

The Crystal and Molecular Structure of the Sodium Bromide Complex of Monensin, $C_{36}H_{62}O_{11} \cdot Na^+ Br^-$

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The Na^+ complex of monensin, prepared in neutral solutions as the bromide, has been shown to be $MonH \cdot Na^+ Br^-$, in which the carboxyl group is not deprotonated, the Na^+ ion is coordinated to six O atoms in a distorted octahedral fashion at an average distance of 2.424 Å and the Br^- ion is hydrogen bonded to a carboxyl and a hydroxyl O atom of one monensin molecule. The colorless crystals are orthorhombic, $P2_12_12_1$, $a = 16.618(4)$, $b = 18.702(4)$, $c = 12.923(3)$ Å, $Z = 4$, $D_x = 1.280$ g cm⁻³. Least-squares refinement {anisotropic Na, Br; isotropic C, O; 206 atomic parameters plus one scale factor; 1929 observed diffractometer data [$I > 3\sigma(I)$]} led to $R = 0.053$. The structure is unique, compared with $MonH$ and $Mon^- Ag^+$, as it is not hydrated; however, the structure is closely related to that of $Mon^- Ag^+ \cdot 2H_2O$.

Introduction

In recent years many very stable alkali-metal complexes have been prepared with ligands such as synthetic mono- and bicyclic polyethers and with some naturally occurring antibiotic compounds such as valinomycin, nigericin and monensin (Ovchinnikov, Ivanov & Shkrob, 1974). The latter compound is a monocarboxylic acid whose structure is shown in Fig. 1. It has been shown that monensin forms complexes with several alkali-metal ions as well as with Ag^+ but it shows a marked specificity for the Na^+ ion (Pressman & Haynes, 1969). It was suggested that the free acid has a non-cyclic configuration (Pressman, 1968) while the metal complex is cyclic (Agtarap, Chamberlin, Pinkerton & Steinrauf, 1967). Crystallographic study of the Ag^+ -monensin complex (Pinkerton & Steinrauf, 1970) showed that the complex is indeed cyclic, that the metal ion is coordinated by six O atoms in a neutral salt, $Mon^- Ag^+$, and that the carboxyl group is deprotonated although the O does not participate in the coordination around the metal ion. Crystallographic study of the free-acid monensin (Lutz, Winkler & Dunitz, 1971) has shown it to be cyclic also.

Recent work has shown, however, that a different type of Na^+ -monensin complex can be prepared in which IR spectra unambiguously indicate that the

carboxyl group is not deprotonated (Gertenbach & Popov, 1975). The general formula of these complexes is $MonH \cdot NaX$ where X is the anion of the Na^+ salt. In conjunction with a broad study of alkali-metal complexes with synthetic and natural ligands it was of interest to us to determine the structure of this new monensin complex and to determine how it differs from the structure of the previously reported $Mon^- Ag^+$ complex.

Experimental

Monensin was obtained as the Na^+ salt, $Mon^- Na^+$, and was purified and converted to the free acid, $MonH$, as previously reported (Gertenbach & Popov, 1975). Colorless crystals of the $NaBr$ complex of monensin, $MonH \cdot Na^+ Br^-$, were obtained by mixing a solution of $MonH$ in chloroform with equimolar $NaBr$ in methanol, evaporating to dryness under vacuum, and recrystallizing from a 1:1 ethyl ether-petroleum ether solution.

A single crystal [described by the indices of the faces and the distance in mm to an origin within the crystal: (110) 0.184, ($\bar{1}\bar{1}0$) 0.216, ($1\bar{1}0$) 0.132, ($\bar{1}10$) 0.242, (011) 0.159, ($0\bar{1}\bar{1}$) 0.152, ($01\bar{1}$) 0.101, and ($0\bar{1}1$) 0.088] (μ for $Mo K\alpha = 10.35$ cm⁻¹) was mounted on a

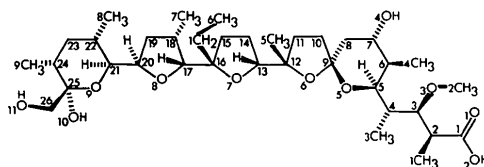


Fig. 1. The molecular structure and the numbering of the atoms in the monensin molecule.

