Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* ($\mathring{A}^2$)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
I1	1.0000	0.28813 (4)	0.2500	0.084 (1)
C2	1.0000	0.5963 (7)	0.2500	0.081 (3)
N3	1.0000	0.7189 (4)	0.2500	0.066 (2)
C4	1.0000	0.9359 (6)	0.2500	0.067 (2)
N5	1.0686 (2)	0.7655 (4)	0.3536 (6)	0.068 (1)
C6	1.0694 (2)	0.8788 (4)	0.3593 (6)	0.063 (1)
C7	1.1461 (2)	0.9296 (4)	0.4837 (6)	0.062 (1)
C8	1.2106 (3)	0.8628 (5)	0.6002 (8)	0.077 (1)
C9	1.2830 (3)	0.9120 (5)	0.7205 (9)	0.084 (2)
C10	1.2919 (3)	1.0254 (6)	0.7251 (9)	0.086 (2)
C11	1.2281 (3)	1.0926 (6)	0.6084 (9)	0.087 (2)
C12	1.1551 (3)	1.0450 (4)	0.4888 (8)	0.074 (1)

Table 2. *Geometric parameters* ($\mathring{A}$, °)

C2—N3	1.469 (10)	C7—C6	1.461 (6)
N3—N5	1.300 (4)	C8—C9	1.392 (7)
C4—C6	1.378 (6)	C9—C10	1.368 (10)
N5—C6	1.358 (6)	C10—C11	1.393 (8)
C7—C12	1.392 (7)	C11—C12	1.391 (8)
C7—C8	1.397 (7)		
N5—N3—C2	115.5 (3)	C12—C7—C6	120.2 (4)
N5—N3—N5'	129.0 (6)	C8—C7—C6	120.3 (4)
C6—C4—C6'	120.4 (7)	C9—C8—C7	119.9 (6)
N3—N5—C6	116.4 (4)	C10—C9—C8	120.6 (5)
N5—C6—C4	118.8 (4)	C9—C10—C11	119.9 (5)
N5—C6—C7	115.6 (4)	C12—C11—C10	120.3 (6)
C4—C6—C7	125.6 (4)	C11—C12—C7	119.8 (5)
C12—C7—C8	119.5 (4)		

tion, 1985*b*). Program(s) used to solve structure: *SAPI*85 (Yao, Zheng, Qian, Han, Gu & Fan, 1985) . Program(s) used to refine structure: *RCRYSTAN*. Molecular graphics: *ACV* (Stardent Computer Inc., 1990). Software used to prepare material for publication: *XPACK* (Yamaguchi, 1987).

The ω-scan width was $(1.3 + 0.14\tan\theta)°$ and the scan speed was $16° \min^{-1}$. Refinement was by the full-matrix least-squares method. The methyl H atoms were refined with occupancy factor 0.5.

References

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Ohsawa, A., Arai, H., Ohnishi, H., Kaihoh, T., Itoh, T., Yamaguchi, K., Igeta, H. & Iitaka, Y. (1985). *Yakugaku Zasshi*, **105**, 1122–1130.

Rigaku Corporation (1985*a*). *AFD*. Diffractometer control program system. Rigaku Corporation, Tokyo, Japan.

Rigaku Corporation (1985*b*). *RCRYSTAN*. X-ray analysis program system. Rigaku Corporation, Tokyo, Japan.

Stardent Computer Inc. (1990). *ACV*. Application chemistry viewer. Stardent Computer Inc., Mewton, MA, USA.

Yamaguchi, K. (1987). *XPACK*. Program for X-ray parameters report. Showa Univ., Tokyo, Japan.

Yamaguchi, K., Ohsawa, A., Arai, H., Ohnishi, H., Igeta, H., & Iitaka, Y. (1983). *Chem. Pharm. Bull.* **31**, 3762–3764.

