

A Neutron Diffraction Study of Barbituric Acid Dihydrate

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A neutron diffraction study of barbituric acid dihydrate, $C_4H_4N_2O_3 \cdot 2H_2O$, has been carried out. The space group is $Pnma$ with $a = 12.759$ (13), $b = 6.264$ (2), $c = 8.902$ (3) Å. The final conventional R value was 0.054 based on 483 reflexions with $F_o^2 > \sigma(F_o^2)$, and all bond lengths have been determined with e.s.d.'s less than 0.02 Å. The barbituric acid molecule is in the triketo form and the water molecules are associated in pairs *via* hydrogen bonds. The structure consists of hydrogen-bonded layers of barbituric acid and water molecules which lie on the crystallographic mirror planes $y = \frac{1}{4}, \frac{3}{4}$. There are two N—H...O and four O—H...O hydrogen bonds in the structure.

Introduction

Voet & Rich (1970) have reported a compilation of the barbiturate crystal structures which have been determined by X-ray diffraction techniques. Recently, a series of X-ray crystal structures involving barbiturate derivatives with non-polar C(5) substituents, such as barbituric acids, 1-methylbarbituric acids, barbiturate anions and barbiturate molecular complexes, have been cited (Gartland & Craven, 1974). The structures of perdeuterated violuric acid monohydrate (Craven & Takei, 1964) and dialuric acid monohydrate (Craven & Sabine, 1969) have been studied by neutron diffraction.

The structure of barbituric acid dihydrate has been solved previously from X-ray diffraction data (Jeffrey, Ghose & Warwicker, 1961), in which approximate positions of the H atoms were estimated on the basis of the 'heavy-atom' positions, but were not refined. A three-dimensional neutron diffraction study of this structure has been carried out to determine precise H-atom positions and to elucidate details of the hydrogen bonding in this compound.

Crystal data

Barbituric acid dihydrate, $C_4H_4N_2O_3 \cdot 2H_2O$, $M_r = 164.14$; orthorhombic, $a = 12.759$ (13), $b = 6.264$ (2), $c = 8.902$ (3) Å, space group $Pnma$, $Z = 4$; $D_c = 1.53$, $D_o = 1.54$ g cm⁻³ (measured by flotation in a mixture of ethyl acetate and carbon tetrachloride). The measured linear absorption coefficient is 1.42 cm⁻¹ and the crystal dimensions are 4.2 × 3.9 × 2.4 mm.

Experimental

Small single crystals were obtained by cooling a saturated solution of barbituric acid (British Drug

House) in an equal-volume mixture of acetone and water. Some of these crystals were used as seeds for growing larger crystals from unsaturated solutions. Two crystalline modifications were observed. The crystal chosen for this study was a parallelepiped approximately 36 mm³ in volume, slightly elongated along **a** and with bounding planes (100), (011) and (01 $\bar{1}$). Upon storage at room temperature the crystal slowly lost water, which resulted in a collapse of the crystal structure. For this reason the crystal was enclosed in a quartz tube during the neutron-data collection. It was mounted on the diffractometer with its **a** axis parallel to the φ axis.

Neutron diffraction data were recorded at room temperature on a paper-tape-controlled four-circle neutron diffractometer (Mitsubishi) at the NRI reactor in Baghdad. The cell parameters were refined on the basis of the optimized 2θ , χ and φ values for 30 strong reflexions, well distributed in the reciprocal lattice, with the program *REFINE* (Srikanta & Sequeira, 1968). Unit-cell parameters obtained in the X-ray study ($a = 12.74$, $b = 6.24$, $c = 8.89$ Å) are smaller than the neutron parameters.

The integrated intensities of 573 independent reflexions within the limit $\sin \theta/\lambda = 0.57$ Å⁻¹ [$\lambda = 1.031$ Å] were recorded in the bisecting position with the θ - 2θ coupled step-scan technique. Three scan lengths were chosen to give 40, 50 or 60 points in each scan, corresponding to 2θ upper limits of 40, 60 or 70° respectively. Two monitor reflexions were measured after every 20 reflexions to provide a check on the experiment. During the course of the experiment, spread over a period of five months, there was a systematic increase of nearly 10% in the intensities of the monitor reflexions. The intensities of all the reflexions were normalized, based on the monitor intensities.

The integrated intensities were then reduced to F_o^2 's by applying the standard Lorentz and absorption corrections with the program *DATARED* (Srikanta, 1968),

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which includes the absorption-correction program *ORABS* (Wehe, Busing & Levy, 1962) as a subroutine. An absorption coefficient of 1.42 cm^{-1} (measured) was used. The transmission factors ranged from 0.600 to 0.689.