Table 1. Crystal data

Sodium bromide complex of monensin
 $C_{36}H_{62}O_{11} \cdot Na^+ Br^-$, FW 773.8, $F(000) = 1648$
Orthorhombic, space group $P2_12_12_1$

$a = 16.618(4)$ Å $V = 4016.3$ Å³
 $b = 18.702(4)$ $Z = 4$
 $c = 12.923(3)$ $D_x = 1.280$ g cm⁻³

Table 2. Atomic parameters

Anisotropic temperature factor is in the form $\exp[-\frac{1}{4} \sum_i \Sigma_j (a_i^* a_j^* h_i h_j B_{ij})]$ where h_i is one of the Miller indices and a_i^* is a reciprocal-cell axis. Positional parameters are multiplied by 10^4 . Thermal parameters are in \AA^2 .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso}		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso}
Br	3263.6 (6)	7352.3 (5)	5565.1 (9)		H(4)	2432	6649	1794	5.000
Na	1077 (2)	6396 (2)	3540 (3)		H(5)	3614	6898	2699	5.000
O(1)	1645 (5)	7998 (4)	1426 (6)	6.2 (2)	H(6)	3564	5934	3931	5.000
O(2)	2695 (4)	8044 (4)	2492 (5)	4.7 (2)	H(7)	2527	5066	3626	5.000
O(3)	4051 (4)	7669 (4)	-219 (5)	5.7 (2)	H(8)	3343	4956	2940	5.000
O(4)	2479 (4)	6379 (4)	3779 (5)	3.9 (1)	H(9)	2121	4165	2178	5.000
O(5)	2747 (4)	5673 (3)	1292 (5)	3.9 (1)	H(10)	2611	4383	1129	5.000
O(6)	1584 (3)	5566 (3)	2322 (4)	3.4 (1)	H(11)	1075	4196	1077	5.000
O(7)	-1 (4)	5553 (3)	2956 (5)	4.1 (1)	H(12)	1501	4794	337	5.000
O(8)	393 (4)	5854 (4)	5047 (5)	3.9 (1)	H(13)	-127	4764	1977	5.000
O(9)	640 (3)	7235 (3)	4870 (4)	3.4 (1)	H(14)	1090	4559	3520	5.000
O(10)	1749 (4)	7839 (3)	4219 (4)	4.2 (1)	H(15)	534	3950	2966	5.000
O(11)	560 (4)	7505 (4)	2844 (5)	5.3 (2)	H(16)	148	4569	4770	5.000
C(1)	2372 (7)	8052 (6)	1581 (9)	4.6 (2)	H(17)	-507	4162	4035	5.000
C(2)	2952 (5)	8106 (5)	680 (8)	4.2 (2)	H(18)	-512	6330	4277	5.000
C(3)	3568 (5)	7507 (5)	690 (7)	3.6 (2)	H(19)	-1483	6045	5422	5.000
C(4)	3242 (6)	6742 (4)	578 (8)	3.9 (2)	H(20)	-606	6350	6980	5.000
C(5)	2937 (5)	6397 (5)	1570 (7)	3.0 (2)	H(21)	-650	6904	6005	5.000
C(6)	3518 (5)	6392 (5)	2477 (7)	3.4 (2)	H(22)	653	5968	6546	5.000
C(7)	3149 (6)	5991 (5)	3377 (7)	3.6 (2)	H(23)	1486	6802	5748	5.000
C(8)	2869 (5)	5268 (5)	3051 (7)	3.4 (2)	H(24)	277	7542	6906	5.000
C(9)	2376 (6)	5272 (5)	2091 (8)	3.7 (2)	H(25)	1793	8124	6286	5.000
