In terms of the vibrational dynamics of the water molecules this compound will probably be the most interesting in the series. Since there are only two water molecules per Zn ion, this is the simplest system in which intermolecular coupling effects between water molecules can be expected. Moreover, although the space group is $P\bar{1}$ with the two water molecules related through an inversion center, the water molecule sits on a site of general symmetry. Therefore this system provides an excellent test of the relative importance of site group effects *versus* correlation field effects.

This material is based upon work supported by the National Science Foundation under grant No. DMR 8319473.

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Structure of a Dihydrated, Di-*tert*-butyl Alcohol Solvated Zinc Acetate Complex with Erythromycin A at 188 K

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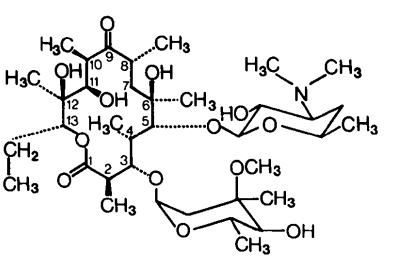
(*Received* 18 *September* 1985; *accepted* 22 *January* 1986)

Abstract. $[Zn(C_2H_3O_2)_2(C_{37}H_{67}NO_{13})(H_2O)].2C_4H_{10}O.2H_2O$, $M_r = 1119{\cdot}72$, orthorhombic, $P2_12_12_1$, $a = 13{\cdot}352\ (3)$, $b = 20{\cdot}013\ (6)$, $c = 22{\cdot}052\ (10)$ Å, $V = 5892{\cdot}6$ Å^3, $Z = 4$, $D_x = 1{\cdot}26$ g cm^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 4{\cdot}95$ cm^{-1}, $F(000) = 2424$, final $R = 0{\cdot}053$ for 3344 unique reflections with $|F| > 3\sigma(|F_o|)$. The absolute structure of the complex was determined. The structure consists of an aquazinc complex and four molecules of solvation, two water molecules and two *tert*-butyl alcohol molecules. The complex has a six-coordinate Zn^{II} ion bonded to two acetate ligands, a water molecule, and the desosamine substituent of the erythromycin A molecule. The important bond lengths are Zn—N 2·124 (6), Zn—O(desosamine) 2·178 (4), Zn—O(water) 2·157 (5) and Zn—O(acetate) 2·024 (6), 2·107 (6) and 2·170 (6) Å.

Introduction. A formulation of erythromycin A (shown below and hereinafter referred to as ER) and zinc acetate has been developed by The Procter & Gamble Company for use as a topical anti-acne medication. The medication was shown in clinical studies (Feucht, Allen & Chalker, 1980) to be safe and effective for acne therapy. The results from a separate clinical investigation (Strauss & Stranieri, 1984) indicated that the mechanism of action of the zinc acetate/ER preparation is probably a direct antibacterial effect on *Propionibacterium acne*. The crystal structure determination was initiated to characterize the interaction between zinc acetate and ER. No other transition-metal complex with ER has been reported.



Erythromycin A

(I)

0108-2701/86/080952-05$01.50

Efforts to grow single crystals from a formulation of the medication in ethanol were unsuccessful. Crystals were eventually obtained fortuitously when the medication was reformulated with *tert*-butyl alcohol as the vehicle.

Experimental. Clear tabular crystals (0·20 × 0·50 × 0·56 mm); Nicolet $P2_1$ four-circle diffractometer; Nicolet LT-1 low-temperature device; graphite-monochromatized Mo $K\alpha$ radiation; cell parameters from setting angles of 16 reflections with $12° < 2\theta < 23°$; corrections for Lorentz and polarization effects, no correction for absorption applied; $\theta_{max} = 21·5°$, $h = 0$ to 13, $k = 0$ to 20, $l = 0$ to 22; standard reflections (004, 040, 210, 111) measured every 100 reflections showed only random variations (<5%) from mean intensities; 3813 unique reflections, 3344 with $|F_o| > 3\sigma|F_o|$; Zn position from a Patterson map, tangent refinement of the heavy-atom phases by direct methods; blocked-cascade refinement on F; hydroxyl, methine, and methyl H atoms refined as rigid groups with common U_{iso}, H atoms on two water and one *tert*-butyl alcohol molecules not located; $R = 0·053$, $wR = 0·059$, $S = 1·77$; $w^{-1} = \sigma^2|F_o| + 0·0005|F_o|^2$; scattering factors and anomalous-dispersion corrections from Ibers & Hamilton (1974); refinement (Rogers, 1981) of f'' multiplier to 0·86 (4) confirms proper enantiomer; mean (max.) shift/σ in final refinement cycle = 0·06 (−0·26); peaks in final difference electron density map from −0·4 to +0·4 e Å^{-3}; Data General Eclipse S-250 computer using *SHELXTL* (Sheldrick, 1981) programs.