Structure refinement

The starting parameters for the refinement were the coordinates given by Jeffrey, Ghose & Warwicker (1961), except for two H atoms (a methylene and an imino H) which were located from a Fourier synthesis computed with the program *FORDAP* (Zalkin, 1962). In order to satisfy the space-group symmetry, the two methylene H atoms must be tetrahedrally disposed above and below the mirror plane. The structure was refined by full-matrix least-squares techniques with

anisotropic temperature factors for all atoms and the program *ORFLS* (Busing, Martin & Levy, 1962). Neutron-scattering lengths used were: $b_C = 0.6626$, $b_H = -0.3727$, $b_N = 0.92$, $b_O = 0.575$ (all $\times 10^{-12} \text{ cm}$). The function minimized was $\sum w |F_o^2 - |F_c|^2|^2$, where $w = 1/\sigma^2$ and $\sigma^2 = \sigma_{\text{count}}^2 + (0.05 F_o^2)^2$. To avoid biasing the results, weak reflexions with $F_o^2 < 0$ were included in the refinements (Hirshfeld & Rabinovich, 1973).

The intensity data showed some moderate extinction effects and correction for secondary extinction was applied in the following way (Zachariasen, 1967): F_o^2 (corrected) = F_o^2/Y , where $Y = (1 + 2X)^{-1/2}$, $X = GQ\bar{T}$ [Q is the reflectivity, \bar{T} is the mean absorption-weighted path length and G is an isotropic extinction parameter, which was refined (Sequeira, Rajagopal & Chidambaram, 1972) with the other parameters]. It became obvious near the end of the refinement that the reflexions 020 and 011 were severely affected by extinction ($Y =$

Table 1. *Final positional and thermal parameters*

The second line given for each atom represents the r.m.s. amplitudes of vibration (in $\text{\AA} \times 10^3$) parallel to the principal axes of the displacement ellipsoids. The form of the anisotropic temperature factor is:

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]. \text{ The } \beta_{ij}\text{'s are multiplied by } 10^4.$$

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11} (Axis 1)	β_{22} (Axis 2)	β_{33} (Axis 3)	β_{12}	β_{13}	β_{23}
N(1)	-0.0015 (2)	0.25	0.2824 (3)	29 (2) 156	396 (11) 281	53 (4) 145	0	-1 (2)	0
C(2)	0.0153 (3)	0.25	0.1287 (4)	29 (2) 156	346 (14) 262	54 (4) 147	0	-8 (3)	0
N(3)	0.1169 (2)	0.25	0.0805 (3)	29 (2) 156	390 (11) 279	43 (5) 132	0	-1 (2)	0
C(4)	0.2034 (3)	0.25	0.1700 (4)	26 (2) 146	394 (16) 280	62 (5) 158	0	-4 (3)	0
C(5)	0.1867 (3)	0.25	0.3371 (4)	32 (2) 162	345 (16) 262	56 (5) 150	0	-8 (3)	0
C(6)	0.0753 (3)	0.25	0.3892 (4)	34 (2) 168	323 (13) 253	49 (5) 141	0	-2 (3)	0
O(7)	-0.0577 (3)	0.25	0.0417 (5)	36 (3) 171	569 (24) 336	62 (6) 158	0	-13 (3)	0
O(8)	0.2898 (3)	0.25	0.1136 (5)	27 (3) 150	818 (32) 403	75 (6) 173	0	1 (3)	0
O(9)	0.0520 (4)	0.25	0.5222 (5)	44 (3) 191	590 (25) 342	51 (6) 142	0	-3 (3)	0
O(w1)	0.1732 (6)	0.25	0.7847 (6)	50 (4) 203	810 (34) 401	50 (8) 142	0	-5 (5)	0
O(w2)	0.3868 (5)	0.25	0.7604 (8)	47 (4) 196	653 (29) 360	74 (8) 172	0	3 (5)	0
H(w11)	0.1400 (7)	0.25	0.6865 (11)	61 (6) 224	659 (46) 362	69 (11) 166	0	-8 (7)	0
H(w12)	0.2455 (8)	0.25	0.7707 (9)	58 (7) 218	489 (34) 312	102 (12) 202	0	4 (7)	0
H(w21)	0.4201 (7)	0.25	0.6651 (11)	67 (6) 234	512 (38) 319	95 (13) 195	0	18 (8)	0
H(w22)	0.4360 (8)	0.25	0.8371 (11)	79 (7) 254	476 (37) 308	118 (13) 218	0	-15 (9)	0
H(1)	-0.0792 (7)	0.25	0.3155 (9)	38 (6) 177	513 (35) 319	101 (9) 201	0	8 (6)	0
H(2)	0.1294 (6)	0.25	-0.0362 (9)	46 (4) 195	496 (35) 314	58 (12) 152	0	-5 (5)	0
H(3)	0.2261 (9)	0.1132 (27)	0.3851 (14)	60 (7) 223	649 (59) 359	129 (17) 227	66 (18)	1 (9)	73 (28)