C(10)	2182 (6)	4530 (5)	1625 (8)	4.6 (2)	H(26)	1100	8541	6949	5.000
C(11)	1397 (6)	4645 (6)	1067 (9)	4.8 (2)	H(27)	258	8530	5536	5.000
C(12)	963 (6)	5241 (5)	1668 (8)	3.9 (2)	H(28)	-118	8118	3763	5.000
C(13)	315 (6)	4975 (6)	2394 (7)	3.9 (2)	H(29)	664	8520	3267	5.000
C(14)	544 (6)	4451 (6)	3241 (8)	4.7 (2)	H(30)	-1707	5112	4009	7.500
C(15)	-99 (7)	4557 (6)	4075 (8)	5.6 (3)	H(31)	-1368	4775	2928	7.500
C(16)	-487 (6)	5286 (6)	3791 (9)	4.6 (2)	H(32)	3645	8883	1438	7.500
C(17)	-427 (5)	5855 (5)	4619 (8)	4.1 (2)	H(33)	2930	9224	725	7.500
C(18)	938 (6)	5851 (5)	5596 (9)	4.6 (2)	H(34)	3742	8906	181	7.500
C(19)	-492 (6)	6412 (6)	6225 (8)	4.7 (2)	H(35)	4882	6909	-69	7.500
C(20)	413 (6)	6264 (5)	5981 (7)	3.9 (2)	H(36)	5138	7675	440	7.500
C(21)	905 (6)	6941 (5)	5834 (8)	3.7 (2)	H(37)	5153	7571	-814	7.500
C(22)	856 (6)	7467 (6)	6736 (8)	4.7 (2)	H(38)	2889	6828	-967	7.500
C(23)	1203 (6)	8188 (6)	6394 (8)	4.5 (2)	H(39)	2166	7016	-156	7.500
C(24)	846 (6)	8460 (5)	5416 (8)	4.4 (2)	H(40)	2428	6185	-351	7.500
C(25)	931 (5)	7916 (5)	4552 (8)	3.3 (2)	H(41)	4593	6338	1615	7.500
C(26)	461 (5)	8063 (5)	3578 (8)	3.7 (2)	H(42)	4259	5552	1956	7.500
1CH ₂	-1357 (7)	5197 (7)	3397 (10)	6.6 (3)	H(43)	4704	6064	2805	7.500
1CH ₃	3356 (7)	8843 (6)	760 (8)	5.5 (2)	H(44)	1040	6018	528	7.500
2CH ₃	4873 (7)	7443 (7)	-159 (9)	7.4 (3)	H(45)	365	6196	1409	7.500
3CH ₃	2629 (6)	6691 (6)	-294 (9)	5.4 (3)	H(46)	182	5593	525	7.500
4CH ₃	4343 (6)	6055 (5)	2187 (8)	4.2 (2)	H(47)	-1371	5888	2199	7.500
5CH ₃	614 (7)	5807 (6)	965 (9)	5.7 (3)	H(48)	-1711	6225	3280	7.500
6CH ₃	-1709 (10)	5794 (9)	2832 (12)	9.9 (4)	H(49)	-2264	5667	2619	7.500
7CH ₃	-1037 (8)	5138 (7)	6158 (10)	7.2 (3)	H(50)	-499	4959	6371	7.500
8CH ₃	1283 (7)	7180 (8)	7703 (10)	7.4 (3)	H(51)	-1300	4790	5680	7.500
9CH ₃	1194 (8)	9178 (7)	5120 (10)	6.7 (3)	H(52)	-1384	5213	6781	7.500
HO(2)	2349	7966	3132	6.000	H(53)	1861	7089	7537	7.500
HO(4)	2725	6685	4338	6.000	H(54)	1021	6718	7911	7.500
HO(10)	2232	7683	4649	6.000	H(55)	1236	7532	8273	7.500
HO(11)	950	7684	2341	6.000	H(56)	1797	9127	5035	7.500
H(1)	2641	8083	23	5.000	H(57)	1091	9528	5695	7.500
H(2)	3910	7547	1326	5.000	H(58)	954	9350	4471	7.500
H(3)	3710	6445	354	5.000					