Discussion. Final atomic coordinates are given in Table 1.* Bond lengths, bond angles, and hydrogen-bond contact distances are presented in Table 2. A drawing of the molecular structure is shown in Fig. 1. A stereoscopic view of the molecular packing is shown in Fig. 2.

The structure consists of complex ions composed of the Zn^{II} ion, a coordinated water molecule, two acetate ligands, and the ER molecule. These complex ions are bridged by the four molecules of solvation. One acetate group functions as a bidentate ligand and the other as a monodentate ligand. The coordination of the Zn^{II} ion is distorted octahedral. As a consequence of the bite geometries of the chelate rings of the acetate and desosamine ligands, the angles subtended by the Zn^{II} ion differ by as much as 27·1° from their ideal values. The Zn—O bond lengths display a range of 0·154 Å; thus the individual Zn—O bond lengths exhibit significant differences from one another. The largest bond lengths, Zn—O(8) and Zn—O(16), have the values 2·178 (4) and 2·170 (6) Å, respectively, and do not

Table 1. *Atom coordinates* (×10⁴) *and temperature factors* (Å² × 10³)

U_{eq} is defined as $\frac{1}{3}$ trace U_{ij}.

	x	y	z	U_{eq}
Zn	3874 (1)	2704 (1)	4609 (1)	39 (1)
N	2665 (4)	3379 (3)	4738 (2)	29 (2)
O(1)	2057 (4)	1381 (3)	276 (2)	49 (2)
O(2)	3676 (3)	1533 (2)	523 (2)	25 (1)
O(3)	1461 (3)	1510 (2)	2147 (2)	24 (1)
O(4)	−176 (3)	1840 (2)	1911 (2)	28 (2)
O(5)	537 (3)	1599 (2)	3394 (2)	30 (2)
O(6)	−1345 (4)	2137 (2)	3390 (2)	38 (2)
O(7)	2516 (3)	3240 (2)	2544 (2)	23 (1)
O(8)	3425 (3)	2827 (2)	3666 (2)	31 (2)
O(9)	1143 (3)	3604 (2)	3058 (2)	28 (1)
O(10)	1795 (3)	3120 (2)	952 (2)	23 (1)
O(11)	2381 (4)	4089 (3)	−135 (2)	38 (2)
O(12)	3041 (3)	2856 (2)	−602 (2)	38 (2)
O(13)	4886 (3)	2422 (2)	−724 (2)	33 (2)
O(14)	4509 (4)	2758 (3)	5507 (2)	52 (2)
O(15)	3037 (4)	1849 (3)	4839 (2)	56 (2)
O(16)	4494 (4)	1726 (3)	4410 (2)	60 (2)
O(17)	5093 (4)	3284 (3)	4464 (3)	61 (2)
O(18)	5206 (4)	3388 (3)	3465 (2)	58 (2)
O(19)	4468 (5)	−646 (3)	2477 (3)	96 (3)
O(20)	4795 (5)	−4370 (3)	2682 (3)	64 (2)
O(21)	−3265 (4)	2384 (3)	3189 (3)	62 (2)
O(22)	−4401 (5)	1324 (3)	3396 (3)	71 (2)
C(1)	2723 (5)	1369 (3)	640 (3)	29 (2)
C(2)	2583 (5)	1175 (3)	1296 (3)	28 (2)
C(3)	2004 (5)	1748 (3)	1624 (3)	24 (2)
C(4)	2712 (5)	2294 (3)	1829 (3)	22 (2)
C(5)	2105 (5)	2919 (3)	2017 (3)	23 (2)
C(6)	1995 (5)	3458 (3)	1511 (3)	21 (2)
C(7)	2986 (5)	3836 (3)	1405 (3)	23 (2)
C(8)	2955 (5)	4330 (3)	874 (3)	30 (2)
C(9)	3030 (5)	3993 (3)	253 (3)	30 (2)
C(10)	3941 (5)	3577 (3)	95 (3)	27 (2)
