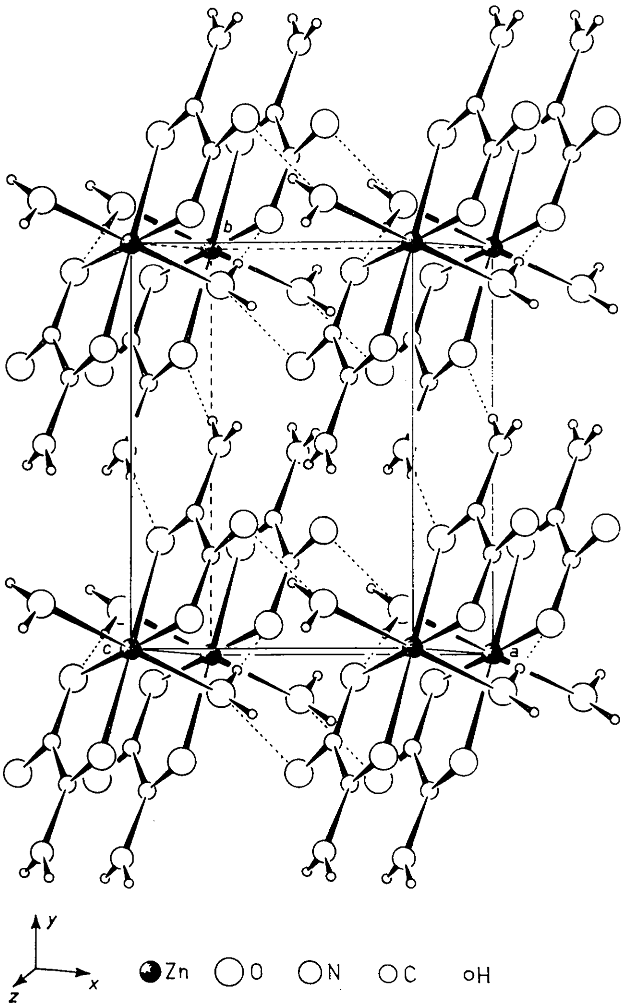

Fig. 1. Clinographic projection of the structure of bis-(amidoxalato-*O*,*O*)-zinc dihydrate.

Table 4. *Environment of the water molecule* $O(4)_w$

$O(4)_w–H(3)$	0·91 (6) Å	$H(3)—O(4)_w—H(4)$	114·3 (5·3)°
$O(4)_w–H(4)$	0·78 (6)	$Zn—O(4)_w—H(3)$	115·8 (3·4)
$O(4)_w–H(3) \cdots O(2^{ii})$	2·674 (9)	$Zn—O(4)_w—H(4)$	115·4 (4·3)
$H(3) \cdots O(2^{ii})$	1·778 (57)	$Zn—O(4)_w—O(2^{ii})$	113·9 (1)
$O(4)_w–H(4) \cdots O(3^{i})$	2·678 (6)	$Zn—O(4)_w—O(3^{i})$	116·3 (1)
$H(4) \cdots O(3^{i})$	1·917 (56)	$O(4)_w—H(3) \cdots O(2^{ii})$	167·7 (5·4)
$Zn—O(4)_w$	2·088 (5)	$O(4)_w—H(4) \cdots O(3^{i})$	166·6 (6·0)
		$O(2^{ii}) \cdots O(4)_w \cdots O(3^{i})$	125·0 (1)

Asymmetric units:
No label $= x, y, z$
i $= x, y, z-1$
ii $= \bar{x}+1, \bar{y}, \bar{z}$

at the midpoint along C–C; this residual peak has been attributed to the overlapping of the electron clouds of carbon atoms around the C–C direction. Beagley & Small (1963) find residual peaks even in the difference map of ammonium amidoxalate obtained with F_c's calculated at the atomic positions as determined by X-rays. In bis(amidoxalato-*O,O*)-zinc dihydrate a residual peak as high as half that of the hydrogen atoms is in fact recognizable in the difference map.