	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
Br	3.09 (4)	4.35 (4)	6.35 (6)	-0.06 (5)	-1.00 (5)	-0.64 (5)
Na	3.7 (2)	3.5 (2)	5.0 (2)	-0.3 (2)	0.3 (2)	-0.6 (2)

glass fiber with epoxy glue. The diffraction conditions $h00$: $h = 2n$, $0k0$: $k = 2n$, $00l$: $l = 2n$, the absence of other conditions, and the orthorhombic symmetry establish the space group as $P2_12_12_1$. Diffraction data were measured at 23°C with a Picker FACS-I automatic diffractometer using Zr-filtered Mo $K\alpha$ radiation. Precise unit-cell parameters were determined by a least-squares fit to the setting angles ($2\theta, \omega, \chi, \phi$) of 12 reflections in the range $35^\circ \leq 2\theta \leq 40^\circ$ for which the $\alpha_1\alpha_2$ doublet was clearly resolved (λ for Mo $K\alpha_1 = 0.70926$ Å). The crystal data are listed in Table 1. For $Z = 4$, the calculated density is 1.280 g cm $^{-3}$. The 3976 unique reflections (including the 2047 'unobserved') in the $h\bar{k}l$ octant were collected for $2\theta \leq 50^\circ$ with the θ - 2θ scan method [$1^\circ (2\theta)$ min $^{-1}$, 10 s background counts at the start and end of each scan, scan ranges of $1.0^\circ (2\theta)$ plus the $\alpha_1\alpha_2$ divergence, and three standard reflections, monitored during data collection, were used to scale the raw intensities].

The data were reduced and standard deviations calculated as a function of counting statistics as reported previously (Wei & Ward, 1976); the least-squares-refinement weights were calculated from the standard deviations of the structure factors by weight = $1/\sigma^2$; an extinction correction was not applied; and an absorption correction (Templeton & Templeton, 1973) was applied giving corrections to F ranging from 1.190 to 1.434.

Structure solution and refinement

The crystal structure was solved by Patterson and Fourier methods; attempts with the program *MULTAN* (Germain, Main & Woolfson, 1971) were unsuccessful. Other programs used in this study include *ORTEP* (Johnson, 1965), the entire system of Zalkin's (1974) programs, *ABSOR* (Templeton & Templeton, 1973) and programs written and/or modified locally. A CDC 6500 computer was used.

The positions of the four H atoms bonded to O atoms were determined from a difference map calculated after an $R = 0.055$ least-squares cycle during which the remaining 58 H atoms were included as fixed contributors with $B_{\text{iso}} = 4.0$ Å 2 . The structure was refined by full-matrix least squares [1929 observed data for which $I \geq 3\sigma(I)$; 206 atomic parameters and one scale factor; anisotropic Na, Br; isotropic C, O; H atoms as fixed contributors with positional parameters calculated prior to each cycle and B_{iso} set to 5.0 Å 2 for those bonded to 'backbone' C atoms, 6.0 Å 2 for those bonded to O atoms and 7.5 Å 2 for those of terminal methyl or ethyl groups] to $R = (\sum |F_o - F_c|) / \sum F_o = 0.053$, R [including 2047 'unobserved' data for which $I < 3\sigma(I)$] = 0.131, $R_{\text{wtd}} = \{[\sum \omega(F_o - F_c)^2] / \sum \omega(F_o)^2\}^{1/2} = 0.049$ and the standard deviation of an observation of unit weight was 1.69. During the final cycle of refinement, the maximum and average shift-to-error