C(11)	3613 (5)	2867 (3)	−51 (3)	26 (2)
C(12)	4442 (5)	2355 (4)	−136 (3)	29 (2)
C(13)	3957 (5)	1645 (3)	−106 (3)	30 (2)
C(14)	477 (5)	1303 (3)	2022 (3)	27 (2)
C(15)	107 (6)	859 (3)	2537 (3)	30 (2)
C(16)	−248 (5)	1226 (3)	3009 (3)	29 (2)
C(17)	−997 (5)	1765 (3)	2890 (3)	29 (2)
C(18)	−512 (5)	2218 (3)	2422 (3)	30 (2)
C(19)	−739 (7)	735 (4)	3539 (3)	47 (3)
C(20)	1371 (6)	1231 (4)	3592 (4)	52 (3)
C(21)	−1246 (6)	2723 (4)	2173 (3)	44 (3)
C(22)	1953 (5)	3152 (3)	3071 (3)	21 (2)
C(23)	2616 (5)	3301 (3)	3617 (3)	26 (2)
C(24)	2014 (5)	3268 (3)	4190 (3)	20 (2)
C(25)	1083 (5)	3724 (3)	4146 (3)	27 (2)
C(26)	501 (5)	3543 (4)	3583 (3)	33 (3)
C(27)	−371 (6)	4011 (5)	3474 (4)	58 (3)
C(28)	2107 (6)	3202 (4)	5293 (3)	42 (3)
C(29)	3033 (6)	4063 (4)	4773 (3)	43 (3)
C(30)	2062 (6)	486 (4)	1301 (4)	51 (3)
C(31)	3460 (5)	2064 (4)	2322 (3)	39 (3)
C(32)	1151 (5)	3926 (3)	1677 (3)	27 (2)
C(33)	3828 (7)	4825 (4)	928 (4)	51 (3)
C(34)	4526 (6)	3925 (4)	−409 (3)	42 (3)
C(35)	5298 (5)	2418 (4)	323 (3)	32 (2)
C(36)	4599 (6)	1068 (4)	−290 (4)	52 (3)
C(37)	4100 (7)	411 (4)	−275 (4)	62 (4)
C(38)	3696 (6)	1472 (4)	4640 (4)	45 (3)
C(39)	3621 (7)	742 (4)	4732 (4)	69 (4)
C(40)	5484 (7)	3494 (4)	3999 (4)	61 (4)
C(41)	6445 (7)	3870 (6)	4108 (5)	88 (5)
C(42)	3664 (7)	−762 (4)	2891 (4)	60 (3)
C(43)	3902 (10)	−1385 (6)	3227 (6)	122 (6)
C(44)	2713 (8)	−841 (5)	2547 (5)	84 (5)
C(45)	3597 (8)	−154 (5)	3260 (5)	95 (5)
C(46)	4003 (6)	−4364 (4)	3110 (3)	48 (3)
C(47)	3751 (8)	−3628 (4)	3216 (4)	76 (4)
C(48)	3145 (8)	−4744 (6)	2866 (5)	92 (5)
C(49)	4396 (8)	−4679 (5)	3693 (4)	79 (4)

*Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond angles (complete) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42783 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

differ significantly. These long bonds are *trans*-related to those involving the O atom of the coordinated water molecule and the N atom of the desosamine moiety. The Zn–O bond lengths of the bidentate acetate ligand show a significant difference, with the shorter bond length, Zn–O(15) [2·107 (6) Å], being *cis* to the Zn–N bond and the longer Zn–O(16) bond being approximately *trans* to the Zn–N bond. The bond length involving the O atom of the monodentate acetate ligand, Zn–O(17) [2·024 (6) Å], has the smallest value of the set of Zn–O bond lengths. The tertiary N atom of the desosamine moiety is an unusual ligand atom, but except for the bond angles Zn–N–C(24) [103·8 (4)°] and C(24)–N–C(29) [112·0 (5)°], the bond angles subtended by the N atom are within 2σ of the idealized tetrahedral value.