0.30 and 0.33 respectively). These two reflexions were removed in the final cycles of refinement. The minimum extinction correction factor is $Y = 0.55$ for the 031 reflexion, and 42 reflexions have values of $Y < 0.85$.

In the last cycle of refinement no parameter shifted by more than 0.1σ . No systematic dependence of values of $w|F_o^2 - F_c^2|^2$ on F_o^2 was observed, as would be expected for a proper weighting scheme. Agreement values are $R = \Sigma |F_o^2 - F_c^2| / \Sigma |F_o^2| = 0.089$ and $R_w = (\Sigma w|F_o^2 - F_c^2|^2 / \Sigma wF_o^4)^{1/2} = 0.126$. The removal of reflexions with $F_o^2 < \sigma$ (88 reflexions) lowered R and R_w to 0.087 and 0.116 respectively, and in this case the value of the conventional agreement index given by $\Sigma |F_o - |F_c|| / \Sigma F_o$ is 0.054. The standard error of fit with all data included is $S = [\Sigma w|F_o^2 - F_c^2|^2 / (n_o - n_v)]^{1/2} = 1.36$, where n_o and n_v are the number of observed reflexions and the number of variables.

As Jeffrey, Ghose & Warwicker (1961) have noted, there is considerable thermal vibration in the **b** direction. Thermal parameters β_{22} are quite high for all atoms located in the mirror plane at $y = \frac{1}{4}$. The O atoms seem to have a systematically higher thermal vibration normal to the layer plane than do the pyrimidine ring atoms. The observed β_{22} parameters for O(7), O(8) and O(9) are 0.057, 0.082 and 0.059, corresponding to thermal motion with r.m.s. amplitudes of 0.336, 0.403 and 0.342 Å respectively (Table 1). Similar effects have been observed in the structure of perdeuterated violuric acid monohydrate (Craven & Mascarenhas, 1964) and in the 1:1 complex between 9-methyladenine and 1-methylthymine (Frey, Koetzle, Lehmann & Hamilton, 1973), both of which have a similar planar structure lying on a mirror plane. In order to check for possible deviations from the mirror plane, additional refinements of the structure in the alternative space group ($Pn2_1a$) would be required. In this case the number of variables would increase from 113 to 171, which would make the refinement meaningless, since the number of reflexions with F_o^2 above σ is only 483. An attempt was made to refine isotropically in this space group, and the origin of the *b* axis was defined by holding the *y* coordinate of one atom fixed. The *y* parameters did not reach convergence but oscillated with shifts as large as their e.s.d.'s, obviously because the matrix of normal equations is nearly singular. No significant decrease was observed in values of the thermal parameters. The resulting coordinates did not imply significant deviation from planarity of the structure, and the maximum displacement from the best least-squares plane passing through all atoms was less than 2σ .

To examine* the alternatives of an ordered structure with high anisotropic thermal vibration and a disordered model, O(8) was displaced off the mirror plane (assigned 50% occupancy) by an amount chosen on the

basis of the apparent vibrational displacement. Least-squares and Fourier methods did not provide a definite answer, indicating that our data could not distinguish between the two models. In any event we believe that the structure is best described in space group $Pnma$.

The refined atomic parameters are given in Table 1. The final value of the extinction parameter G is $0.019(2) \times 10^4$.*

The calculations described in this paper have been performed on an IBM 370 computer with programs from the Nuclear Research Institute Crystallographic Computing Library which have been described by Sequeira (1975). Bond lengths and angles have been calculated with the programs *SADIAN* (from Brookhaven National Laboratory Crystallographic Computing Library) and *MGEOM* (Wood, 1964) (for the calculation of standard deviations in bond lengths and angles).

