

The coordination geometry in (2) is more difficult to describe. Each Cu<sup>II</sup> ion is coordinated in a distorted square-planar fashion by four 1,2-dmi ligands. The Cu<sup>II</sup> ions are also nearest neighbours to the perchlorate group O atoms O(1) and O(5), suggesting the possibility of axial coordination. If axial coordination is present, geometric considerations suggest that it must be very weak. The Cu—O(ClO<sub>4</sub>) distances in (2) are substantially longer than those reported for tetragonally coordinated Cu<sup>II</sup> complexes containing 'semi-coordinated' perchlorate ligands [range 2.495 (6)–2.667 (5) Å; Sekizaki (1981); Fawcett, Rudich, Toby, Lalancette, Potenza & Schugar (1980)]. Moreover, the effectiveness of perchlorate as a ligand should be dependent on the Cu—O(ClO<sub>4</sub>)—Cl angle. If one assumes sp<sup>3</sup> hybridization at O, maximum bonding would be expected for angles near 109°. In (2), the Cu—O—Cl angles are far removed from this value while with tetragonal copper complexes known to involve axial coordination by perchlorate, the tetrahedral angle is approached much more closely. For example, in Cu{N,N'-bis(2-aminoethyl)-1,3-propanediamine}-(ClO<sub>4</sub>)<sub>2</sub>, the Cu—O(ClO<sub>4</sub>)—Cl angles were 118.9 (3) and 121.1 (3)° (Fawcett *et al.*, 1980). The apparent weakness of axial coordination in (2) may result in part from the presence of the bulky methyl groups on the 1,2-dmi ligands. In tetrakis(1,4,5-trimethylimidazole)-copper(II) diperchlorate [(3), Bernarducci *et al.* (1983)], a complex closely related to (2) chemically but with sterically more demanding trimethylated imidazole ligands, all Cu—O(ClO<sub>4</sub>) distances were found to be greater than 4 Å and axial coordination was absent.

Excluding the disordered atom N(7'), the Cu—N distances in (2) are equivalent to each other and to the Cu—N lengths reported [2.004 (7), 1.995 (7) Å] for (3). These distances are typical of those observed for Cu—N(azole) ligands. The imidazole groups are planar

to within ±0.01 Å. Their planes (I–IV, Fig. 2) make dihedral angles of 50.0 (2), 50.1 (2), 52.0 (3) and 52.0 (3)°, respectively, with the planar (±0.03 Å) CuN<sub>4</sub> unit; dihedral angles ranging from 18.7 to 85.7° have been observed for tetragonal Cu<sup>II</sup>im<sub>4</sub>X<sub>2</sub> complexes, where im = imidazole or substituted imidazole and X is an axial ligand bonded to Cu by means of an O atom (Bernarducci *et al.*, 1983).

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### Structure of Sodium (–)-Shikimate Dihydrate

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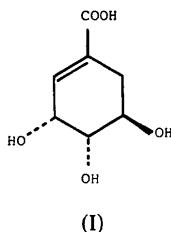
**Abstract.** Sodium (–)-3α,4α,5β-trihydroxy-1-cyclohexene-1-carboxylate dihydrate, Na<sup>+</sup>·C<sub>7</sub>H<sub>9</sub>O<sub>7</sub><sup>-</sup>·2H<sub>2</sub>O, M<sub>r</sub> = 232.2, monoclinic, C<sub>2</sub>, a = 15.806 (2), b = 7.139 (1), c = 17.395 (3) Å, β = 100.05 (2)°, V =

1932.7 (4) Å<sup>3</sup>, Z = 8, D<sub>x</sub> = 1.595 Mg m<sup>-3</sup>, Cu Kα, λ = 1.54178 Å, μ = 1.575 mm<sup>-1</sup>, F(000) = 976, T = 293 K, R = 0.066 for 2252 observed reflections [I > 3σ(I)] and 318 parameters. A clear indication of absolute configuration [η = 1.25 (23)] is in accord with the chemical assignment. The cyclohexene ring adopts a

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half-chair conformation. The overall non-H geometries of the two independent (–)-shikimate ions are closely comparable: mean differences in bond lengths, valence angles and torsion angles are 0.011 Å, 1.5 and 3.9° respectively. The carboxylate group, however, is twisted out of the plane of the endocyclic double bond by 12.4 (4)° (molecule *A*) and by 19.4 (4)° (molecule *B*), whilst the 5β(O–H) bond adopts very different orientations in the two molecules. Crystal packing is dominated by a network of 12 O–H···O hydrogen bonds with O···O in the range 2.674 (6)–2.928 (6) Å.

