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The Crystal Structure of Bis-(β-alaninato)copper(II) Tetrahydrate

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Crystals of bis-(β-alaninato)copper(II) tetrahydrate ($CuC_6N_2O_8H_{20}$) belong to the space group $P\bar{1}$ with the unit-cell dimensions, $a=9{\cdot}164$ (7), $b=10{\cdot}000$ (7), $c=7{\cdot}041$ (7) Å, $\alpha=99{\cdot}89$ (9), $\beta=102{\cdot}21$ (9) and $\gamma=91{\cdot}42$ (9)°. The atomic parameters were refined to a final R value of 0·061 for 2092 reflexions. The crystal contains two different complex molecules *A* and *B*. Both complexes assume a distorted octahedron with the copper ion at the centre of symmetry as found in bis-(β-alaninato)copper(II) hexahydrate. The two β-alanine residues are coordinated *trans* to each other forming an equatorial square. The apical coordination sites are occupied by water molecules in complex *B*, while in complex *A* they are occupied by carbonyl oxygen atoms of the β-alanine residues belonging to the adjacent complex *B*.

Introduction

While crystal structures of many metal–amino acid complexes have been elucidated so far, few data are available for the complexes with β-alanine, that is, bis-(β-alaninato)copper(II) hexahydrate (Tomita, 1961) and bis-(β-alaninato)nickel(II) dihydrate (Jose, Pant & Biswas, 1964). The conclusions derived from these earlier studies are: (1) β-alanine behaves as a bidentate chelating agent, the two β-alanine residues being *trans* to each other, (2) the four donor atoms (probably in the forms of NH_2 and COO^-) form an approximate square about the metal, and octahedral coordination is completed by two water molecules, (3) characteristic for Cu^{II}, the bonds to the two apical oxygen atoms of water molecules are longer than those to the donor atoms in the coordination square. These studies, however, are based on two-dimensional intensity data visually estimated from the Weissenberg photographs. We report here a structure analysis of the title compound which seems to be precise enough to allow one to discuss the details of the structure. Like Cu^{II} complexes with histamine or histidine (Asato, Komano, Okuyama & Satake, 1967) the bis-(β-alaninato)copper(II) complex has been shown to have a peroxidase activity as indicated by hypochromism of indigo disodium sulphonate (Sakaguchi, unpublished result).

Experimental

Deep blue crystals of the complex were obtained by: (1) mixing an aqueous solution of β-alanine (0·01 *M*) with copper nitrate (0·005 *M*), (2) warming the solution at 40°C for 30 min after adjusting the *p*H to 8 with ammonia, (3) adding isopropyl alcohol after cooling to room temperature and (4) drying the precipitate *in vacuo*. The melting point of the crystals recrystallized from water was 225°C (dec.) (Sakaguchi, 1976).

A block of the crystal with irregularly cleaved surfaces was shaped to a roughly spherical specimen, with a diameter of about 0·15 mm, by soaking in water and methanol for a few minutes. The space group and the lattice constants were determined by Weissenberg photographs, the latter being refined later by mea-