Unusual Conformation of (*R*,*R*)-*N*,*N*,*N*',*N*'-Tetramethyltartramide (I) and its *O*,*O*'-Dibenzoyl Derivative (II)†

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Abstract

Despite the conformational stability of optically active tartaric acid and its salts, all of which adopt the energetically preferred $-$synclinal conformation in the solid state, the tetramethyl amide derivatives (I) and (II) adopt an unprecedented $+$synclinal conformation. In this conformation both hydroxy (or benzoyloxy) and amide groups are in *gauche* arrangements, and the H atoms are *trans*. Compound (I) has a twofold rotation axis coinciding with the crystallographic diad axis lying at $(x, 0, \tfrac{1}{6})$. A three-dimensional network of O—H$\cdots$O hydrogen bonds connects the molecules of (I) in the crystal while the molecules of (II) are mainly held together by van der Waals forces.

Comment

It is generally accepted that for optically active tartaric acid and its derivatives as well as for its salts there is a strong preference for a planar carbon-chain conformation. When applied to the *O*,*O*'-dibenzoyl derivative of (*R*,*R*)-*N*,*N*,*N*',*N*'-tetramethyltartramide, the exciton chirality method revealed the presence of a bent carbon-chain conformation (Gawroński, Gawrońska & Rychlewska, 1989). In order to compare the circular dichroism conformational results in solution with the conformation of tartramides in the solid state, the X-ray analysis of (*R*,*R*)-*N*,*N*,*N*',*N*'-tetramethyltartramide (I) and its *O*,*O*'-dibenzoyl derivative (II) was undertaken. The

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† Alternative nomenclature: (I) (*R*,*R*)-2,3-dihydroxy-*N*,*N*,*N*',*N*'-tetramethylbutanediamide; (II) (*R*,*R*)-2,3-dibenzoyloxy-*N*,*N*,*N*',-*N*'-tetramethylbutanediamide.

appropriate derivatives were obtained in the Laboratory of Natural Products Chemistry, A. Mickiewicz University, Poznań (Gawroński, Gawrońska & Rychlewska, 1989). Crystals suitable for X-ray analysis were grown from methanol/ethyl acetate in the case of (I), and ethyl acetate/ethyl ether in the case of (II).

(I) R = H
(II) R = COPh
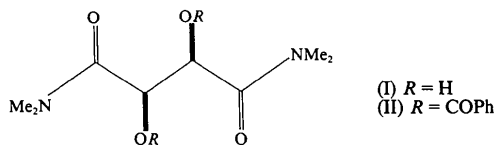
Perspective views of (I) and (II) with their atom-numbering schemes are shown in Fig. 1. In (I) the molecule sits on a crystallographic twofold axis, the second half of the molecule being generated by the symmetry operation $x - y + 1$, $-y + 2$, $-z$, whereas in (II) there is no crystallographically imposed symmetry. Fractional atomic coordinates and isotropic displacement coefficients for non-H atoms are given in Table 1. The atomic coordinates and all drawings are in accordance with the known chirality of the compounds investigated (Gawroński, Gawrońska & Rychlewska, 1989). Selected bond lengths, valency angles and torsional angles are provided in Table 2.
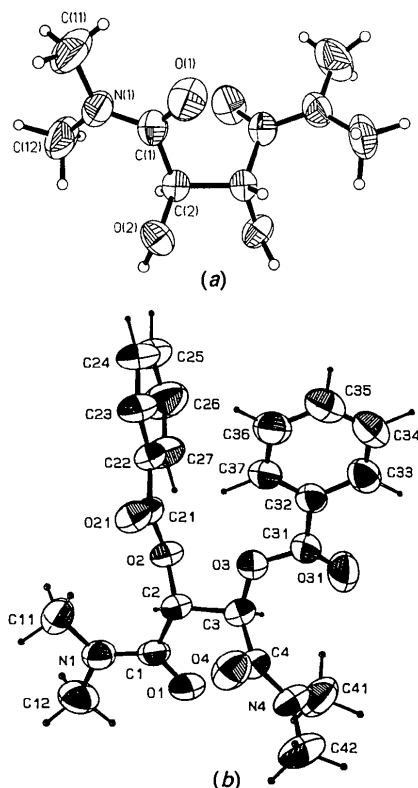

(a)

(b)

Fig. 1. Perspective views of (a) (R,R)-N,N,N',N'-tetramethyltartramide and (b) its O,O'-dibenzoyl derivative with atom-numbering schemes.