Table 2. *Bond lengths* (Å), *bond angles* (°), *and hydrogen-bond contact distances* (Å)

Zn–N	2·124 (6)	Zn–O(8)	2·178 (4)
Zn–O(14)	2·157 (5)	Zn–O(15)	2·107 (6)
Zn–O(16)	2·170 (6)	Zn–O(17)	2·024 (6)
N–C(24)	1·505 (8)	N–C(28)	1·477 (9)
N–C(29)	1·457 (9)	O(1)–C(1)	1·199 (8)
O(2)–C(1)	1·339 (8)	O(2)–C(13)	1·455 (7)
O(3)–C(3)	1·444 (7)	O(3)–C(14)	1·406 (8)
O(4)–C(14)	1·405 (8)	O(4)–C(18)	1·428 (8)
O(5)–C(16)	1·442 (8)	O(5)–C(20)	1·405 (9)
O(6)–C(17)	1·409 (8)	O(7)–C(5)	1·438 (7)
O(7)–C(22)	1·395 (7)	O(8)–C(23)	1·442 (8)
O(9)–C(22)	1·410 (8)	O(9)–C(26)	1·445 (8)
O(10)–C(6)	1·432 (7)	O(11)–C(9)	1·232 (8)
O(12)–C(11)	1·435 (7)	O(13)–C(12)	1·433 (7)
O(15)–C(38)	1·238 (9)	O(16)–C(38)	1·285 (9)
O(17)–C(40)	1·224 (11)	O(18)–C(40)	1·252 (11)
O(19)–C(42)	1·428 (11)	O(20)–C(46)	1·418 (10)
C(1)–C(2)	1·510 (9)	C(2)–C(3)	1·560 (9)
C(2)–C(30)	1·543 (10)	C(3)–C(4)	1·514 (9)
C(4)–C(5)	1·547 (9)	C(4)–C(31)	1·545 (9)
C(5)–C(6)	1·559 (8)	C(6)–C(7)	1·543 (9)
C(6)–C(32)	1·510 (9)	C(7)–C(8)	1·534 (9)
C(8)–C(9)	1·529 (9)	C(8)–C(33)	1·534 (11)
C(9)–C(10)	1·515 (10)	C(10)–C(11)	1·523 (9)
C(10)–C(34)	1·527 (10)	C(11)–C(12)	1·520 (9)
C(12)–C(13)	1·562 (10)	C(12)–C(35)	1·532 (9)
C(13)–C(36)	1·494 (10)	C(14)–C(15)	1·524 (9)
C(15)–C(16)	1·517 (9)	C(16)–C(17)	1·542 (10)
C(16)–C(19)	1·528 (10)	C(17)–C(18)	1·518 (9)
C(18)–C(21)	1·511 (10)	C(22)–C(23)	1·523 (9)
C(23)–C(24)	1·499 (9)	C(24)–C(25)	1·545 (9)
C(25)–C(26)	1·510 (9)	C(26)–C(27)	1·514 (11)
C(36)–C(37)	1·475 (11)	C(38)–C(39)	1·479 (11)
C(40)–C(41)	1·508 (13)	C(42)–C(43)	1·485 (15)
C(42)–C(44)	1·488 (14)	C(42)–C(45)	1·468 (14)
C(46)–C(47)	1·528 (11)	C(46)–C(48)	1·476 (14)
C(46)–C(49)	1·526 (12)		
N–Zn–O(8)	81·2 (2)	N–Zn–O(14)	98·3 (2)
O(8)–Zn–O(14)	168·3 (2)	N–Zn–O(15)	94·6 (2)
