



Crystal structure and FT-IR study of aqualithium 1-naphthylmethyl ester of monensin A perchlorate

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ABSTRACT

The crystal [MON8–LiClO₄–H₂O] containing the neutral molecule of 1-naphthylmethyl ester of monensin A (MON8), lithium perchlorate and one water molecule was obtained and its structure was examined using X-ray diffraction and discussed in detail. The MON8–LiClO₄–H₂O supramolecular complex is crystallized in the non-centrosymmetric space group of the orthorhombic system (*P*2₁2₁2₁) with four molecules in the unit cell. Within MON8–LiClO₄–H₂O complex the Li⁺ cation is square-pyramidally coordinated by four oxygen atoms of the MON8 molecule and by the oxygen atom of the water molecule. The oxygen atoms (O9 and O14) of the two OH groups are involved in two intramolecular O(14)–H···O(9) and O(9)–H···O(14) hydrogen bonds of similar strength stabilizing a pseudo-cyclic structure of MON8. Additionally the coordinated water molecule acts as proton donor in the two hydrogen bonds. The FT-IR spectrum of the crystal provides spectroscopic evidence for the complex formation and it is discussed in detail.

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1. Introduction

Monensin A isolated from *Streptomyces cinnamonensis* is a well-known polyether ionophore antibiotic. It forms lipid-soluble pseudo-macrocyclic complexes with monovalent metal cations able to transport these cations across natural and artificial lipid membranes [1–7]. Sodium salt of monensin is used commercially as a coccidiostat for poultry and growth promoting agent for cattle [8–13].

The structures of monensin A complexes with several monovalent cations such as Li⁺, Na⁺, K⁺, Rb⁺ and Ag⁺ have been determined using X-ray crystallography [14–20].

Up to now, we have synthesised several new esters and amides of monensin and studied their abilities to form complexes with monovalent and divalent metal cations using mass spectrometry, spectroscopic and semiempirical methods [21–34]. We have also shown that various modifications of monensin influence the affinity of the new derivatives of monensin towards monovalent and divalent cations as well as the stability of the respective complexes. Some of these monensin esters and amides have been tested in view of their antimicrobial properties. They show a certain activity against *Gram-positive* bacteria, however no activity against *Gram-negative* bacteria and *Candida* [32–35].

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As a continuation of these studies, a new supramolecular complex of aqualithium 1-naphthylmethyl ester of monensin A (MON8) perchlorate (MON8–LiClO₄–H₂O) has been obtained in solid state and studied by X-ray crystallography and FT-IR spectroscopy.

2. Experimental

2.1. Synthesis of MON8

MON8 was obtained according to our method described in Ref. [31]. The purity of this compound was controlled by elemental analysis, FT-IR, ¹H and ¹³C NMR spectroscopic methods [31].

2.2. Synthesis of MON8–LiClO₄–H₂O complex

The appropriate lithium perchlorate (1.0 mmol) was dissolved in warm acetonitrile (5 cm³) and added to the solution of MON8 (1.0 mmol) in warm acetonitrile (5 cm³) and the crystals suitable for X-ray crystallography were obtained by very slow crystallization at room temperature.

2.3. X-ray measurements

A colourless single crystal of the MON8–LiClO₄–H₂O (1:1:1) complex with the edges of 0.34 × 0.18 × 0.10 mm was measured on a KUMA KM-4 CCD diffractometer with graphite monochroma-