Tartaric acid and its derivatives have been extensively studied and some generalizations concerning the molecular structure and stereochemistry of tartrates have been made (Kroon, 1982; Tapscott, 1982). So far for optically active tartaric acid, as well as its salts, only one conformation has been found in the solid state by X-ray diffraction techniques. The preferred conformational isomer has a staggered conformation with a planar carbon chain and the carboxyl groups opposite each other, the $-$synclinal conformation according to Klyne & Prelog (1960) rules. In both of the compounds investigated, the conformation around the $C(sp^3)$—$C(sp^3)$ bond is $+$synclinal which means that the two dimethylamide groups are adjacent to each other and the two H atoms are opposite each other. This conformation is maintained in solution, as evidenced for (II) by the exciton chirality method (Gawroński, Gawrońska & Rychlewska, 1989). The result is rather unexpected, since an antiperiplanar relationship between the two bulky amide units would seem to be favoured and indeed such a conformation has been observed in (R,R)-N,N'-diisopropyltartramide (Dobashi, Hara & Iitaka, 1988).

Moreover, in (I) and (II), the conformation around the $C(sp^2)$—$C(sp^3)$ bond is different from other tartaric acid derivatives. In both molecules the amide carbonyl is not eclipsed by the α-hydroxyl group. In (I), the α-hydroxyl appears to move towards an intermediate position between the amide O and N atoms. The O(1)—C(1)—C(2)—O(2) torsion angle is 90.5 (3)°. In (II) which, in contrast to its parent compound, does not possess C_2 molecular symmetry and therefore has two distinct $C(sp^2)$—$C(sp^3)$ bonds, the conformation in one case tends towards anticlinal [O(1)—C(1)—C(2)—O(2) 115.6 (2)°] and in the other towards synclinal [O(3)—C(3)—C(4)—O(4) 57.7 (3)°]. Consequently, in the former it is the $C(\alpha)$—$C(\beta)$ bond which eclipses the carbonyl group, while in the latter both $C(\alpha)$—$C(\beta)$ and $C(\alpha)$—OH bonds are synclinal with respect to the carbonyl group. A few examples of amides derived from R^1R^2CH—COOH-type carboxylic acids suggest that in these molecules there is a tendency for the two $C(\alpha)$—$C(\beta)$ bonds to be $\pm$synclinal with respect to the carbonyl group rather than for one to be synplanar to it.

Within the amide group, deviations of the torsion angles from 0 or 180° are less than 4.2 (4)° and the out-of-plane rotations are always greater than the twist angle around the $C(sp^2)$—N bond. In (I) bending at C(1) is more pronounced than at N(1) and there is approximately 3° of twisting around the N(1)—C(1) bond. In (II), the out-of-plane rotations are at N atoms. Practically no twisting is observed around the C(4)—N(4) bond and, consequently, bending at N(4) is more severe than that at N(1).
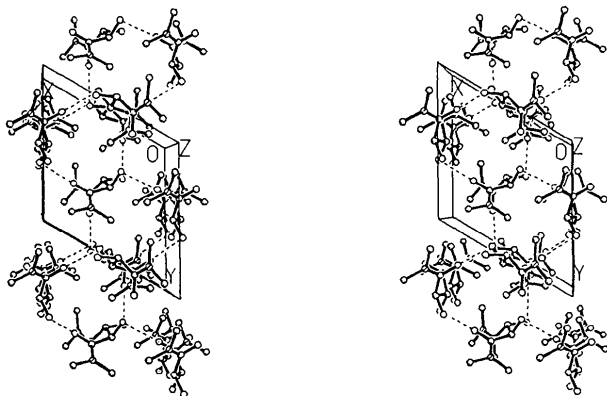
Fig. 2. Stereoscopic view of the crystal packing of compound (I). H atoms have been omitted. Hydrogen bonds are indicated by broken lines.