Table 5. *Analysis of planarity in the amidoxalato anion*

The plane of best fit is defined by atoms with an asterisk.
Equation of the plane of the amidic group:

$$3{\cdot}1876x-3{\cdot}3317y-3{\cdot}2535z-0{\cdot}0431=0.$$

	Δ	σ	Group of atoms
Zn	−0·0431 Å	0·0000	O(1)
*O(1)	−0·0002	0·0025	\
O(2)	−0·0304	0·0031	C(1)—N
O(3)	0·0184	0·0023	/
*N	−0·0003	0·0037	C(2)
*C(1)	0·0009	0·0036	
*C(2)	−0·0002	0·0036	$\Sigma\left(\frac{\Delta}{\sigma}\right)^2 = 0{\cdot}079$
O(4)$_w$	2·0410	0·0031	

Equation of the plane of the carboxylic group:

$$3{\cdot}2855x-3{\cdot}1942y-3{\cdot}2160z-0{\cdot}1009=0.$$

	Δ	σ	Group of atoms
Zn	−0·1009 Å	0·0000	C(1)
O(1)	−0·0276	0·0025	/
*O(2)	−0·0010	0·0031	O(3)—C(2)
*O(3)	−0·0005	0·0023	\
N	0·0216	0·0037	O(2)
*C(1)	−0·0009	0·0036	
*C(2)	0·0036	0·0036	$\Sigma\left(\frac{\Delta}{\sigma}\right) = 1{\cdot}214$
O(4)$_w$	1·9802	0·0031	

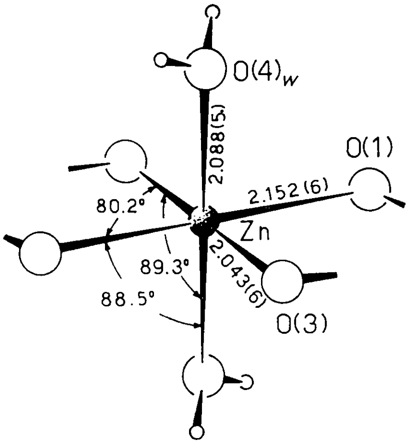

Fig. 2. *trans*-Octahedral complex around zinc.

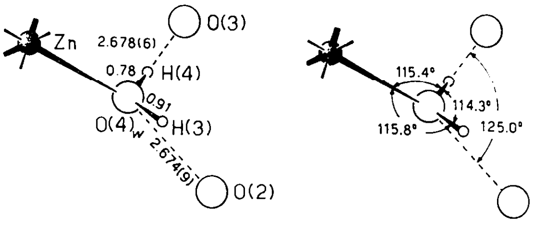

Fig. 3. Coordination around O(4)$_w$.

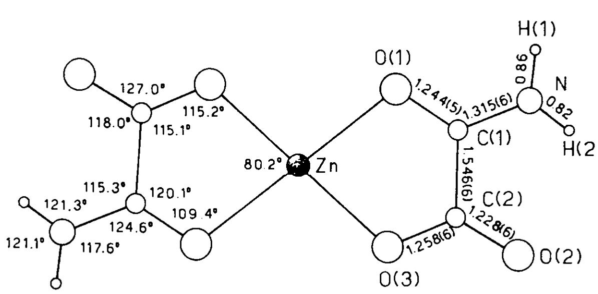

Fig. 4. Diagram of the pentatomic chelate ring, with distances (in Å) and angles.

The carboxylic group with distances C(2)–O(2) = 1·228 and C(2)–O(3) = 1·258 Å shows that the difference in a single–double bond character is much less than in dimethyl oxalate where C–O(CH_3) = 1·31 and C=O = 1·19 Å (Dougill & Jeffrey, 1953) and in α-oxalic acid dihydrate where C–OH = 1·285 and C=O = 1·212 Å (Delaplane & Ibers, 1969), but is greater than in ionic carboxylic groups where the two bonds are equal as in ammonium amidoxalate (C–O = 1·256, 1·257 Å, Beagley & Small, 1963) and ammonium oxalate monohydrate (C–O = 1·252, 1·263 Å, Robertson, 1965).