Table 1. *Atomic parameters*

(*a*) Non-hydrogen atoms. Values are × 10⁴. Anisotropic temperature factors are of the form:
$T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
CU	0 (0)	0 (0)	0 (0)	47 (1)	36 (1)	47 (2)	8 (1)	9 (1)	12 (1)
CU′	5000 (0)	0 (0)	5000 (0)	45 (1)	30 (1)	60 (2)	−8 (1)	−6 (1)	20 (1)
N	−604 (5)	1543 (4)	−1320 (6)	60 (5)	44 (4)	59 (9)	6 (4)	20 (5)	16 (5)
O(1)	459 (4)	1176 (4)	2708 (5)	67 (5)	51 (4)	62 (7)	26 (3)	11 (5)	7 (4)
O(2′)	2563 (4)	280 (4)	−485 (5)	60 (5)	96 (5)	69 (8)	−19 (4)	−5 (5)	45 (5)
N′	5805 (5)	1846 (4)	4912 (6)	60 (5)	42 (4)	88 (10)	−2 (4)	−6 (6)	19 (5)
O(1′)	3760 (4)	−239 (3)	2316 (5)	58 (4)	43 (4)	81 (8)	−8 (3)	−8 (5)	25 (4)
O(3)	2773 (4)	1186 (4)	6164 (5)	64 (5)	87 (5)	99 (9)	−1 (4)	16 (5)	46 (5)
C(1)	−361 (6)	2141 (5)	3157 (7)	59 (6)	46 (5)	86 (11)	5 (5)	19 (7)	15 (6)
C(2)	−904 (6)	3053 (5)	1691 (8)	78 (7)	48 (5)	97 (12)	20 (5)	36 (7)	21 (6)
C(3)	−187 (6)	2896 (5)	−74 (7)	77 (7)	44 (5)	82 (11)	3 (5)	29 (7)	22 (6)
O(2)	−721 (5)	2385 (4)	4792 (6)	158 (7)	95 (5)	88 (9)	56 (5)	86 (7)	46 (5)
C(1′)	3543 (5)	563 (5)	1073 (7)	46 (6)	50 (5)	72 (11)	6 (4)	19 (6)	18 (6)
C(2′)	4517 (7)	1859 (6)	1455 (8)	112 (9)	62 (6)	103 (13)	−15 (6)	3 (8)	38 (7)
C(3′)	4842 (7)	2608 (6)	3554 (8)	104 (8)	45 (6)	121 (13)	4 (5)	5 (8)	26 (7)
O(4)	−3668 (5)	4424 (5)	−1501 (7)	120 (7)	102 (6)	161 (11)	20 (5)	59 (7)	16 (6)
O(5)	−3208 (5)	5956 (5)	2467 (6)	119 (7)	83 (5)	143 (10)	5 (5)	21 (7)	10 (6)
O(6)	−1996 (5)	4825 (4)	−4282 (7)	116 (6)	70 (5)	175 (11)	−1 (4)	49 (7)	13 (6)

Table 1 (*cont.*)

(*b*) Hydrogen atoms. Positional parameters are × 10³. Thermal parameters are × 10.

Attached to	Atom	x	y	z	B (Å²)
C(2)	H(1)	−69 (6)	403 (6)	251 (8)	19 (11)
	H(2)	−207 (7)	286 (7)	121 (10)	34 (14)
C(3)	H(3)	−36 (8)	361 (7)	−85 (10)	35 (15)
	H(4)	93 (7)	304 (6)	40 (9)	25 (12)
N	H(5)	−35 (7)	136 (6)	−233 (9)	25 (13)
	H(6)	−171 (8)	144 (7)	−171 (10)	36 (15)
C(2′)	H(7)	388 (9)	258 (8)	86 (12)	55 (20)
	H(8)	569 (8)	156 (7)	112 (11)	42 (16)
C(3′)	H(9)	533 (8)	360 (8)	369 (11)	47 (18)
	H(10)	375 (8)	285 (7)	395 (11)	43 (16)
N′	H(11)	576 (8)	234 (7)	616 (11)	47 (17)
	H(12)	673 (12)	158 (11)	473 (16)	99 (29)
O(3)	H(13)	264 (7)	75 (6)	706 (9)	23 (12)
	H(14)	193 (9)	100 (8)	517 (11)	49 (18)

surements on the diffractometer. The space group is $P\bar{1}$ with $a=9{\cdot}164$ (7), $b=10{\cdot}000$ (7), $c=7{\cdot}041$ (7) Å, $\alpha=99{\cdot}89$ (9), $\beta=102{\cdot}21$ (9), $\gamma=91{\cdot}42$ (9)°. The unit cell with the volume of 593·61 Å³ contains two complex molecules, $2[Cu(C_3H_6NO_2)_2]$, and eight water molecules ($Cu_2C_{12}N_4O_{16}H_{40}$, F.W. 623·0) with $D_x=1{\cdot}74$ g cm^{-3}. The intensities were measured on a Rigaku four-circle diffractometer using Ni-filtered Cu $K\alpha$ radiation. Intensities of reflexions with 2θ values up to 132° were collected by the θ–2θ scan method with a 2θ scan rate of 2° min^{-1}. The background was measured at each end of the scan range for 10 s. The intensities were corrected for Lorentz and polarization factors but not for absorption factors. The total number of independent observed reflexions above the $2\sigma(F)$ level was 2092 out of 2165 theoretically possible reflexions.