O(8)–Zn–O(15)	100·2 (2)	O(14)–Zn–O(15)	91·6 (2)
N–Zn–O(16)	152·9 (2)	O(8)–Zn–O(16)	90·8 (2)
O(14)–Zn–O(16)	94·7 (2)	O(15)–Zn–O(16)	61·2 (2)
N–Zn–O(17)	105·6 (2)	O(8)–Zn–O(17)	90·3 (2)
O(14)–Zn–O(17)	78·5 (2)	O(15)–Zn–O(17)	158·5 (2)
O(16)–Zn–O(17)	100·3 (2)	Zn–N–C(24)	103·8 (4)
C(24)–N–C(28)	109·9 (5)	Zn–N–C(28)	110·0 (4)
C(24)–N–C(29)	112·0 (5)	Zn–N–C(29)	110·4 (4)
C(1)–O(2)–C(13)	117·8 (5)	C(28)–N–C(29)	110·6 (5)
C(5)–O(7)–C(22)	114·3 (5)	C(3)–O(3)–C(14)	114·2 (5)
Zn–O(16)–C(28)	87·7 (4)	Zn–O(8)–C(23)	110·7 (3)
O(1)–C(1)–O(2)	124·8 (6)	Zn–O(15)–C(38)	91·8 (4)
O(2)–C(1)–C(2)	111·5 (6)	Zn–O(17)–C(40)	132·2 (6)
C(1)–C(2)–C(30)	107·0 (6)	O(1)–C(1)–C(2)	123·7 (6)
O(3)–C(3)–C(2)	112·1 (5)	C(1)–C(2)–C(3)	108·4 (5)
C(2)–C(3)–C(4)	111·1 (5)	C(3)–C(2)–C(30)	115·5 (6)
C(3)–C(4)–C(31)	113·5 (5)	O(3)–C(3)–C(4)	108·2 (5)
O(7)–C(5)–C(4)	112·2 (5)	C(3)–C(4)–C(5)	109·7 (5)
C(4)–C(5)–C(6)	114·7 (5)	C(5)–C(4)–C(31)	113·0 (5)
O(10)–C(6)–C(7)	105·1 (5)	O(7)–C(5)–C(6)	107·8 (5)
O(10)–C(6)–C(32)	111·3 (5)	O(10)–C(6)–C(5)	107·8 (5)
C(7)–C(6)–C(32)	111·9 (5)	C(5)–C(6)–C(7)	111·5 (5)
C(7)–C(8)–C(9)	113·4 (5)	C(5)–C(6)–C(32)	109·0 (5)
C(9)–C(8)–C(33)	107·8 (6)	C(6)–C(7)–C(8)	114·1 (5)
O(11)–C(9)–C(10)	119·3 (6)	C(7)–C(8)–C(33)	109·6 (6)
C(9)–C(10)–C(11)	109·3 (5)	O(11)–C(9)–C(8)	120·5 (6)
C(11)–C(10)–C(34)	114·8 (5)	C(8)–C(9)–C(10)	120·0 (6)
O(12)–C(11)–C(12)	105·8 (5)	C(9)–C(10)–C(34)	109·1 (5)
O(13)–C(12)–C(11)	110·5 (5)	O(12)–C(11)–C(10)	110·2 (5)
C(11)–C(12)–C(13)	107·8 (5)	C(10)–C(11)–C(12)	116·5 (5)
C(11)–C(12)–C(35)	113·9 (5)	O(13)–C(12)–C(13)	107·2 (5)
O(2)–C(13)–C(12)	106·7 (5)	O(13)–C(12)–C(35)	106·3 (5)
C(12)–C(13)–C(36)	116·9 (6)	C(13)–C(12)–C(35)	111·0 (5)
		O(2)–C(13)–C(36)	106·7 (5)