**Introduction.** Naturally occurring (–)-shikimic acid (**I**) was first isolated from *Illicium religiosum* Sieb. by Eijckmann (1885). Its structure was established by Fischer & Dangschat (1934, 1935) and the absolute stereochemistry derived by degradation and correlation with glucose derivatives (Fischer & Dangschat, 1937). The conformation of the cyclohexene ring in solution was shown to be a half-chair by NMR spectroscopy (Hall, 1964). (–)-Shikimic acid occupies a key position on the pathway to the aromatic amino acids in plants and micro-organisms (Weiss & Edwards, 1980; Conn, 1986). This pathway is of considerable agrochemical interest as a potential target for herbicides. In order to provide accurate structural data for molecular modelling purposes, we are carrying out a series of X-ray analyses of molecules which are on, or related to, this biosynthetic route. We begin the series by reporting the crystal structure of sodium (–)-shikimate dihydrate.



**Experimental.** Colourless prismatic crystals obtained by vapour diffusion from water/acetone. Crystal 0.35 × 0.37 × 0.42 mm; Nicolet R3mμ diffractometer; graphite-monochromatized Cu Kα radiation; cell parameters refined from diffractometer settings of 25 centred reflections (45 < 2θ < 55°). Intensity data collected by θ–2θ scans for 4994 reflections with 5 < 2θ < 116° (*h*–16/0, *k*–7/7, *l*–18/18); 3 standard reflections measured in every 100 showed no significant crystal decay; absorption neglected; 2252 unique reflections (*R*<sub>int</sub> = 0.069) with *I* > 3σ(*I*) used in analysis. Initial structural fragment obtained by multiresolution direct methods and elaborated by Δ*F* syntheses. Blocked-cascade least-squares refinement on *F*, anisotropic thermal parameters for all non-H atoms. H atoms from Δ*F* synthesis: C–H riding on C at 0.96 Å, O–H

(hydroxyl) positions refined, H–O–H riding on O with O–H = 0.96 and H···H = 1.56 Å, separate overall *U*'s for different types of H atoms. 318 parameters, *R* = 0.066, *wR* = 0.082, *w*<sup>–1</sup> = σ<sup>2</sup>(*F*<sub>o</sub>) + 0.0005*F*<sub>o</sub><sup>2</sup>, *S* = 2.26, Δ/σ = 0.053 (mean) and 0.180 (max.), Δρ within +0.54 and –0.46 e Å<sup>–3</sup>.

Owing to the favourably high proportion of O, Na and the use of Cu Kα radiation, we have examined the predictive ability of the Rogers (1981) η parameter for this molecule of known absolute configuration. Two refinements were performed using the correct enantiomorph and a starting η of (*a*) –1.0 and (*b*) +1.0, to yield final η values of (*a*) 1.28 (23) and (*b*) 1.25 (23). No oscillatory behaviour of η was observed following initial shifts of 9.2σ (*a*) and 0.9σ (*b*). Simple enantiomorph inversion yielded *R*, *wR* = 0.0658, 0.0822 (correct) and 0.0662, 0.0822 (incorrect). With a value of (1 + |η|)/σ(η) (Rogers, 1981) of 9.8, the η indication may be regarded as decisive, despite the fact that Friedel equivalents were not measured, and is consistent with chemical knowledge (Fischer & Dangschat, 1937).

The *SHELXTL* program system (Sheldrick, 1983) was used throughout. Scattering factors and *f*', *f*'' correction terms were taken from *International Tables for X-ray Crystallography* (1974).

**Discussion.** Final atomic coordinates are given in Table 1\* and relevant molecular geometry is presented in Table 2. A perspective view of one of the two independent (–)-shikimate ions is shown in Fig. 1, molecular packing is illustrated in Fig. 2. The crystallographic numbering is based on IUPAC–IUB (1968) recommendations for cyclitols.

The two independent ions have closely comparable geometries (Table 2, Fig. 1). Mean differences in bond lengths, valence angles and torsion angles for the C,O framework are 0.011 Å, 1.5 and 3.9° respectively. The cyclohexene ring adopts a half-chair conformation, in agreement with the NMR solution studies of Hall (1964). The mean absolute torsion angle is 32.4 (molecule *A*) and 31.8 (molecule *B*) or 32.1° (overall). These values are close to the 30.3° obtained from energy-minimization studies (Bucourt & Hainaut, 1965). Bond lengths in the ions are normal by comparison with standard mean values for organic compounds recently derived from the Cambridge Structural Database (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987).