Table 3. *Interatomic distances (Å) and angles (°)*

O(1)-C(1)	1.228 (12)	C(3)-O(3)-2CH ₃	114.9 (8)
O(2)-C(1)	1.295 (11)	C(5)-O(5)-C(9)	114.3 (8)
O(3)-C(3)	1.455 (10)	C(9)-O(6)-C(12)	111.2 (8)
O(3)-2CH ₃	1.433 (13)	C(13)-O(7)-C(16)	109.4 (9)
O(4)-C(7)	1.427 (10)	C(17)-O(8)-C(20)	109.7 (8)
O(5)-C(5)	1.436 (11)	C(21)-O(9)-C(25)	119.4 (8)
O(5)-C(9)	1.417 (11)	O(1)-C(1)-O(2)	123.7 (9)
O(6)-C(9)	1.455 (10)	O(1)-C(1)-C(2)	120.5 (9)
O(6)-C(12)	1.466 (11)	O(2)-C(1)-C(2)	115.8 (8)
O(7)-C(13)	1.403 (11)	C(1)-C(2)-C(3)	112.0 (8)
O(7)-C(16)	1.437 (12)	C(1)-C(2)-1CH ₃	106.6 (8)
O(8)-C(17)	1.471 (10)	C(3)-C(2)-1CH ₃	111.6 (7)
O(8)-C(20)	1.431 (11)	O(3)-C(3)-C(2)	102.2 (6)
O(9)-C(21)	1.432 (11)	O(3)-C(3)-C(4)	108.2 (7)
O(9)-C(25)	1.424 (10)	C(2)-C(3)-C(4)	116.7 (7)
O(10)-C(25)	1.433 (10)	C(3)-C(4)-C(5)	115.7 (8)
O(11)-C(26)	1.420 (11)	C(3)-C(4)-3CH ₃	111.3 (8)
C(1)-C(2)	1.515 (13)	C(5)-C(4)-3CH ₃	112.0 (8)
C(2)-C(3)	1.516 (12)	O(5)-C(5)-C(4)	105.2 (7)
C(2)-1CH ₃	1.536 (14)	O(5)-C(5)-C(6)	109.2 (7)
C(3)-C(4)	1.536 (12)	C(4)-C(5)-C(6)	116.1 (8)
C(4)-C(5)	1.522 (13)	C(5)-C(6)-C(7)	109.8 (7)
C(4)-3CH ₃	1.523 (13)	C(5)-C(6)-4CH ₃	112.1 (7)
C(5)-C(6)	1.518 (11)	C(7)-C(6)-4CH ₃	110.0 (7)
C(6)-C(7)	1.514 (12)	O(4)-C(7)-C(6)	110.2 (7)
C(6)-4CH ₃	1.555 (13)	O(4)-C(7)-C(8)	108.7 (6)
C(7)-C(8)	1.491 (12)	C(6)-C(7)-C(8)	111.0 (7)
C(8)-C(9)	1.487 (12)	C(7)-C(8)-C(9)	113.8 (8)
C(9)-C(10)	1.547 (14)	O(5)-C(9)-O(6)	110.1 (6)
C(10)-C(11)	1.506 (13)	O(5)-C(9)-C(8)	111.7 (7)
C(11)-C(12)	1.538 (14)	O(5)-C(9)-C(10)	106.3 (7)
C(12)-C(13)	1.513 (13)	O(6)-C(9)-C(8)	109.2 (6)
C(12)-5CH ₃	1.511 (15)	O(6)-C(9)-C(10)	103.3 (6)
C(13)-C(14)	1.518 (14)	C(8)-C(9)-C(10)	115.8 (8)
C(14)-C(15)	1.531 (14)	C(9)-C(10)-C(11)	103.8 (8)
C(15)-C(16)	1.554 (15)	C(10)-C(11)-C(12)	105.5 (8)
C(16)-C(17)	1.512 (14)	O(6)-C(12)-C(11)	105.2 (6)
C(16)-1CH ₃	1.542 (15)	O(6)-C(12)-C(13)	106.3 (6)
C(17)-C(18)	1.522 (14)	O(6)-C(12)-5CH ₃	109.1 (7)
C(18)-C(19)	1.521 (14)	C(11)-C(12)-C(13)	114.2 (9)
C(18)-7CH ₃	1.528 (16)	C(11)-C(12)-5CH ₃	112.6 (9)
C(19)-C(20)	1.562 (13)	C(13)-C(12)-5CH ₃	109.2 (8)
C(20)-C(21)	1.518 (14)	O(7)-C(13)-C(12)	109.6 (7)
C(21)-C(22)	1.527 (13)	O(7)-C(13)-C(14)	102.6 (7)
C(22)-C(23)	1.530 (14)	C(12)-C(13)-C(14)	118.7 (8)
C(22)-8CH ₃	1.536 (15)	C(13)-C(14)-C(15)	104.4 (8)
C(23)-C(24)	1.486 (14)	C(14)-C(15)-C(16)	103.7 (8)
C(24)-C(25)	1.517 (13)	O(7)-C(16)-C(15)	104.4 (7)
C(24)-9CH ₃	1.511 (16)	O(7)-C(16)-C(17)	104.5 (7)
C(25)-C(26)	1.506 (13)	O(7)-C(16)-1CH ₃	108.5 (8)
1CH ₂ -6CH ₃	1.457 (18)	C(15)-C(16)-C(17)	115.0 (9)
Na-O(4)	2.349	C(15)-C(16)-1CH ₂	111.8 (9)
Na-O(6)	2.366	C(17)-C(16)-1CH ₂	111.9 (9)
Na-O(7)	2.503	O(8)-C(17)-C(16)	109.0 (7)
Na-O(8)	2.471	O(8)-C(17)-C(18)	101.9 (7)
Na-O(9)	2.438	C(16)-C(17)-C(18)	123.1 (9)
Na-O(11)	2.419	C(17)-C(18)-C(19)	99.7 (7)
O(4)-Na-O(6)	74.1 (3)	C(17)-C(18)-7CH ₃	117.3 (9)
O(4)-Na-O(7)	137.8 (4)	C(19)-C(18)-7CH ₃	113.6 (9)
O(4)-Na-O(8)	110.3 (3)	C(18)-C(19)-C(20)	103.9 (8)
O(4)-Na-O(9)	102.2 (3)	O(8)-C(20)-C(19)	104.1 (7)
O(4)-Na-O(11)	114.4 (3)	O(8)-C(20)-C(21)	110.8 (7)
O(6)-Na-O(7)	69.0 (2)	C(19)-C(20)-C(21)	113.3 (9)
O(6)-Na-O(8)	114.8 (3)	O(9)-C(21)-C(20)	105.3 (6)
O(6)-Na-O(9)	175.9 (3)	O(9)-C(21)-C(22)	113.5 (7)
O(6)-Na-O(11)	116.2 (3)	C(20)-C(21)-C(22)	114.4 (8)
O(7)-Na-O(8)	69.5 (2)	C(21)-C(22)-C(23)	109.1 (8)