Discussion

A stereoscopic view of the barbituric acid molecule, drawn with the program *ORTEP* (Johnson, 1965), is shown in Fig. 1. Covalent bond lengths and angles are given in Table 2, which for comparison includes results from the prior X-ray study (Jeffrey, Ghose & Warwicker, 1961). The general features of the non-hydrogen backbone in the present neutron study and in the X-ray study are the same and bond parameters agree to within 2σ (X-ray). All distances and angles fall within the ranges for barbiturate bonding parameters cited in a review of purine, pyrimidine and barbiturate crystal structures (Voet & Rich, 1970). Average bond distances in the pyrimidine ring are C—N 1.370 and C—C 1.499 Å. The mean of the C—N—C angles within the ring is 125.6° , significantly larger than those at the C atoms (average 117.3°).

The C—O distances in the barbituric acid molecule correspond to normal carbonyl groups, as would be expected for the triketo form. The average C—O bond length is 1.214 Å. The triketo form has also been found in the structure of anhydrous barbituric acid (Bolton, 1963) and in the barbiturate ion (Craven, 1964).

The two imino N—H bond lengths are N(1)—H(1) 1.033 (9) and N(3)—H(2) 1.051 (17) Å, corresponding to a difference of about 2σ , which is probably significant. C(5)—H(3) is 1.082 (15) Å and C(4)—C(5)—H(3) and C(6)—C(5)—H(3) are $109.0(9)$ and $108.6(9)^\circ$ respectively, very close to the tetrahedral value. The average O—H distance in the water molecules is 0.945 Å, while the average H—O—H angle is 109.5° . Similar

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32311 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* This question was brought to our attention by a referee.

values have been observed for the water bond parameters in precision neutron diffraction structural studies (e.g. Verbist, Lehmann, Koetzle & Hamilton, 1972).

The bond lengths given in Table 2 have not been corrected for the foreshortening effects of thermal motion. Thus, they are expected to be slightly underestimated.

H-atom positions given in the X-ray study (Jeffrey, Ghose & Warwicker, 1961) have been calculated according to the positions of the 'heavy' atoms, but they have not been refined. Thus it is not appropriate to make a comparison between the present neutron study and the X-ray study for the results involving H atoms.

The crystal structure and hydrogen bonding

With fourfold occupancy, space group *Pnma* requires all atoms, except the methylene and water H atoms, to lie on the mirror planes at $y = \frac{1}{4}, \frac{3}{4}$. The H atoms of both water molecules are also found to lie on the mirror planes, so that the barbituric acid and water molecules are coplanar and hydrogen-bonded, forming a relatively compact layer structure (Fig. 2). The separation between layers is 3.13 Å (one-half the *b* translation of the unit cell), comparable to the 3.11 Å separation in violuric acid monohydrate (Craven & Mascarenhas, 1964) and to the mean separation of 3.22 Å in 5-nitrobarbituric acid trihydrate (Craven, Martínez-Carrera & Jeffrey, 1964). Adjacent layers are displaced with respect to each other by the symmetry operation of the *n* and *a* glide planes perpendicular to the *a* and *c* axes respectively.

With the two imino groups and two water molecules there are six H atoms available for hydrogen-bond formation. The three carbonyl O atoms act as hydrogen-bond acceptors and the two imino groups as hydrogen-bond donors, but both water molecules act as donors and acceptors at the same time (Table 3). The water

molecules are linked in pairs *via* the hydrogen bond $O(w1)-H(w12)\cdots O(w2)$. One water molecule of the pair is hydrogen-bonded to two carbonyl O atoms on different neighbouring molecules, the other is bonded to a carbonyl and an imino group on two different neighbouring barbituric acid molecules. The sixth hydrogen bond is formed between a carbonyl O and an imino H on adjacent molecules. The carbonyl O(9) is involved in two hydrogen bonds *via* H(w11) and H(w22) of adjacent water molecules (Fig. 2). Among the six hydrogen bonds mentioned, $N(3)-H(2)\cdots O(w1)$ is the strongest, the distances $N(3)\cdots O(w1)$ and $H(2)\cdots O(w1)$ being 2.729(6) and