Determination and refinement of the structure

From a single strong peak at $u=0{\cdot}5$, $v=0$, $w=0{\cdot}5$ on the three-dimensional Patterson map, the two Cu ions were placed at (0,0,0) and (0·5,0,0·5). The alternative solution, (0·25,0,0·25) and (−0·25,0,−0·25), was discarded because of larger R values when several ligand atoms were added. The first Fourier map based on the Cu ions alone showed a superposition of the two different sets of ligand atoms which was gradually resolved during the several successive Fourier syntheses as usual. Refinement of the structure was carried out by the block-diagonal least-squares method (program by Okaya & Ashida, 1967). All 14 hydrogen atoms attached to the β-alanine molecules and to the water molecules coordinated to the Cu ion, but not those attached to the other three water molecules of crystallization, were located on the difference electron density map calculated at the stage where R was 0·075. Subsequent least-squares refinement in which anisotropic thermal motions were assumed for non-hydrogen atoms and isotropic for hydrogen atoms gave $R=0{\cdot}061$. The weighting scheme was: $\sqrt{w}=30/F_o$, when $F_o\geq 30$ and $\sqrt{w}=1$ otherwise. The atomic scattering factors for Cu$^{\text{II}}$, C, N and O were those cited in *International Tables for X-ray Crystallography* (1962) as SX-67, SX-6, 7 and 8 respectively, and for H that given by Stewart, Davidson & Simpson (1965). The real part of the anomalous dispersion, $\Delta f'=-2{\cdot}1$, was taken into consideration for the Cu$^{\text{II}}$ ion.* The final atomic coordinates are listed in Table 1.

Description of the structure and discussion

There are two different complex molecules (denoted as complex *A* and *B* in Figs. 1 and 2) in a unit cell, each having coordination number 6. Each complex has a

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31518 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Cu ion at the crystallographic centre of symmetry. By necessity, the copper ion CU is precisely on the three planes formed by [N,O(1),N*,O(1)*], [O(1),O(2′), O(1)*,O(2′)*] and [N,O(2′),N*,O(2′)*], the equivalent situation being present for the other copper ion CU′. β-Alanine is coordinated to the copper ion through its amino nitrogen and carboxyl oxygen atoms. The two β-alanine residues are coordinated *trans* to each other forming a square planar coordination plane.

The two hydrogen atoms H(5) and H(6) attached to N make a roughly tetrahedral arrangement with the bonds N–CU and N–C(3) showing that the amino group is in the form NH_2. Much the same argument can be made with respect to H(11), H(12), N′, CU′ and C(3′). On the other hand, the carboxyl groups C(1), O(1), O(2) and C(1′), O(1′), O(2′) are clearly in the ionized form COO^-. In both complexes, the C–O (coordinated to Cu ion) bond lengths in the carboxyl group are significantly longer than the C–O (uncoordinated) bond lengths [1·276 (6) and 1·250 (7) Å respectively for the complex *A* and 1·274 (7) and 1·247 (5) Å respectively for the complex *B*] showing the partial polarization induced by the metal ion as found in many metal–amino acid complexes (see, for example, Mitsui, Watanabe, Iitaka & Kimura, 1975). The reverse bond length relationship reported earlier for $Ni(\beta\text{-Ala})_2.2H_2O$ (Jose, Pant & Biswas, 1964) and for $Cu(\beta\text{-Ala})_2.6H_2O$ (Tomita, 1961) is probably due to the limited quality of the intensity data. The planarity of the carboxyl group is complete, the sum of the three bond angles around C(1) or C(1′) being equal to 360·0° within the limit of standard errors. The apical coordination site in complex *B* is occupied by the oxygen atom O(3) of a free water molecule as in the crystals of $Cu(\beta\text{-Ala})_2.6H_2O$ and $Ni(\beta\text{-Ala})_2.2H_2O$. In complex *A*, however, the apical site is occupied by the carbonyl oxygen atom O(2′) belonging to the adjacent complex *B*. The apical bond lengths are 2·460 (4) and 2·596 (4) Å for complexes *A* and *B* respectively, seriously distorting the conformation of both the complexes from a regular octahedron. The averages of the four equatorial bond lengths, on the other hand, are 1·991 and 1·974 Å for *A* and *B* respectively. In both complexes, the apical bonds deviate significantly from the normal to the equatorial plane as, for example, shown by the bond angles O(1)–CU–O(2′) and N′–CU′–O(3) in Table 2. All the bond lengths and angles associated with the β-alanine residue are normal. In Table 3, the torsion angles within the six-membered chelate ring CU–C(1)–C(2)–C(3)–N–CU are compared with the available data. While there seems to be some similarity between the conformation in the complex *B* of the present crystal and that in $Cu(\beta\text{-Ala})_2.6H_2O$ and between the conformation in the complex *A* and that in $Ni(\beta\text{-Ala})_2.2H_2O$, there are apparently no fixed standard conformations for the β-alanine chelate rings.