Table 3 (cont.)

O(7)-Na-O(9)	113.9 (3)	C(21)-C(22)-8CH ₃	111.7 (9)
O(7)-Na-O(11)	100.0 (3)	C(23)-C(22)-8CH ₃	111.7 (9)
O(8)-Na-O(9)	64.7 (2)	C(22)-C(23)-C(24)	113.4 (8)
O(8)-Na-O(11)	118.8 (3)	C(23)-C(24)-C(25)	111.1 (9)
O(9)-Na-O(11)	66.7 (3)	C(23)-C(24) 9CH ₃	111.6 (9)
		C(25)-C(24) 9CH ₃	111.9 (8)
		O(9)-C(25)-O(10)	108.6 (6)
		O(9) C(25)-C(24)	110.8 (7)
		O(9) C(25)-C(26)	103.2 (6)
		O(10)-C(25)-C(24)	112.1 (7)
		O(10) C(25)-C(26)	105.1 (6)
		C(24)-C(25)-C(26)	116.4 (9)
		O(11)-C(26)-C(25)	111.3 (7)
		C(16)-1CH ₂ -6CH ₃	117.3 (11)

Hydrogen bonding		H-O...Br	O...O, Br
O(2)	HO(2)-O(10)	[1.74]	2.757
O(4)	HO(4)-Br	[2.21]	3.216
O(10)	HO(10)-Br	[2.17]	3.193
O(11)	HO(11)-O(1)	[1.75]	2.732

Contacts around Br ion

Br-C(7)	3.809	Br-C(19) ^b	3.869
Br-C(10) ^a	3.849	Br-C(23)	3.914
Br-C(11) ^a	3.832	Br-C(26) ^b	3.893
Br-C(18) ^b	3.912		

(a) Atom at: $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$. (b) Atom at: $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$.

ratios were 2.92 and 0.48. Because of the small number of observed data relative to the number of parameters and also the high cost and poor convergence of the refinement, the refinement was terminated when the *R* factor ceased to improve. The final difference map showed densities ranging from +0.34 to -0.31 e Å⁻³ with no indication of incorrectly placed or missing atoms. The scattering factors of Doyle & Turner (1968) were used for the non-hydrogen atoms, those of Stewart, Davidson & Simpson (1965) for H, the anomalous scattering factors of Cromer & Liberman (1970) for the non-hydrogen atoms and anomalous scattering factors of zero were assumed for H.* Atomic parameters are listed in Table 2; interatomic distances and angles are listed in Table 3.

Two additional cycles of full-matrix least-squares refinement of the opposite enantiomorph (achieved by reversing the sign of the $\Delta f''$ terms rather than by transforming the positional parameters from *x, y, z* to $-x, -y, -z$; all other refinement parameters as above)

* A table of structure factors and a table of torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32928 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