The amide group is planar in accordance with results in amides and peptides (Marsh & Donohue, 1967). The distances between nitrogen and hydrogen atoms (N–H(1) = 0·86, N–H(2) = 0·82 Å are again shorter than distances determined in other compounds by neutron diffraction. The hydrogen atoms are found to be displaced H(1) = 0·013 and H(2) = −0·017 Å from the plane of the whole group. The bonds (Tables 6 & 7) C(1)–O(1) = 1·244 and C(1)–N = 1·315 Å are very close to the average values in peptides (C–O = 1·24, C–N = 1·325 Å, Marsh & Donohue, 1967) and to the values in ammonium amidoxalate (Beagley & Small, 1963). Therefore the anion does not change appreciably as a result of chelation. The $-NH_2$ group (Fig. 5) forms only one hydrogen bond N–H(1)···O(1) = 3·057 Å with the angle N–H(1)···O(1) = 176·3°. The other H atom is directed toward O(2) but the distance N···O(2) = 3·305 Å is so long that hydrogen bonding can be excluded. On the other hand a contact N···O(4)$_w$ = 3·072 Å should not be considered as a hydrogen bond because no hydrogen peak has been found in between.

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Table 6. *Bond distances and angles in amidoxalato anion*

C(1)–O(1)	1·244 (5) Å	O(1)–C(1)–N	124·6 (4)°
C(1)–N	1·315 (6)	O(1)–C(1)–C(2)	120·1 (3)
C(1)–C(2)	1·546 (6)	N—C(1)–C(2)	115·3 (3)
C(2)–O(2)	1·228 (6)	C(1)–C(2)–O(2)	118·0 (3)
C(2)–O(3)	1·258 (6)	C(1)–C(2)–O(3)	115·1 (3)
		O(3)–C(2)–O(2)	127·0 (4)

Table 7. *Environment of amidic group*

N—H(1)	0·86 (5) Å	C(1)—N—H(1)	117·6 (3·9)°
N—H(2)	0·82 (6)	C(1)—N—H(2)	121·3 (4·4)
N—H(1)···O(1$^{\text{iii}}$)	3·057 (8)	H(1)—N—H(2)	121·1 (5·9)
H(1)···O(1$^{\text{iii}}$)	2·200 (54)	N—H(1)···O(1$^{\text{iii}}$)	176·3 (4·8)
N—H(2)···O(2$^{\text{iv}}$)	3·305 (9)	N—H(2)···O(2$^{\text{iv}}$)	173·0 (5·9)
H(2)···O(2$^{\text{iv}}$)	2·486 (64)	C(1)—N·····O(1$^{\text{iii}}$)	116·3 (3)
N···O(4$^{\text{v}}$)$_w$	3·072 (12)	C(1)—N·····O(2$^{\text{iv}}$)	125·9 (3)
N—C(1)	1·315 (6)	O(1$^{\text{iii}}$)···N·····O(2$^{\text{iv}}$)	117·4 (1·3)

Asymmetric units:
No label $= x, y, z$
iii $= \bar{x}, \bar{y}+1, \bar{z}-1$
iv $= \bar{x}+1, \bar{y}+1, \bar{z}$
v $= x, y+1, z$

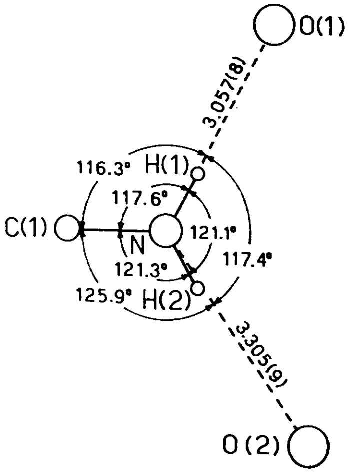

Fig. 5. Environment of $-NH_2$ group.

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