The three $C(sp^2)$—N distances are equal within experimental error and compare well with the standard value of 1.346 (10) Å quoted by Chakrabarti & Dunitz (1982) for tertiary monocyclic amides. The $C(sp^3)$—$C(sp^3)$ distances are in the range 1.523 (20)–1.542 (7) Å observed in both (R,R)- and meso-tartaric acid isomers (Okaya, Stemple & Kay, 1966; Bootsma & Schoone, 1967).

The three amide carbonyl bonds differ in length. The C=O distance in (I) [1.244 (2) Å] is longer than the corresponding bond distances in (II). Presumably this is a result of the involvement of the carbonyl group in (I) in a strong intermolecular hydrogen bond and the absence of such interactions in (II). In (II) the aromatic rings are oriented in such a way that the normals of their planes form an angle of 75.2 (1)°. The two rings form angles of 5.1 (2) and 2.6 (32)° with the respective carboxylic moieties. The geometrical parameters of the aromatic rings, which are planar within experimental error, are normal. In (I) the molecular packing is determined by a three-dimensional hydrogen-bonding network involving the hydroxyl O(2) atom and the carbonyl O(1) atom in the equivalent position y, $x + 1$, z [O(2)—H(O2) = 1.04 (3), H(O2)···O(1') = 1.80 (3), O(2)···O(1') = 2.677 (2) Å, and O(2)—H(O2)···O(1') = 140 (3)°]. The molecular packing for (I) is shown in the stereo-pair diagrams of Fig. 2. Each molecule uses two of its hydroxyl groups and two of its carbonyl groups to form hydrogen bonds with four nearest neighbours. Viewed in a different way, each molecule participates in two helical hydrogen-bonded systems running along the 3_2 screw axes.

Experimental

Compound (I)

Crystal data

$C_8H_{16}N_2O_4$
$M_r = 204.23$

$Z = 3$
$D_x = 1.23$ Mg m^{-3}

Trigonal
$P3_221$
$a = 9.437$ (1) Å
$b = 9.437$ (1) Å
$c = 10.690$ (1) Å
Cell parameters from 15 reflections
$\theta = 12.6–16.8°$
$V = 824.5$ (1) Å^3

$D_m = 1.23$ Mg m^{-3}
Cu $K\alpha$
$\lambda = 1.54178$ Å
$\mu = 0.796$ mm^{-1}
$T = 295$ K
Cube
0.35 × 0.35 × 0.3 mm
Transparent

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$
1667 measured reflections
767 independent reflections
736 observed reflections
$[I \geq 1.96\sigma(I)]$
$R_{int} = 0.028$
$\theta_{max} = 58°$

$h = -10 \rightarrow 0$
$k = 0 \rightarrow 10$
$l = -11 \rightarrow 11$
2 standard reflections monitored every 100 reflections
intensity variation: ±2%

Refinement

Refinement on F
Final $R = 0.035$
$wR = 0.050$
$S = 4.0$
734 reflections
80 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{max} = 0.12$
$\Delta\rho_{max} = +0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Extinction correction:
$F_c^* = F_c(1 - xF_c^2/\sin\theta)$
Extinction coefficient:
2.0 (1) × 10^{-5}

Density was measured by flotation in a CCl_4/n-hexane mixture. The background and integrated intensity for each reflection were evaluated from a profile analysis according to Lehmann & Larsen (1974) using the program PRARA (Jaskólski, 1982). No absorption correction was made. All H atoms were located on a $\Delta\rho$ map except for two methyl H atoms, the positions of which were calculated geometrically. Methyl groups were refined as rigid groups and their H atoms were assigned a common isotropic temperature factor which refined to a value of $U = 0.181$ (9) Å^2. The remaining H atoms were refined isotropically. Scattering factors were taken from International Tables for X-ray Crystallography (1974, Vol. IV).