Table 2 (*cont.*)

Intramolecular hydrogen bonds			
O(8)···O(18)	2·666 (6)	H(8′)···O(18)	1·50 (2)
O(11)···O(12)	2·814 (7)	H(12′)···O(11)	2·13 (2)
O(12)···O(13)	2·625 (7)	H(13′)···O(12)	1·87 (2)
Intermolecular hydrogen bonds			
O(6)···O(14^{i})	2·695 (6)		
O(10)···O(13^{ii})	2·815 (6)	H(10′)···O(13^{ii})	1·74 (2)
O(16)···O(22^{iii})	2·797 (5)		
O(21)···O(22^{iv})	2·648 (6)		
O(18)···O(21^{iii})	2·927 (7)		
O(18)···O(19^{v})	2·872 (6)		
O(19)···O(20^{v})	2·758 (5)	H(20t)···O(19^{v})	1·67 (2)
O(20)···O(22^{vi})	2·803 (6)		

Symmetry code: (i) $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (ii) $-\frac{1}{2}+x, \frac{1}{2}-y, -z$; (iii) $1+x, y, z$; (iv) x, y, z; (v) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vi) $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Adjacent molecules of the complex associate through an extended hydrogen-bonding network, involving the ER molecule, the acetate ligands, and the molecules of solvation. An unequivocal characterization of the details of the hydrogen-bonding network was precluded by the inability to locate the hydroxyl H atoms of the two water molecules [O(21) and O(22)] and of one of the *tert*-butyl alcohol molecules [O(19)]. Table 2 gives the pertinent contact distances. Hydroxyl groups [O(10) and O(13)] of adjacent ER ligands form a hydrogen bond. The H···O contact distance, H(10′)···O(13), is 1·74 (2) Å. The non-coordinated O atom, O(18), of the monodentate acetate ligand is hydrogen-bonded to the coordinated O atom, O(8), of the ER molecule within the same asymmetric unit and is probably involved in a chain of hydrogen bonds through the two water molecules of hydration to an O atom of the bidentate acetate ligand, forming the association O(16)···O(22)···O(21)···O(18). The *tert*-butyl alcohol molecules form a hydrogen bond, as indicated by the contact distances, O(19)···O(20) [2·758 (5) Å] and H(20*t*)···O(19) [1·67 (2) Å]. The O(18)···O(19) contact distance, 2·872 (6) Å, suggests that atom O(18) is associated with one of the *tert*-butyl alcohol molecules forming the chain, O(18)···O(19)···O(20). The contact distance O(20)···O(22) indicates that a hydrogen bond exists between one of the water molecules and one of the *tert*-butyl alcohol molecules. The four molecules of solvation thus appear to be linked together into a complex network. The non-bonded contact distance given in Table 2 between the coordinated water molecule, O(14), and atom O(6) of the

ER molecule suggests that a hydrogen bond exists. The O atoms, O(11), O(12) and O(13), of the ER molecule are intramolecularly hydrogen-bonded forming a C=O···H–O···H–O unit. The involvement of the two *tert*-butyl alcohol molecules in the hydrogen-bonding network that holds the structure intact may be responsible for the growth of good crystals from this solvent and the failures to obtain acceptable crystals from ethanolic solution.

The absolute structure determined for the ER ligand in this work is consistent with that previously reported for erythromycin hydroiodide dihydrate (Harris, McGeachin & Mills, 1965). The absolute configurations of the asymmetric centers, C(2), C(3), C(4), C(5), C(6), C(8), C(10), C(11), C(12) and C(13), of the aglycone ring are *R, S, S, R, R, R, R, R, S* and *R*, respectively. The β-D-desosamine sugar is connected to the aglycone ring through a β-glycosidic linkage. The α-L-cladinose sugar is bonded to the aglycone ring through an α-glycosidic linkage. A detailed comparison of the geometry of the ER molecule in this study with that of erythromycin hydroiodide dihydrate was not possible since the atomic coordinates were unavailable from either the authors or the Cambridge Crystallographic Database.

The conformations of the aglycone rings and the desosamine substituents of several macrocyclic antibiotic molecules are compared in Table 3. The conformation angles within the aglycone rings differ by less than 16°, except for those involving the bonds C(2)–C(3), C(4)–C(5), C(5)–C(6) and C(7)–C(8), whose ranges of conformation angles are 35, 22, 20 and 46°, respectively. The atoms involved in these bonds are near the sugar residues; therefore the greater variabilities in conformations are probably the consequences of steric interactions. The comparison of the geometries of four desosamine moieties shows similar chair conformations for the six-membered rings. The torsion angles also reveal that only a minor rotation about the C(2′)–N bond is required for chelation to the Zn^{II} ion.