Table 2. *Bond lengths* (Å) *and angles* (°)

Standard deviations are referred to the last digits.

Complex *A*		Complex *B*	
CU—O(1)	2·015 (3)	CU′—O(1′)	1·960 (4)
CU—N	1·967 (4)	CU′—N′	1·987 (3)
CU—O(2′)	2·460 (4)	CU′—O(3)	2·596 (4)
O(1)—C(1)	1·276 (6)	O(1′)–C(1′)	1·274 (7)
C(1)—O(2)	1·250 (7)	C(1′)–O(2′)	1·247 (5)
C(1)—C(2)	1·507 (8)	C(1′)–C(2′)	1·507 (8)
C(2)—C(3)	1·511 (8)	C(2′)–C(3′)	1·503 (8)
C(3)—N	1·473 (6)	C(3′)–N′	1·483 (7)
O(2′)—CU—O(1)	94·0 (1)	O(3)†–CU′—O(1′)	93·4 (2)
O(2′)*–CU—O(1)	86·0 (1)	O(3)—CU′—O(1′)	86·6 (2)
O(2′)—CU—N	90·9 (2)	O(3)†–CU′—N′	93·4 (2)
O(2′)*–CU—N	89·1 (2)	O(3)—CU′—N′	86·6 (2)
N—CU—O(1)	92·9 (2)	N′†—CU′—O(1′)	93·4 (2)
N*—CU—O(1)	87·1 (2)	N′—CU′—O(1′)	86·6 (2)
CU—O(1)–C(1)	121·1 (3)	CU′—O(1′)–C(1′)	131·1 (3)
O(1)—C(1)–O(2)	122·7 (5)	O(1′)–C(1′)–O(2′)	121·3 (5)
O(1)—C(1)–C(2)	119·5 (5)	O(1′)–C(1′)–C(2′)	119·7 (5)
O(2)—C(1)–C(2)	117·8 (5)	O(2′)–C(1′)–C(2′)	119·0 (5)
C(1)—C(2)–C(3)	115·3 (5)	C(1′)–C(2′)–C(3′)	114·7 (5)
C(2)—C(3)–N	110·5 (4)	C(2′)–C(3′)–N′	111·8 (5)
C(3)—N—CU	115·0 (3)	C(3′)–N′—CU′	116·0 (3)

* Inverted at (0,0,0).
† Inverted at (½,0,½).

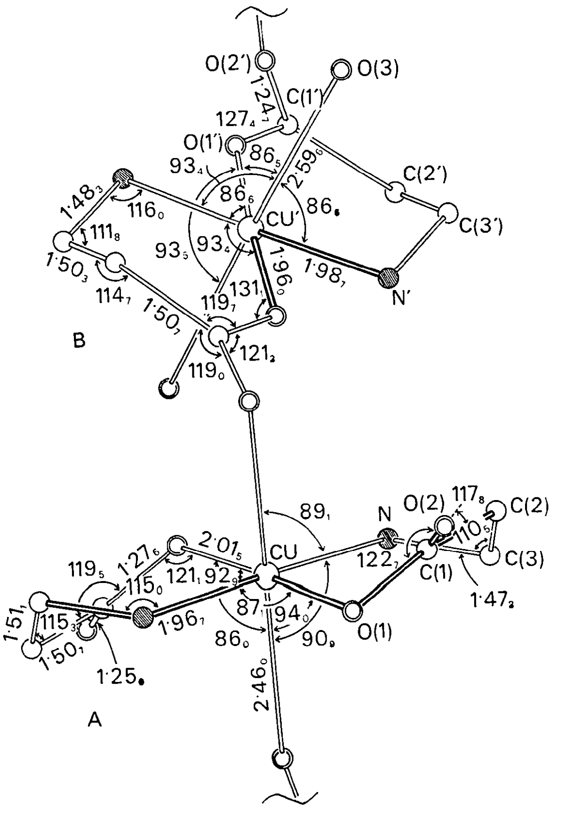

Fig. 1. Nomenclature and geometry of the two complex ions in the crystal. The two copper ions are on the crystallographic centres of symmetry.