Compound (II)

Crystal data

$C_{22}H_{24}N_2O_6$
$M_r = 412.44$
Monoclinic
$P2_1$
$a = 9.578$ (1) Å
$b = 13.692$ (1) Å
$c = 8.508$ (1) Å
$\beta = 102.783$ (9)°
Cell parameters from 15 reflections
$\theta = 8.0–16.1°$

$V = 1088.1$ (2) Å^3
$Z = 2$
$D_x = 1.26$ Mg m^{-3}
$D_m = 1.26$ Mg m^{-3}
Cu $K\alpha$
$\lambda = 1.54178$ Å
$\mu = 0.73$ mm^{-1}
$T = 295$ K
Needle
0.55 × 0.35 × 0.3 mm
Transparent

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$
2941 measured reflections

$h = 0 \rightarrow 10$
$k = -14 \rightarrow 14$
$l = -9 \rightarrow 9$

2906 independent reflections
2810 observed reflections
   $[I \geq 1.96\sigma(I)]$
$R_{int} = 0.024$
$\theta_{max} = 58°$

2 standard reflections
monitored every 100
reflections
intensity variation: ±3%

Refinement

Refinement on F
Final $R = 0.036$
$wR = 0.050$
$S = 3.4$
2795 reflections
280 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F) + 0.0001F^2]$

$(\Delta/\sigma)_{max} = 0.16$
$\Delta\rho_{max} = +0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Extinction correction:
$F_c^* = F_c(1 - xF_c^2/\sin\theta)$
Extinction coefficient:
1.37 (1) × 10^{-5}

Density was measured by flotation in an aqueous solution of KI. The background and integrated intensity for each reflection were evaluated from a profile analysis according to Lehmann & Larsen (1974) using the program *PRARA* (Jaskólski, 1982). No absorption correction was made. Methyl H atoms were located on a $\Delta\rho$ map, except for two atoms, the positions of which were calculated geometrically. The remaining H atoms were placed at calculated positions, and allowed to ride on the parent C atoms. Methyl and phenyl H atoms were assigned common isotropic temperature factors which refined to values of $U= 0.168$ (5) and 0.099 (3) Å^2, respectively. The H atoms at asymmetric centers were given a fixed isotropic temperature factor $U= 0.065$ Å^2. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Programs used for (I) and (II): *PRARA* (Jaskólski, 1982), *SHELX*76 (Sheldrick, 1976), *SHELXS*86 (Sheldrick, 1986), *OR-TEP* (Johnson, 1965), *PLUTO* (Motherwell & Clegg, 1978), *PARST* (Nardelli, 1983), *CRYSRULER* (Rizzoli, Sangermano, Calestani & Andretti, 1986).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Compound (I)				
C(1)	0.3559 (3)	0.9938 (3)	0.0315 (2)	0.051 (1)
C(2)	0.5131 (2)	1.0377 (2)	0.1012 (2)	0.042 (1)
C(11)	0.2095 (4)	1.0428 (5)	−0.1319 (3)	0.098 (2)
C(12)	0.5039 (4)	1.2471 (5)	−0.0916 (3)	0.113 (2)
O(1)	0.2294 (2)	0.8641 (2)	0.0590 (2)	0.074 (1)
O(2)	0.5957 (2)	0.9710 (2)	0.0337 (1)	0.055 (1)
N(1)	0.3602 (3)	1.0927 (3)	−0.0591 (2)	0.066 (1)
Compound (II)				
C(1)	0.5331 (2)	0.7552 (2)	0.5578 (3)	0.057 (1)
C(2)	0.4684 (2)	0.8143 (2)	0.4074 (3)	0.056 (1)
C(3)	0.5824 (2)	0.8398 (2)	0.3133 (3)	0.061 (1)
C(4)	0.6930 (2)	0.9109 (2)	0.4083 (3)	0.066 (1)
C(11)	0.2957 (3)	0.7534 (3)	0.6310 (4)	0.084 (1)
C(12)	0.5085 (4)	0.6675 (3)	0.7952 (4)	0.087 (1)
C(21)	0.2398 (2)	0.7995 (2)	0.2267 (3)	0.057 (1)
C(22)	0.1520 (2)	0.7365 (2)	0.1005 (3)	0.063 (1)
C(23)	0.0288 (3)	0.7766 (3)	0.0053 (4)	0.084 (1)
C(24)	−0.0568 (4)	0.7193 (4)	−0.1139 (4)	0.104 (2)
C(25)	−0.0191 (4)	0.6256 (4)	−0.1378 (4)	0.108 (2)
C(26)	0.1032 (4)	0.5874 (3)	−0.0463 (5)	0.111 (2)
C(27)	0.1893 (3)	0.6418 (3)	0.0735 (4)	0.085 (1)
C(31)	0.5577 (3)	0.9034 (2)	0.0473 (3)	0.064 (1)
C(32)	0.4594 (3)	0.9584 (2)	−0.0823 (3)	0.061 (1)
C(33)	0.5033 (3)	0.9770 (2)	−0.2245 (3)	0.071 (1)