tized Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation at room temperature. The final unit cell parameters were refined by the least-square methods on the basis of 1251 reflections. 65,001 reflections (12,573 independent, 6554 observed ($F^2 \geq 4\sigma(F^2)$), $R_{\text{int}} = 0.0797$) were measured up to 58.90° in 2θ covering over 95% of the Ewald sphere. Data collections were made using the CrysAlis CCD program [36], integration, scaling of the reflections and absorption corrections were performed with CrysAlis Red program [36]. The structure was solved by direct methods using the SHELXS-97 and refined using the SHELXL-97 program [37]. The hydrogen atoms were geometrically positioned with $U_{\text{iso}} = 1.5U_{\text{eq}}$ (or $U_{\text{iso}} = 1.2U_{\text{eq}}$ for aromatic C) of the C atoms joined H, and a riding model was used in the refinement process. The final differences Fourier maps showed no peaks of chemical significance. The largest peaks on the final $\Delta\rho$ map were at $+0.427$ and $-0.288 \text{ e \AA}^{-3}$. Visualization of the structure was made with the Diamond 3.0 program [38]. Details on data collection and structure refinement are collected in Table 1. Selected geometrical parameters are listed in Table 2.

2.4. FT-IR measurements

The FT-IR spectra of MON8 and its 1:1 mixture with LiClO_4 were recorded in acetonitrile solution and the crystals of $\text{MON8-LiClO}_4\text{-H}_2\text{O}$ (1:1:1) complex were recorded in potassium bromide as pellets. A cell with Si windows and wedge-shaped layers was used to avoid interferences (mean layer thickness $170 \mu\text{m}$). The spectra were taken on an IFS 113v FT-IR spectrophotometer (Bruker, Karlsruhe) equipped with a DTGS detector; resolution 2 cm^{-1} , NSS = 64. The Happ-Genzel apodization function was used.

3. Results and discussion

3.1. X-ray studies

The aqualithium 1-naphthylmethyl ester of monensin A perchlorate supramolecular complex crystallizes in the non-centrosymmetric space group $P2_12_12_1$ of the orthorhombic system with

Table 1
Crystal data, data collection, refinement.

Crystal data	
Formula	$\text{C}_{47}\text{H}_{72}\text{LiO}_{12}\text{ClO}_4$
M (g mol^{-1})	935.44
Crystal size	$0.38 \times 0.22 \times 0.14$
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (No. 19)
a (\AA)	17.703(2)
b (\AA)	13.737(3)
c (\AA)	30.301(6)
V (\AA^3)	1013.4(4)
Z	4
μ (mm^{-1})	0.015
ρ_{obs} ; ρ_{calc} (g cm^{-3})	1.27; 1.275
Data collection	
Radiation, λ (\AA)	Mo K α (0.71073)
θ_{max} ($^\circ$)	29.50
Absorpt. correct. (T_{min} ; T_{max})	0.9491; 0.9805
No. collected reflections	65,001 ($R_{\text{int}} = 0.0797$)
No. unique reflections	12,573
No. observed reflections	6554
Refinement	
R [$F^2 > 2\sigma(F^2)$]	0.0706
$wR(F^2)^{a,b}$	0.1095
Goof	1.034
Absolute structure Flack parameter	0.08(9)
$\Delta\rho_{\text{min}}$; $\Delta\rho_{\text{max}}$ (e \AA^{-3})	+0.427; -0.288

^a $w = 1/[\sigma^2(F_o^2) + (0.017P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

^b All reflections.

Table 2
Selected geometrical parameters (\AA , $^\circ$).

Li–O9	1.984(6)	Li–O10	1.955(7)
Li–O11	2.280(6)	Li–O12	2.080(7)
Li–O1W	2.027(7)	Cl1–O3	1.344(3)
Cl1–O2	1.358(2)	Cl1–O4	1.416(2)
Cl1–O1	1.442(2)		
O9–Li–O10	88.2(3)	O9–Li–O12	105.2(3)
O10–Li–O11	77.0(2)	O11–Li–O12	77.0(2)
O9–Li–O1W	98.7(2)	O10–Li–O1W	114.6(3)
O11–Li–O1W	99.0(3)	O12–Li–O1W	107.9(3)
O1–Cl1–O2	113.06(15)	O1–Cl1–O3	107.28(16)
O1–Cl1–O4	110.77(15)	O2–Cl1–O3	111.26(17)
O2–Cl1–O4	111.49(17)	O3–Cl1–O4	102.40(17)

four molecules in the unit cell. The molecular dimensions (bond lengths and angles) are in agreement with the structural formula shown in Scheme 1 (Table 2).