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* Inverted at (0,0,0).

Crystal structure

The *c* axis projection is shown in Fig. 2. The complexes *A* and *B* share a common carboxyl group of the β-alanine residue as the apical and equatorial ligand respectively. In addition the two complexes are connected by two hydrogen bonds N′···O(2) and O(3)···O(1) (Nos. 10 and 1 in Table 4, respectively). Also the two complexes *A* and *B* are connected to their own counterparts translated along the *c* axis by the hydrogen bonds O(2)···N and O(2′)···O(3) (Nos. 6 and 4 in Table 4, respectively), forming the sheet of complex ions parallel to (010). Between the sheets thus formed, there are water molecules interconnected by three strong hydrogen bonds O(4)···O(5),

Table 3. *Torsion angles* (°) *of β-amino acid chelate rings*

	Complex *A*	Complex *B*	Zn(Asp).3H$_2$O†	Cu(β-Ala)$_2$.6H$_2$O†	Cu(β-NH$_2$But)$_2$.2H$_2$O†	Ni(β-Ala)$_2$.2H$_2$O†
O(1)-M*—N—C(3)	14	26	47	22	6	10
M*—N—C(3)-C(2)	−60	−59	−80	−55	−50	−56
N—C(3)-C(2)-C(1)	66	68	60	62	67	74
C(3)-C(2)-C(1)-O(1)	−11	−42	−6	−39	−28	−27
C(2)-C(1)-O(1)-M*	−42	11	−14	−6	−23	−29
C(1)-O(1)-M*—N	39	−3	−7	9	32	35
Reference	Present study		Doyne (1957), Doyne, Pepinsky & Watanabe (1957)	Tomita (1961)	Bryan, Poljak & Tomita (1961)	Jose *et al.* (1964)

* Metal.

† Calculations of torsion angles for these compounds have been made by Freeman (1967).