The largest angular discrepancies between ions *A* and *B* occur in the peripheral –OH and –COO<sup>–</sup> groups. In

\* Lists of structure factors, H-atom coordinates, anisotropic thermal parameters, and the geometry of the Na environment have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44846 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

$U_{eq}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{eq}$
Na(1)	4461 (1)	5437	7963 (1)	27 (1)
Na(2)	4219 (1)	202 (2)	7803 (1)	33 (1)
C(1)*	7327 (2)	3143 (4)	9763 (3)	16 (1)
C(2)	6532 (2)	2873 (5)	9892 (3)	21 (1)
C(3)	5757 (2)	2764 (5)	9252 (3)	25 (1)
C(4)	6036 (2)	2402 (5)	8473 (3)	21 (1)
C(5)	6734 (2)	3764 (5)	8354 (3)	19 (1)
C(6)	7526 (2)	3372 (5)	8963 (3)	20 (1)
C(7)	8073 (2)	3134 (5)	10435 (3)	20 (1)
O(3)	5244 (1)	4440 (4)	9212 (2)	31 (1)
O(4)	5296 (1)	2581 (3)	7863 (2)	21 (1)
O(5)	6950 (1)	3589 (4)	7597 (2)	31 (1)
O(7)	7939 (1)	3215 (4)	11123 (2)	28 (1)
O(8)	8814 (1)	3012 (4)	10262 (2)	34 (1)
C(11)	8684 (2)	1986 (5)	4832 (2)	20 (1)
C(12)	8623 (2)	451 (5)	5238 (3)	22 (1)
C(13)	8530 (2)	476 (5)	6087 (3)	24 (1)
C(14)	8327 (2)	2435 (5)	6369 (2)	18 (1)
C(15)	8915 (2)	3849 (5)	6065 (3)	23 (1)
C(16)	8710 (2)	3910 (5)	5189 (3)	27 (1)
C(17)	8733 (2)	1841 (5)	3980 (3)	27 (1)
O(13)	9294 (1)	-255 (3)	6574 (2)	27 (1)
O(14)	8433 (1)	2481 (3)	7203 (2)	25 (1)
O(15)	8777 (2)	5641 (3)	6407 (2)	31 (1)
O(17)	8952 (2)	297 (4)	3713 (2)	33 (1)
O(18)	8555 (2)	3263 (4)	3552 (2)	41 (1)
O(90)	3248 (2)	2901 (5)	7906 (2)	44 (1)
O(91)	4516 (1)	-1616 (5)	8932 (2)	37 (1)
O(92)	5541 (1)	-2074 (4)	7723 (2)	29 (1)
O(93)	531 (2)	6614 (4)	6314 (2)	36 (1)

\* C(1)-O(8) are shikimate A, C(11)-O(18) are shikimate B.

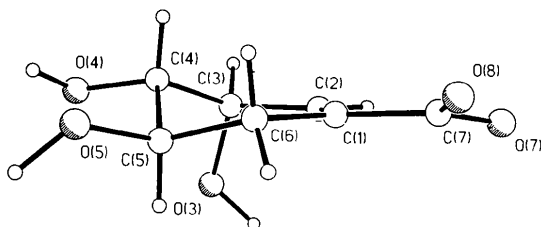


Fig. 1. A view of shikimate ion A showing atomic labelling. Atoms of ion B have 10 added to the numeric part of the label.

particular, the O-H bond of the  $5\beta$ -OH group is rotated from its position in molecule A by  $77(3)^\circ$  in molecule B. Thus, O(5)-H(5O) is approximately antiperiplanar/anticlinal to C(6)-C(5) in molecule A [ $C(6)-C(5)-O(5)-H(5O) = -149(3)$ ;  $C(4)-C(5)-O(5)-H(5O) = 91(4)^\circ$ ], but this situation is reversed in molecule B [ $C(16)-C(15)-O(15)-H(15O) = -72(3)$ ;  $C(14)-C(15)-O(15)-H(15O) = 168(4)^\circ$ ]. The carboxylate group also exhibits conformational differences between the two ions. The carboxylate [C(7), O(7), O(8)] plane is twisted out of the plane of the C(1)-C(2) double bond [defined by C(1), C(2), C(3), C(6), C(7)] by  $12.4(4)^\circ$  in molecule A, and by  $19.4(4)^\circ$  in molecule B.