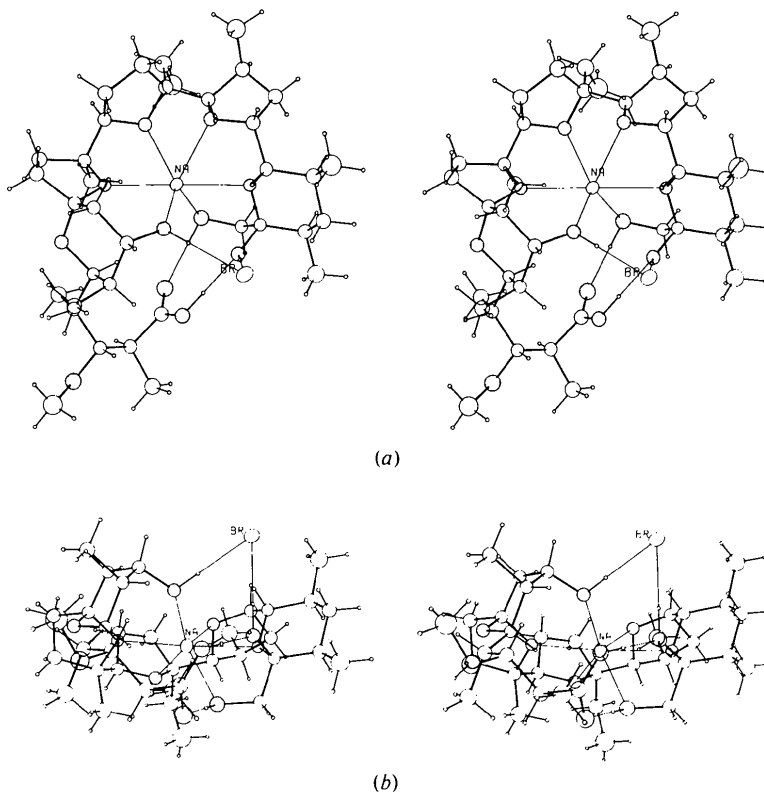


Fig. 2. The sodium bromide complex of monensin (ORTEP, Johnson, 1965) (oxygen atoms are shaded) (a) viewed approximately normal to the plane of the monensin molecule, (b) viewed approximately parallel to the plane of the monensin molecule.

led to $R = 0.077$, R (all data) = 0.156, $R_{\text{wtd}} = 0.077$ and the standard deviation of an observation of unit weight was 2.64. During the last cycle of refinement, the maximum and average shift-to-error ratios were 2.15 and 0.30. The estimated standard deviations of the resulting bond lengths and angles averaged approximately 0.02 Å and 1.2°.

The structure and hydrogen bonding

The molecular structure and the numbering of the atoms are shown in Fig. 1. All atoms lie in general positions. The crystal structure contains a Br^- ion and a neutral molecule of monensin coordinated to a Na^+ ion.

Two intramolecular hydrogen bonds, $\text{O}(2)\text{---HO}(2)\cdots\text{O}(10)$ and $\text{O}(11)\text{---HO}(11)\cdots\text{O}(1)$, join the two ends of the monensin molecule together; two additional hydrogen bonds, $\text{O}(4)\text{---HO}(4)\cdots\text{Br}$ and $\text{O}(10)\text{---HO}(10)\cdots\text{Br}$, associate the Br^- ion to one monensin molecule. The Na^+ ion is coordinated in a distorted octahedral fashion to six of the O atoms of the monensin molecule. Intermolecular contacts are of the van der Waals type. Table 3 lists the distances and angles of the coordination and hydrogen bonding. Fig. 2(a) and (b) are stereo drawings illustrating the structure of the complex, the hydrogen bonding and the Na^+ ion coordination viewed approximately normal to and parallel to the average plane of the monensin molecule.

The structure and configuration of the monensin molecule are essentially the same as reported for the free acid (Lutz, Winkler & Dunitz, 1971) and for the Ag^+ salt (Pinkerton & Steinrauf, 1970); the absolute configuration of the monensin molecule (see Fig. 1), as determined from the refinements of both enantiomorphs, is also the same as that reported for MonH and Mon^-Ag^+ . Because of the differences in the hydrogen bonding, the degree of hydration, the metal-ion coordination and the presence or absence of the carboxyl H atom and the Br^- ion in the three structures, differences were expected in the details of the conformation of the monensin molecule. These differences can be seen in the comparison of torsion angles.* The torsion angles of the Na^+ complex and the free acid differ by less than 19° (average 5.3°) and those of the Na^+ complex and the Ag^+ salt by less than 16° (average 3.3°). The largest differences in torsion angles between the Na^+ complex and the Ag^+ salt, other than those involving atom 6CH_3 , which is disordered in the Ag^+ salt, are ones which involve O(10) and O(9); these differences probably reflect the coordination of metal ions whose radii differ by about 0.1 Å and the differences in hydrogen bonding. The largest torsion-angle differences between the Na^+ complex and the free acid are those involving O(7),

O(8), O(9), O(10); again, these probably reflect the metal-ion coordination and hydrogen-bonding differences.