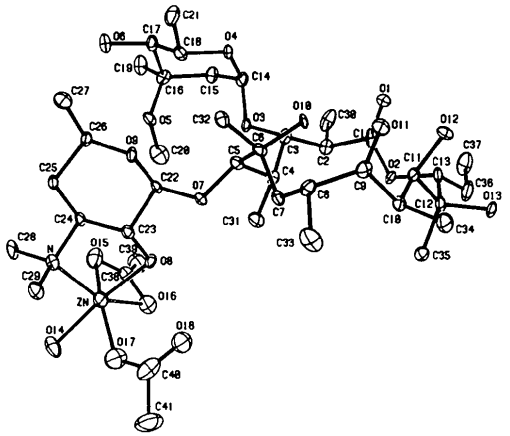


Fig. 1. A perspective drawing of the structure illustrating 30% probability ellipsoids for the non-hydrogen atoms. Hydrogen atoms are omitted for the sake of clarity.

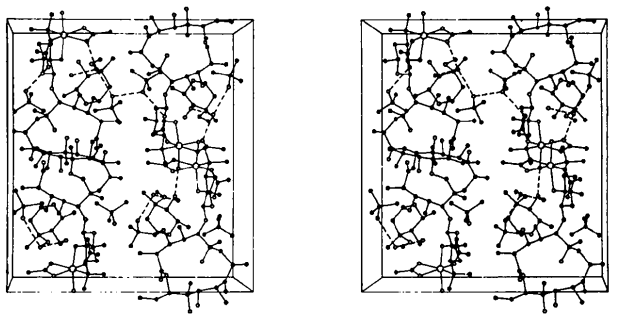


Fig. 2. Stereoview of the molecular packing. The O and N atoms are represented as small circles, the Zn atoms as larger circles. The dashed lines represent hydrogen bonds.

Table 3. *Torsion angles* (°) *for the aglycone and desosamine substituents of several macrocyclic antibiotic molecules*

Aglycones				
Torsion angle[a]	This work	LANK[b]	MEGA[c]	
O–C(1)–C(2)–C(3)	107·5 (6)	117	111	
C(1)–C(2)–C(3)–C(4)	−84·1 (6)	−113	−79	
C(2)–C(3)–C(4)–C(5)	167·2 (5)	161	168	
C(3)–C(4)–C(5)–C(6)	−95·7 (6)	−74	−88	
C(4)–C(5)–C(6)–C(7)	−73·0 (6)	−90	−71	
C(5)–C(6)–C(7)–C(8)	174·8 (5)	178	172	
C(6)–C(7)–C(8)–C(9)	−77·2 (7)	−54	−100	
C(7)–C(8)–C(9)–C(10)	−59·8 (8)	−64	−52	
C(8)–C(9)–C(10)–C(11)	120·7 (6)	119	106	
C(9)–C(10)–C(11)–C(12)	−171·9 (5)	178	−164	
C(10)–C(11)–C(12)–C(13)	165·0 (5)	173	177	
C(11)–C(12)–C(13)–O	−71·5 (6)	−71	−69	
C(12)–C(13)–O–C(1)	125·4 (6)	116	113	
C(13)–O–C(1)–C(2)	172·0 (5)	−172	175	

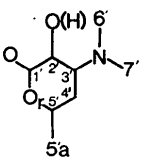
Desosamines				
Torsion angle[d]	This work	MEGA[c]	BPIK[e]	PIKR[f]
O_r–C(1′)–C(2′)–C(3′)	56·9 (6)	48	56	60
C(1′)–C(2′)–C(3′)–C(4′)	−55·6 (5)	−50	−54	−56
C(2′)–C(3′)–C(4′)–C(5′)	55·4 (5)	62	56	55
C(3′)–C(4′)–C(5′)–O_r	−58·6 (7)	−68	−58	−58
C(4′)–C(5′)–O_r–C(1′)	62·2 (5)	70	63	62
C(5′)–O_r–C(1′)–C(2′)	−62·7 (6)	−62	−63	−63
O–C(1′)–C(2′)–O(H)	−64·8 (6)	−71	−68	−64
O(H)–C(2′)–C(3′)–N	55·0 (5)	48	67	60
C(2′)–C(3′)–N–C(6′)	68·8 (5)	77	60	40

(*a*) Endocyclic torsion angles are defined using the standard ring numbering scheme.

(*b*) 3-(β-L-Mycarose)-5-(β-D-4,6-dideoxy-3-ketoallose)-13-(β-D-mycinose)-lankamycin-11α-hydroxyisovalerate ester (Arnoux, Pascard, Raynaud & Lunel, 1980).