The angular differences noted above are almost certainly due to the different packing environments of individual ions. These environments are dominated by a three-dimensional network of O-H...O hydrogen

Table 2. Molecular geometry for shikimate ions A and B

Distances are in  $\text{\AA}$ , angles in  $^\circ$ , with e.s.d.'s in parentheses.

	A	B	A	B	
C(1)-C(2)	1.329 (5)	1.316 (5)	C(2)-C(1)-C(6)	122.3 (3)	122.5 (4)
C(1)-C(6)	1.488 (6)	1.505 (6)	C(2)-C(1)-C(7)	120.3 (4)	119.5 (4)
C(1)-C(7)	1.508 (5)	1.502 (6)	C(6)-C(1)-C(7)	117.4 (3)	117.9 (3)
C(2)-C(3)	1.506 (5)	1.510 (7)	C(1)-C(2)-C(3)	123.6 (4)	122.9 (3)
C(3)-C(4)	1.518 (6)	1.534 (5)	C(2)-C(3)-C(4)	110.1 (3)	112.6 (3)
C(4)-C(5)	1.513 (5)	1.528 (5)	C(3)-C(4)-C(5)	110.2 (3)	108.5 (3)
C(5)-C(6)	1.518 (5)	1.501 (7)	C(4)-C(5)-C(6)	108.6 (3)	109.5 (3)
C(3)-O(3)	1.440 (4)	1.447 (4)	C(5)-C(6)-C(1)	113.0 (3)	112.2 (3)
C(4)-O(4)	1.441 (4)	1.431 (5)	C(2)-C(3)-O(3)	111.8 (3)	110.8 (3)
C(5)-O(5)	1.422 (6)	1.444 (5)	C(4)-C(3)-O(3)	110.3 (3)	110.0 (3)
C(7)-O(7)	1.253 (6)	1.267 (5)	C(3)-C(4)-O(4)	108.5 (2)	110.5 (3)
C(7)-O(8)	1.261 (4)	1.261 (5)	C(5)-C(4)-O(4)	111.1 (3)	111.4 (3)
			C(4)-C(5)-O(5)	111.7 (3)	107.3 (3)
			C(6)-C(5)-O(5)	109.2 (3)	111.8 (3)
			C(1)-C(7)-O(7)	120.0 (3)	119.1 (4)
			C(1)-C(7)-O(8)	116.7 (4)	118.8 (4)
			O(7)-C(7)-O(8)	123.3 (3)	122.1 (4)
			A	B	
C(6)-C(1)-C(2)-C(3)	0.1 (6)	3.1 (5)			
C(1)-C(2)-C(3)-C(4)	17.3 (5)	11.9 (4)			
C(2)-C(3)-C(4)-C(5)	-49.8 (4)	-44.6 (4)			
C(3)-C(4)-C(5)-C(6)	65.5 (5)	64.6 (4)			
C(4)-C(5)-C(6)-C(1)	-46.5 (5)	-50.0 (4)			
C(5)-C(6)-C(1)-C(2)	14.9 (5)	16.5 (5)			
C(2)-C(1)-C(7)-O(7)	-13.1 (5)	-19.6 (5)			
C(2)-C(1)-C(7)-O(8)	165.8 (3)	160.6 (3)			
C(6)-C(1)-C(7)-O(7)	169.8 (3)	160.5 (3)			
C(6)-C(1)-C(7)-O(8)	-11.2 (5)	-19.3 (4)			

Hydrogen-bond geometry, H-atom positions normalized to O-H = 0.983  $\text{\AA}$  (e.s.d.'s for O...O are in the range 0.005-0.008  $\text{\AA}$ , and ca 0.04  $\text{\AA}$  and  $3^\circ$  for distances and angles involving H)

	$d(\text{H}\cdots\text{O})$	$d(\text{O}\cdots\text{O})$	O-H...O
O(4)-H...O(93 <sup>i</sup> )	1.93	2.870	158
O(5)-H...O(17 <sup>ii</sup> )	1.81	2.750	160
O(13)-H...O(17 <sup>iii</sup> )	1.97	2.928	165
O(14)-H...O(3)	1.70	2.674	174
O(15)-H...O(93 <sup>iv</sup> )	2.02	2.892	146
O(90)-H(B)...O(7 <sup>v</sup> )	1.81	2.743	157
O(91)-H(A)...O(8 <sup>vi</sup> )	1.82	2.747	156
O(91)-H(B)...O(8 <sup>vii</sup> )	1.81	2.778	168
O(92)-H(A)...O(18 <sup>viii</sup> )	1.89	2.854	164
O(92)-H(B)...O(7 <sup>ix</sup> )	1.90	2.856	163
O(93)-H(A)...O(17 <sup>x</sup> )	1.99	2.757	133
O(93)-H(B)...O(18 <sup>x</sup> )	1.97	2.787	139