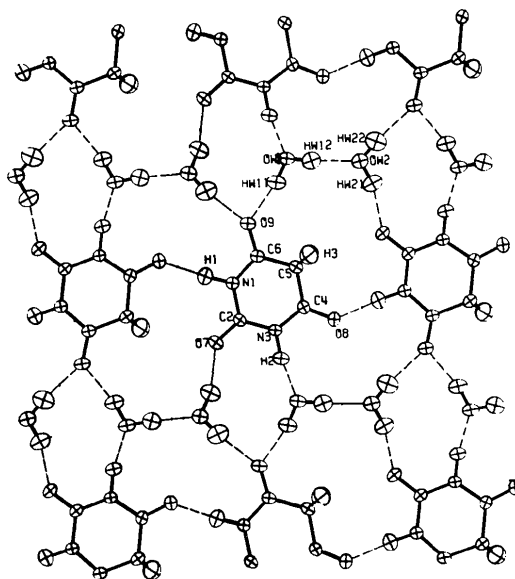


Fig. 2. A single hydrogen-bonded layer in the crystal structure of barbituric acid dihydrate, viewed down *b*. Only one of the methylene H atoms is shown. Covalent bonds are solid and hydrogen bonds are dashed.

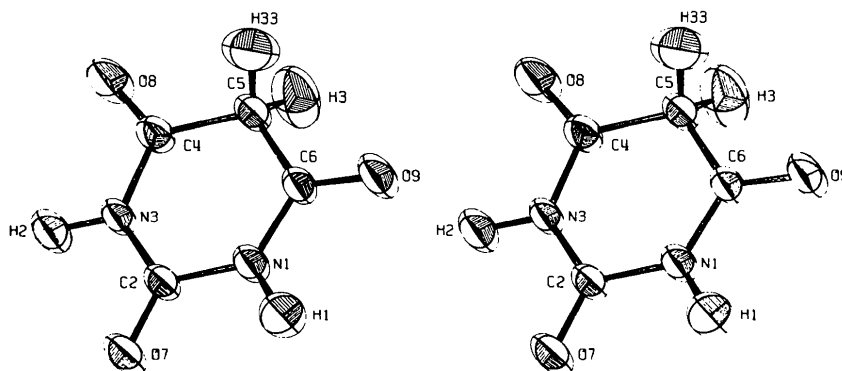


Fig. 1. A stereoscopic drawing of the barbituric acid molecule, with thermal ellipsoids drawn on a 50% probability scale. H(3) and H(33) are related by mirror symmetry.

Table 2. Covalent bond lengths (Å) and angles (°)

Bonds	Neutron	X-ray*	Angles	Neutron	X-ray*
N(1)—H(1)	1.033 (9)		C(2)—N(1)—C(6)	125.2 (2)	125.2
N(1)—C(2)	1.385 (4)	1.386	C(2)—N(1)—H(1)	115.5 (4)	
N(1)—C(6)	1.366 (4)	1.368	C(6)—N(1)—H(1)	119.3 (1)	
C(2)—O(7)	1.211 (5)	1.217	N(1)—C(2)—N(3)	117.2 (1)	118.1
C(2)—N(3)	1.366 (4)	1.351	N(1)—C(2)—O(7)	120.8 (1)	119.7
N(3)—H(2)	1.051 (17)		N(3)—C(2)—O(7)	122.0 (2)	122.2
N(3)—C(4)	1.361 (4)	1.386	C(2)—N(3)—C(4)	125.9 (1)	125.0
C(4)—O(8)	1.212 (5)	1.208	C(2)—N(3)—H(2)	117.0 (4)	
C(4)—C(5)	1.503 (5)	1.511	C(4)—N(3)—H(2)	117.1 (8)	
C(5)—H(3)	1.082 (15)		N(3)—C(4)—C(5)	117.7 (2)	117.8
C(5)—C(6)	1.495 (5)	1.495	N(3)—C(4)—O(8)	119.7 (1)	118.3
C(6)—O(9)	1.220 (6)	1.226	C(5)—C(4)—O(8)	122.6 (1)	123.9
O(w1)—H(w11)	0.971 (11)		C(4)—C(5)—C(6)	116.3 (0)	115.8
O(w1)—H(w12)	0.931 (13)		C(4)—C(5)—H(3)	109.0 (9)	
O(w2)—H(w21)	0.949 (12)		C(6)—C(5)—H(3)	108.6 (9)	
O(w2)—H(w22)	0.928 (12)		H(3)—C(5)—H(33)	104.8 (10)	
			C(5)—C(6)—N(1)	117.8 (1)	118.1
			C(5)—C(6)—O(9)	122.2 (1)	121.9
			N(1)—C(6)—O(9)	120.1 (2)	120.0
			H(w11)—O(w1)—H(w12)	108.2 (10)	
			H(w21)—O(w2)—H(w22)	110.8 (8)	

* Data of Jeffrey, Ghose & Warwicker (1961) recalculated with the unit-cell dimensions from this work.