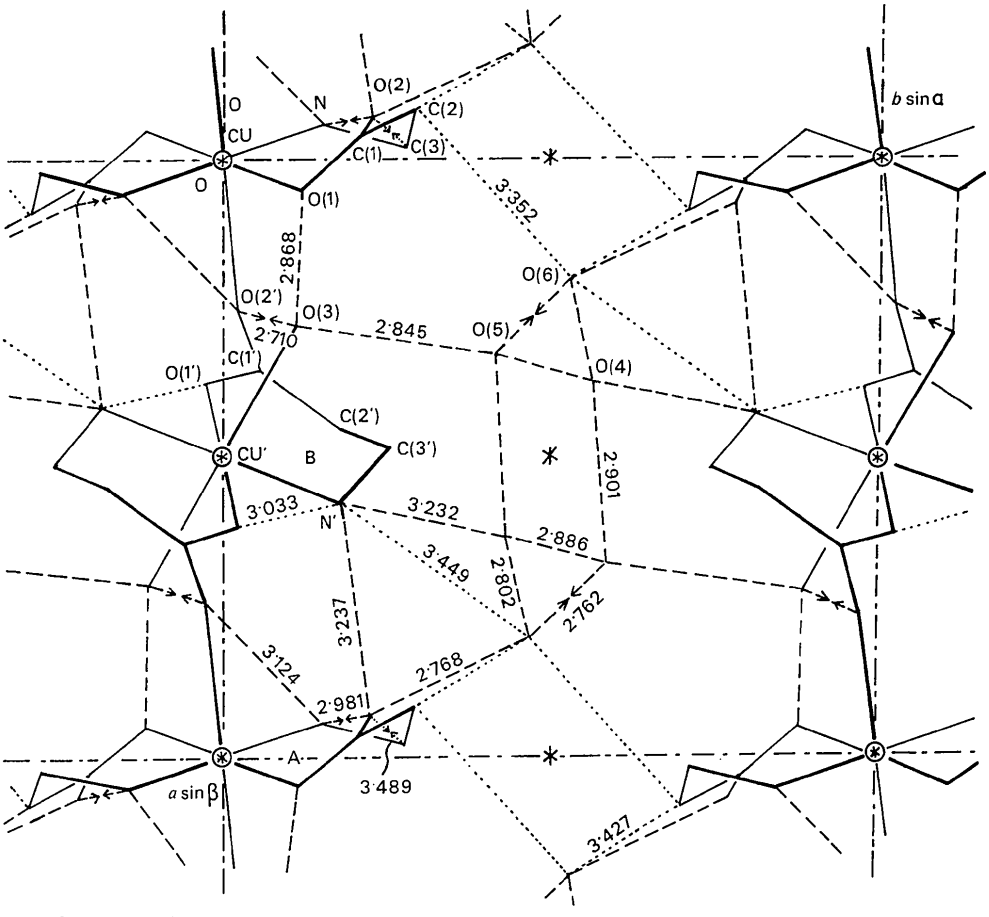

Fig. 2. Projection of the crystal structure along the *c* axis. Centres of symmetry are denoted by *. Hydrogen bonds are shown by broken lines, other intermolecular interactions less than 3·5 Å are shown by dotted lines. Labelled atoms correspond to those given in Table 1 except for O(4), O(5) and O(6) for which the symmetry operation ($\bar{x},\bar{y},\bar{z}$) and a translation (0,1,0) have been given.

Table 4. *Important intermolecular interactions less than* 3·5 Å

No.	From†	To	Distance
1	O(1)	O(3^{i})	2·868 (6)*
2	O(4)	O(5^{i})	2·886 (6)*
3	O(4)	O(6^{i})	2·802 (7)*
4	O(3)	O($2'^{i}$)	2·710 (6)*
5	C(2)	O(6^{i})	3·427 (7)
6	O(2)	N	2·981 (6)*
7	O(2)	C(3^{i})	3·489 (7)
8	O(2)	O(6^{i})	2·768 (6)*
9	O(5)	O(6^{i})	2·762 (7)*
10	N′	O(2^{iii})	3·237 (7)*
11	N′	O(4^{iv})	3·232 (6)*
12	N′	O(6^{iv})	3·449 (6)
13	C(2)	O(6^{ii})	3·352 (6)
14	O(3)	O(5^{v})	2·845 (6)*
15	O(4)	O(5^{vi})	2·901 (6)*

* Hydrogen-bond suggested.
† Atom at (i).

Key to the symmetry operation: (i) x,y,z; (ii) $-x,1-y,-z$; (iii) $1+x,y,z$; (iv) $1+x,y,1+z$; (v) $-x,1-y,1-z$; (vi) $1-x,1-y,-z$.

O(5)···O(6) and O(6)···O(4) (Nos. 2, 9 and 3 in Table 4, respectively) to form a triangular pillar infinitely extending along the c axis. The two triangular pillars related by a centre of symmetry at $(\frac{1}{2},0,\frac{1}{2})$ are connected by hydrogen bonds O(4)···O(5) (No. 15 in Table 4) to form a pair of pillars. The pair of pillars is connected to the complex ions by the two strong and one weak hydrogen bonds O(5)···O(3), O(6)···O(2) and O(4)···N′ (Nos. 14, 8 and 11 in Table 4, respectively). Between the pairs of pillars, however, there is no direct interaction which might result in relatively large temperature factors associated with atoms O(4), O(5) and O(6). The hydrogen atoms attached to these have not appeared clearly on the difference Fourier map.

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The Molecular Structure of a Compound with the Lycoctonine Skeleton, $C_{21}H_{31}O_2N$*

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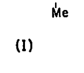
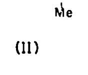
The compound $C_{21}H_{31}O_2N$ was synthesized from an aconite alkaloid, atisine. It has the lycoctonine skeleton. The crystals are orthorhombic, space group $P2_12_12_1$ with $a=10·404$, $b=22·040$ and $c=7·666$ Å. Data were collected with an automatic Picker diffractometer. The structure was solved by direct phasing methods and the refinement was carried out by least-squares procedure to the final R value of 0·049.

Introduction

The structure of the first C_{20} aconite alkaloid, atisine (I), was deduced chemically by Wiesner, Armstrong, Bartlett & Edwards (1954) and the structure of lycoctonine, the C_{19} aconite alkaloid, was determined by X-ray analysis by Przybylska & Marion (1956). Since then a possible biosynthetic transformation of atisine type starting materials into lycoctonine type alkaloids was postulated. Recently T.Y.R. Tsai and K. Wiesner succeeded in transforming the compound (II), which was prepared from atisine by Johnston & Overton (1972), into the compound (III).



(I)



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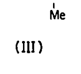

(III)

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* Issued as N.R.C.C. No. 15106.