The crystal structure of the Na^+ complex is very similar to that of the Ag^+ salt; the Br^- ion coordinates correspond to those of $2\text{H}_2\text{O}$ in the Ag^+ salt and no atom was found corresponding to $1\text{H}_2\text{O}$. The six $\text{O}\cdots\text{Na}^+$ distances in the Na^+ complex average 2.424 Å, 0.09 Å less than the average $\text{O}\cdots\text{Ag}^+$ distance in the Ag^+ salt.

A half-normal probability plot (Abrahams & Keve, 1971) comparing the positional parameters of the Na^+ complex with those of the Ag^+ salt is shown in Fig. 3. Except for the two points corresponding to the x and y coordinates of Na^+ and Ag^+ , the plot is smooth and linear; the deviation of these two points from the straight line may be due to slight differences in the coordination geometry due to the different size of the ions or it may be an artifact related to the very small estimated standard deviations of these parameters compared with those for other atoms. The linearity and zero intercept of the plot indicate that there are no systematic errors in the postulate that the crystal structures of the Na^+ complex and the Ag^+ salt are the same. However, the slope of 9.1 would then indicate that the estimated standard deviations of the positional parameters of both structures have been underestimated by approximately that factor. This interpretation of the slope is unreasonable – considering the quality of both structure determinations and also the chemical differences between the two – and leads to the conclusion that these two structures are only ‘closely related’. A comparison of the unit-cell parameters for four monensin structures is given in Table 4; the unit-cell volumes differ as expected for the different cell contents and the similarity of the cell parameters is evident for the Na^+Br^- complex and the Ag^+ salt.

It is especially interesting to note the similarities in the crystal structures of the Na^+ complex and the Ag^+

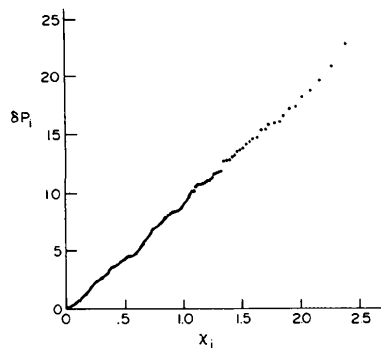


Fig. 3. Half-normal probability plot of 145 of 147 non-hydrogen atom positional parameters of $\text{MonH}\cdot\text{Na}^+\text{Br}^-$ and $\text{Mon}^-\text{Ag}^+\cdot 2\text{H}_2\text{O}$. Two points not shown are for the x and y parameters of Na^+ , Ag^+ at coordinates (2.55, 37.3) and (2.87, 46.5) respectively.

* See deposition footnote on p. 113.

Table 4. Comparison of cell parameters of structures of monensin

	Na ⁺ Br ⁻ complex ^a	Ag ⁺ salt ^b	Free acid ^c	Na ⁺ ClO ₄ complex ^d
<i>a</i> (Å)	16.618 (4)	16.46	15.15	17.832 (9)
<i>b</i> (Å)	18.702 (4)	18.81	23.61	22.257 (10)
<i>c</i> (Å)	12.923 (3)	12.73	10.65	10.367 (6)
Space group	<i>P</i> 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁
<i>V</i> (Å ³)	4016.3	3941.4	3809.4	4114.5

References: (a) Present study. (b) Pinkerton & Steinrauf (1970). (c) Lutz, Winkler & Dunitz (1971). (d) Present authors, unpublished results.

salt in light of their chemical differences (Pinkerton & Steinrauf, 1970): The Ag⁺ salt was prepared in water-ethanol solutions from a Na⁺ salt prepared in basic water-ethanol solutions while the Na⁺ complex was prepared in neutral pH non-aqueous solutions; the Ag⁺ salt crystallizes with two waters of hydration while the Na⁺ complex is anhydrous; the monensin carboxyl group is deprotonated in the Ag⁺ salt while it is not deprotonated in the Na⁺ complex. Yet, in spite of all these differences, the crystal structures are very similar.

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