Table 3. Distances (Å) and angles (°) involving the hydrogen bonds

X—H...Y	X...Y	H...Y	∠X—H...Y
O(w1)—H(w11)...O(9) ⁱ	2.802 (8)	1.844 (10)	168.4 (6)
O(w1)—H(w12)...O(w2) ⁱⁱ	2.734 (9)	1.805 (9)	175.2 (4)
O(w2)—H(w21)...O(7) ⁱⁱⁱ	2.780 (8)	1.862 (11)	162.1 (7)
O(w2)—H(w22)...O(9) ⁱⁱⁱ	2.862 (8)	1.938 (11)	172.8 (7)
N(3)—H(2)...O(w1) ^{iv}	2.729 (6)	1.689 (17)	169.4 (1)
N(1)—H(1)...O(8) ^v	2.818 (5)	1.787 (21)	175.9 (2)

Symmetry code

- (i) x, y, z (iv) $x, y, z - 1$
(ii) $\frac{1}{2} + x, y, \frac{1}{2} - z$ (v) $x - \frac{1}{2}, y, \frac{1}{2} - z$
(iii) $\frac{1}{2} + x, y, \frac{3}{2} - z$

1.689 (17) Å respectively (Table 3). This is consistent with the observed lengthening of N(3)—H(2) relative to N(1)—H(1) (Table 2).

Bond distances and angles determined in this study have standard deviations approximately two to three times larger than those found in the most precise neutron diffraction structure refinements. This is probably attributable to the small number of measured intensity data. There were about four reflections above σ for each refined parameter. To avoid biasing the results we have refined on F^2 and included all weak reflexions in the refinement (Hirshfeld & Rabinovich, 1973).

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L-(+)₅₄₆-L-Phenylalaninatobis(acetylacetonato)cobalt(III)–Chloroform

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The crystal structure of L-(+)₅₄₆-L-phenylalaninatobis(acetylacetonato)cobalt(III)–chloroform, $\text{Co}(\text{C}_{19}\text{H}_{24}\text{O}_6\text{N})\cdot\text{CHCl}_3$, has been determined and refined by three-dimensional least-squares techniques. The space group is $P3_1$ with unit-cell dimensions $a = b = 12.319$ (1), $c = 14.504$ (2) Å. The final weighted R value for all 1793 data is 0.060. The structure is the Δ -*cis* isomer, in agreement with the identification made by Laurie [*J. Chem. Soc. Dalton* (1972), pp. 573–576] from spectroscopic data. The Co ion is in a distorted octahedral environment with the amino acid and acetylacetonate ions acting as bidentate ligands.

Introduction and experimental

The synthesis of the title compound has been reported by Laurie (1968). Recrystallization from chloroform–*n*-hexane yielded violet, hexagonal needles. The data crystal had the dimensions $0.086 \times 0.121 \times 0.129 \times 0.535$ mm. All X-ray measurements were made at room temperature (22 °C) with an Enraf–Nonius CAD-4 diffractometer and Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) with a Zr filter. The space group was determined as $P3_1$ from the systematic absences, $000l$ ($l \neq 3n$), and the known absolute configuration of the amino acid used in the formation of the compound. Least-square cell dimensions were determined from averages of $+2\theta$ and -2θ values of 30 reflections. The reported uncertainties are three times the calculated standard deviations. Intensities of 1793 independent reflections ($\theta \leq 23^\circ$) were measured with θ – 2θ scans. The data were corrected for background radiation. Lorentz,

polarization and absorption corrections ($\mu = 10.51 \text{ cm}^{-1}$) were applied with the program of Coppens, Leiserowitz & Rabinovich (1965) for 216 sampling points. Intensities of 336 data could not be distinguished from the background, being less than $1.4 T^{1/2}$ ($T = \text{total count}$). They were assigned intensities of $0.63T^{1/2}$ for the purpose of least-squares refinement. Each structure amplitude was assigned a weight of $w_F = \sigma_F^{-2}$, where σ_F is the standard deviation of the amplitude and is given by $\sigma_F = \frac{1}{2} \{[\sigma^2 + (0.05P)^2]/(\text{Lp})P\}^{1/2}$, in which: $\sigma = VT^{1/2}$, $V = \text{scan speed}$, $\text{Lp} = \text{Lorentz-polarization factor}$, $P = V(\text{background-corrected peak count})$.

Structure determination and refinement

The x and y coordinates of Co were determined from a Patterson map and z was set at 0.10. The remaining non-hydrogen atoms were located from difference Fourier maps. The structure was refined by full-matrix

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