C(34)	0.4154 (4)	1.0290 (2)	−0.3472 (3)	0.079 (1)
C(35)	0.2836 (4)	1.0615 (2)	−0.3288 (3)	0.081 (1)
C(36)	0.2391 (3)	1.0438 (3)	−0.1878 (3)	0.080 (1)
C(37)	0.3268 (3)	0.9914 (2)	−0.0641 (3)	0.067 (1)
C(41)	0.8941 (3)	0.8003 (3)	0.3864 (5)	0.102 (1)
C(42)	0.9336 (4)	0.9578 (4)	0.5335 (5)	0.118 (2)
O(1)	0.6606 (2)	0.7340 (2)	0.5846 (2)	0.075 (1)
O(2)	0.3628 (1)	0.7552	0.3017 (2)	0.056 (1)
O(3)	0.5003 (2)	0.8926 (2)	0.1758 (2)	0.069 (1)
O(4)	0.6490 (2)	0.9861 (2)	0.4571 (3)	0.091 (1)
O(21)	0.2059 (2)	0.8802 (2)	0.2611 (2)	0.071 (1)
O(31)	0.6743 (2)	0.8748 (2)	0.0428 (2)	0.096 (1)
N(1)	0.4475 (2)	0.7293 (2)	0.6559 (2)	0.065 (1)
N(4)	0.8333 (2)	0.8894 (2)	0.4343 (3)	0.083 (1)

Table 2. *Selected bond lengths* (Å), *valency angles* (°) *and torsional angles* (°) *with e.s.d.'s in parentheses*

Compound (I)

C(1)—C(2)	1.521 (3)	C(11)—N(1)	1.477 (4)
C(1)—O(1)	1.244 (2)	C(12)—N(1)	1.452 (4)
C(1)—N(1)	1.332 (4)	C(2)—C(2')	1.529 (3)
C(2)—O(2)	1.420 (3)		

O(1)—C(1)—N(1)	122.6 (3)	C(1)—N(1)—C(12)	124.3 (3)
C(2)—C(1)—N(1)	118.8 (2)	C(1)—N(1)—C(11)	118.2 (3)
C(2)—C(1)—O(1)	118.5 (2)	C(1)—C(2)—C(2')	110.7 (2)
C(1)—C(2)—O(2)	107.9 (2)	C(2')—C(2)—O(2)	108.1 (2)
C(11)—N(1)—C(12)	117.5 (3)		

O(1)—C(1)—N(1)—C(11)	−2.0 (4)	O(1)—C(1)—C(2)—C(2')	−27.6 (3)
C(2)—C(1)—N(1)—C(11)	175.8 (3)	N(1)—C(1)—C(2)—C(2')	154.5 (2)
O(1)—C(1)—N(1)—C(12)	178.2 (3)	C(1)—C(2)—C(2')—C(1')	−52.4 (2)
C(2)—C(1)—N(1)—C(12)	−4.1 (4)	C(1)—C(2)—C(2')—O(2')	−170.4 (2)
O(1)—C(1)—C(2)—O(2)	90.5 (3)	O(2)—C(2)—C(2')—O(2')	71.6 (2)
N(1)—C(1)—C(2)—O(2)	−87.4 (3)		