Symmetry code: (i)  $-0.5 + x, 0.5 + y, z$ ; (ii)  $1.5 - x, 0.5 + y, 1 - z$ ; (iii)  $2 - x, -y, 2 - z$ ; (iv)  $1 - x, -y, z$ ; (v)  $1 - x, -y, 2 - z$ ; (vi)  $-0.5 + x, -0.5 + y, z$ ; (vii)  $1.5 - x, 0.5 + y, 2 - z$ ; (viii)  $1.5 - x, -0.5 + y, 1 - z$ ; (ix)  $1 - x, 1 + y, 1 - z$ ; (x)  $1 - x, -y, 1 - z$ .

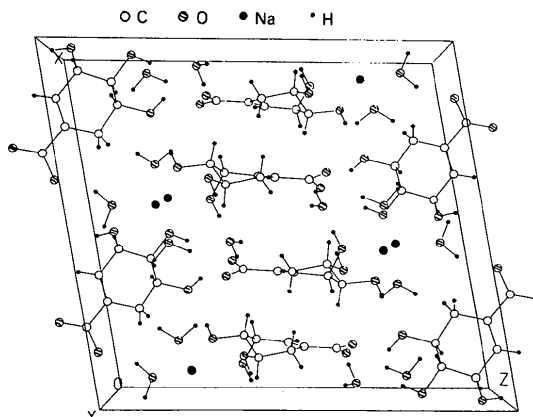


Fig. 2. Packing diagram for sodium shikimate dihydrate.

bonds which links shikimate ions and water molecules. All O—H act as H-bond donors except for H(3O) and H(90A) to yield 12 interactions with O...O in the range 2.674 (6)–2.928 (6) Å (Table 2). The O—H...O angles range from 146 (3) to 174 (3)° with the exception of two angles of 133 (5) and 139 (5)° involving water O(93)—H donors. The water molecules play a key role in the network, being involved in nine of the interactions.

The Na<sup>+</sup> ions have different oxygen environments. Na(1) has seven Na...O contacts (two from each shikimate, three from waters) in the range 2.402 (4)–2.687 (4) Å, forming a distorted pentagonal bipyramid. Na(2) has six Na...O (three from shikimates, three from waters) in the range 2.332 (3)–2.669 (4) Å forming an approximate octahedron.

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### **catena-(N,N,N',N'-Tetramethylethylenediamine)-di-μ-thiocyanato-N,S-cadmium(II)**

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**Abstract.** [Cd(C<sub>6</sub>H<sub>16</sub>N<sub>2</sub>)(NCS)<sub>2</sub>], *M<sub>r</sub>* = 344.68, monoclinic, *C2/c*, *a* = 14.672 (3), *b* = 8.520 (2), *c* = 11.164 (3) Å, β = 100.69 (2)°, *V* = 1371.3 (6) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.67 Mg m<sup>-3</sup>, λ(Mo *Kα*) = 0.71073 Å, μ = 1.72 mm<sup>-1</sup>, *F*(000) = 688, *T* = 296 K, *R* = 0.043 for 722 observed reflections. The Cd<sup>II</sup> ion, mounted on a twofold axis, is octahedrally coordinated by two S and two N atoms of four symmetry-related thiocyanate groups [Cd—N = 2.340 (8), Cd—S = 2.704 (3) Å] and two N atoms of the tetramethylethylenediamine ligand, which is also sited on the twofold axis [Cd—N = 2.415 (8) Å]. The thiocyanate ions constitute double

bridges, thereby building infinite chains of thiocyanate-linked Cd<sup>II</sup> ions along the *c* axis.

**Introduction.** The complexes formed by the IIb metal salts and nitrogen-containing ligands are found in a variety of coordination numbers and geometries (Dean, 1978). In particular, the thiocyanate ion is known to form metal–nitrogen and metal–sulfur bonds and also bridges through atoms —N—, —S— or through —N,S (e.g. Cingi, Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1985). As part of a systematic investigation of a series of *MX<sub>2</sub>(tmen)* complexes, *M* = Zn<sup>II</sup>, Cd<sup>II</sup>, Hg<sup>II</sup>; *X*