(*c*) 4″-*O*-(4-Iodobenzoyl)megalomycin A dihydrate (Bartner *et al.*, 1979).

(*d*) Torsion angles are defined according to:



(*e*) *p*-Bromobenzoylpikromycin monohydrate (Furuhata, Ogura, Yoshinori & Iitaka, 1977).

(*f*) Pikromycin (Furusaki, Matsumoto, Furuhata & Ogura, 1982).

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Structure of 2-Methylpyridinium β-Octamolybdate(VI)

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(*Received* 25 *November* 1985; *accepted* 11 *March* 1986)

Abstract. $[C_6H_8N]_4[Mo_8O_{26}]$, $M_r = 1560{\cdot}05$, triclinic, $P\bar{1}$, $a = 10{\cdot}011$ (1), $b = 10{\cdot}453$ (3), $c = 10{\cdot}540$ (2) Å, $\alpha = 94{\cdot}83$ (2), $\beta = 84{\cdot}39$ (2), $\gamma = 113{\cdot}97$ (2)°, $V = 1001{\cdot}8$ (4) Å^3, $Z = 1$, $D_m = 2{\cdot}60$ (1), $D_x = 2{\cdot}59$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}459$ mm^{-1}, $F(000) = 748$, room temperature, $R = 0{\cdot}025$ for 4848 observed reflections. The title compound is the product of the reaction between 3-ethylpyridinium β-octamolybdate and 2-methylpyridine. The structure comprises $Mo_8O_{26}^{4-}$ anions in the well characterized conformation and 2-methylpyridinium cations. Eight MoO_6 distorted octahedra share edges with short terminal Mo—O bonds (1·693–1·749 Å), bonds of intermediate length (1·895–2·014 Å) and long bonds (2·156–2·484 Å). Octamolybdate polyanions are H-bonded [N···O: 2·82 (5) Å] to two crystallographically independent cations.

Introduction. This work forms part of a series of studies on molybdates of pyridinium, alkylpyridinium (Román, González-Aguado, Esteban-Calderón & Martínez-Ripoll, 1984; Román, Jaud & Galy, 1981; Román, Martínez-Ripoll & Jaud, 1982; Román, Vegas, Martínez-Ripoll & García-Blanco, 1982) and aminopyridinium ions (Gutiérrez-Zorrilla, 1984).

Reaction of 3-ethylpyridinium octamolybdate with pyridine (Esteban-Calderón, Martínez-Ripoll, García-Blanco & Román, 1984) and 3-methylpyridine (Román, González-Aguado, Esteban-Calderón, Martínez-Ripoll & García-Blanco, 1983) gives the corresponding substituted octamolybdate. Attempts have been made to prepare single crystals of these salts from the reaction between MoO_3 with pyridine or n-alkylpyridine where $n = 2$, 3 and 4. The same octamolybdates have been obtained with both methods. This paper deals with the structure of the title compound.

Experimental. 3-Ethylpyridinium octamolybdate (3 g) heated under reflux for 8 h with water (800 ml); then 2-methylpyridine (3 ml) added with stirring during 1 h at the same temperature; resulting solution filtered and cooled. Colourless prismatic crystals separated after 48 h; stable to air, light and X-ray exposure. Density by method of Archimedes (CCl_4 + $CHBr_3$) (Román & Gutiérrez-Zorrilla, 1985); CAD-4 four-circle diffractometer, graphite-monochromated Mo $K\alpha$; approximately 0·25 × 0·15 × 0·10 mm. Unit-cell parameters refined using 25 high-angle reflections ($20 < 2\theta < 40°$); $\omega/2\theta$ scans, $2\theta_{max} = 60°$; two standard reflections, no intensity variation; 5731 reflections measured, 4848 with $I > 3\sigma(I)$, $h < 14$, $-14 < k < 13$, $-14 < l < 14$. No absorption corrections were made in spite of the rather high μ value. Coordinates of a group of four Mo atoms obtained from Patterson function, remaining non-H atoms from successive Fourier maps. Refinement: full-matrix least squares, unit weights [flat

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0108-2701/86/080956-03$01.50