Compound (II)

C(1)—C(2)	1.525 (4)	C(3)—C(4)	1.531 (3)
C(1)—O(1)	1.227 (3)	C(4)—O(4)	1.220 (4)
C(2)—O(2)	1.444 (2)	C(3)—O(3)	1.450 (3)
C(1)—N(1)	1.341 (3)	C(4)—N(4)	1.345 (3)
C(11)—N(1)	1.460 (4)	C(41)—N(4)	1.449 (5)
C(12)—N(1)	1.468 (4)	C(42)—N(4)	1.468 (5)
C(2)—C(3)	1.530 (3)		

O(1)—C(1)—N(1)	122.9 (2)	O(4)—C(4)—N(4)	122.5 (3)
C(2)—C(1)—N(1)	118.2 (2)	C(3)—C(4)—N(4)	119.8 (2)
C(2)—C(1)—O(1)	119.0 (2)	C(3)—C(4)—O(4)	117.8 (2)
C(1)—C(2)—O(2)	108.9 (2)	C(4)—C(3)—O(3)	107.3 (2)
C(1)—C(2)—C(3)	110.8 (2)	C(2)—C(3)—C(4)	111.1 (2)
C(3)—C(2)—O(2)	106.5 (2)	C(2)—C(3)—O(3)	102.3 (2)
C(11)—N(1)—C(12)	116.9 (2)	C(41)—N(4)—C(42)	116.5 (3)
C(1)—N(1)—C(12)	117.8 (2)	C(4)—N(4)—C(42)	117.3 (3)
C(1)—N(1)—C(11)	125.2 (2)	C(4)—N(4)—C(41)	126.0 (2)

O(1)—C(1)—N(1)—C(11)	179.3 (3)	O(2)—C(2)—C(3)—O(3)	60.3 (2)
C(2)—C(1)—N(1)—C(11)	−0.2 (4)	O(2)—C(2)—C(3)—C(4)	174.5 (2)
O(1)—C(1)—N(1)—C(12)	−4.1 (4)	C(2)—C(3)—C(4)—O(4)	−53.4 (3)
C(2)—C(1)—N(1)—C(12)	176.4 (2)	C(2)—C(3)—C(4)—N(4)	127.0 (2)
O(1)—C(1)—C(2)—O(2)	115.6 (2)	O(3)—C(3)—C(4)—N(4)	−121.9 (3)
O(1)—C(1)—C(2)—C(3)	−1.3 (3)	O(3)—C(3)—C(4)—O(4)	57.7 (3)
N(1)—C(1)—C(2)—O(2)	−64.9 (3)	C(3)—C(4)—N(4)—C(41)	−3.1 (4)
N(1)—C(1)—C(2)—C(3)	178.2 (2)	C(3)—C(4)—N(4)—C(42)	−176.8 (3)
C(1)—C(2)—C(3)—C(4)	−67.2 (3)	O(4)—C(4)—N(4)—C(41)	177.3 (3)
C(1)—C(2)—C(3)—O(3)	178.6 (2)	O(4)—C(4)—N(4)—C(42)	3.6 (4)

References

Bootsma, G. A. & Schoone, J. C. (1967). *Acta Cryst.* **B22**, 522–532.

Chakrabarti, P. & Dunitz, J. D. (1982). *Helv. Chim. Acta*, **65**, 1555–1562.

Dobashi, Y., Hara, S. & Iitaka, Y. (1988). *J. Org. Chem.* **53**, 3894–3896.

Gawroński, J., Gawrońska, K. & Rychlewska, U. (1989). *Tetrahedron Lett.* **30**, 6071–6074.