The molecular structure of the $\text{MON8-LiClO}_4\text{-H}_2\text{O}$ supramolecular complex with the labelling scheme is illustrated in Fig. 1. All the atoms of this complex lie in general positions. The crystal structure contains a neutral molecule of MON8 coordinated to the aqualithium cation ($\text{Li(H}_2\text{O)}^+$) and ClO_4^- anion with slightly distorted tetrahedral geometry. The attractive interaction of the Li^+ cation with the three ether oxygen atoms and one oxygen atom of the hydroxyl group with formation of Li–O coordination bonds has induced formation of a pseudo-cyclic structure of the MON8 molecule within the complex (Fig. 1). Furthermore, this pseudo-cyclic structure is stabilised by two intramolecular $\text{O}(14)\text{-H}\cdots\text{O}(9)$ and $\text{O}(9)\text{-H}\cdots\text{O}(14)$ hydrogen bonds of similar strength and one $\text{O-H}\cdots\text{O}$ hydrogen bond between the coordinated water molecule and $\text{O}(15)\text{-H}$ oxygen atom of the monensin ester molecule (Table 3).

The Li^+ cation is equatorially coordinated in a distorted square fashion to the four oxygen atoms of monensin ester molecule and to the oxygen atom of water molecule in an axial position (Fig. 2). Thus, the Li^+ cation exhibits distorted square pyramidal environment. The five Li–O coordination bonds are in the range from 1.955(7) to 2.281(6) \AA (Table 2). The interaction of Li^+ cation with water molecule with formation of the axial Li–O coordination bond leads its to deviation by 0.519(5) \AA from the average plane defined by the four equatorially bonded oxygen atoms of the monensin ester molecule (Fig. 2).

The arrangement of the aqualithium 1-naphthylmethyl ester of monensin cations $[\text{MON8-Li(H}_2\text{O)}]^+$ and perchlorate anions in the unit cell is mainly determined by the ionic and van der Waals forces. In addition, $[\text{MON8-Li(H}_2\text{O)}]^+$ cations related by a screw 2_1 axis parallel to the $[1\ 0\ 0]$ direction interact through intermolecular $\text{O-H}\cdots\text{O}$ hydrogen bond between the coordinated to Li^+ water molecule of one $[\text{MON8-Li(H}_2\text{O)}]^+$ cation and the methoxy oxygen atom (O7) of the other $[\text{MON8-Li(H}_2\text{O)}]^+$ cation forming two dimensional double layers of $\{[\text{MON8-Li(H}_2\text{O)}]^+\}_n$ parallel to the $(0\ 0\ 1)$ crystallographic plane at $z = 0, \frac{1}{2}, \dots$ (Fig. 3).

3.2. FT-IR studies

In Fig. 4a the FT-IR spectrum of crystalline $\text{MON8-LiClO}_4\text{-H}_2\text{O}$ complex recorded in KBr pellets is compared with the corresponding spectra of water free MON8 (dashed line) and 1:1 MON8-LiClO_4 complex (dashed-dotted line) both in acetonitrile. In Fig. 4b and c, the same spectra are shown in the ranges of the $\nu(\text{OH})$ and $\nu(\text{C=O})$ vibrations respectively, on expanded scale.

The most characteristic in the FT-IR spectrum of water free MON8 are the bands assigned to the $\nu(\text{OH})$ vibrations of the $\text{O}(14)\text{H}$ and $\text{O}(15)\text{H}$ groups at 3506 cm^{-1} , and of the $\text{O}(9)\text{H}$ group at ca. 3320 cm^{-1} as well as the band assigned to the $\nu(\text{C=O})$ vibra-

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