Jaskólski, M. (1982). *Collected Abstracts, Symposium on Organic Crystal Chemistry*, edited by Z. Kałuski, p. 70. UAM: Poznań.

Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Klyne, W. & Prelog, V. (1960). *Experientia*, **16**, 521–523.

Kroon, J. (1982). *Molecular Structure and Biological Activity*, edited by J. F. Griffin & W. L. Duax, pp. 151–163. New York: Elsevier Biomedical.

Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* **A30**, 580–584.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO78.* Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Okaya, Y., Stemple, N. R. & Kay, M. I. (1966). *Acta Cryst.* **B21**, 237–243.

Rizzoli, C., Sangermano, V., Calestani, G. & Andretti, G. D. (1986). *CRYSRULER Package.* Version 1.0. Univ. of Parma, Italy.

Sheldrick, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELXS86.* Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Tapscott, R. E. (1982). *Transition Metal Chemistry*, Vol. 8, edited by G. A. Melson & B. N. Figgis, pp. 253–429. New York: Marcel Dekker.

Structure of Aqua[N,N'-ethylenebis(N-carbamoylmethylglycinato)]copper(II) Dihydrate

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Abstract

The structure consists of a copper(II) cation octahedrally coordinated to the polyaminocarboxylate ligand through five ligating atoms: one N atom of the ethylenediamine ring, two carboxylate O atoms and a molecule of water form a square plane, while one amide O and the other ethylenediamine-ring N atom are above and below the plane. The latter two atoms display tetragonal distortion. Eight inter-

molecular hydrogen bonds involve H, N and O atoms of the complex as well as the two water molecules of crystallization.

Comment

DL-[1,2-Bis(3,5-dioxo-1-piperazinyl)ethane (1) is a well known anti-tumor agent (Camerman, Hempel & Camerman, 1984; Creighton, Hellmann & Whitecross, 1969). Methyl substitution on the ethylenediamine backbone also yields an immunoreactive agent (2); however, the ethyl-substituted derivative (3) shows no such effect. The biological activity of these compounds is thought to be due to the role of their hydrolysis products, (4), (5) and (6), respectively, which act as intracellular chelators for biologically essential metals such as copper(II), iron(III) and zinc(II). To gain insight into the mechanism of activity, structure–function relationships have been probed (Hasinoff, 1990; Huang, May, Quinlan, Williams & Creighton, 1982). Copper(II) complexes, in particular, have received considerable attention. Relatively high thermodynamic stability constants (Smith & Martell, 1989; Huang, May, Quinlan, Williams & Creighton, 1982) and crystal structures (Prout, Sanderson & Couldwell, 1979) for the copper(II) complexes of ligands (5) and (6) have been reported. Also, Houghton & Williams (1982) have shown that copper(II) promotes the rapid hydrolysis of (1) to form the stable metal–(4) complex, Cu(EDTA-BA). In this paper we report the coordination geometry for copper(II) chelated to (4), and compare the structure with those determined for (5), (6) and structurally related EDTA ligands.
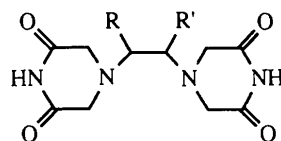
(1) R = H, R' = H
(2) R = CH₃, R' = H
(3) R = C₂H₅, R' = H
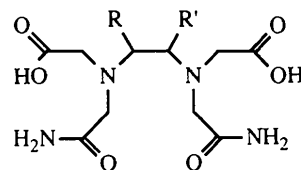
(4) R = H, R' = H
(5) R = CH₃, R' = H
(6) R = C₂H₅, R' = H

Atomic coordinates and equivalent isotropic displacement coefficients for [Cu(EDTA-BA)(H₂O)].2H₂O are listed in Table 1. A stereoview of the asymmetric unit and the atom-numbering scheme are shown in Fig. 1 and selected bond distances and angles are given in Table 2. Ligand (4) acts as a pentadentate ligand, binding a single copper(II) cation, with the sixth coordination site occupied by a molecule of water. Amido O-atom