

Chemistry of 1,3-Dioxepins. XIV.¹ Structural Studies of 4,7-Dihydro-(4,7-dihydro-1,3-dioxepin-2-yl)-1,3-dioxepin and Their Metal Complexes*

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The coordination properties and conformational behaviour of 4,7-dihydro-(4,7-dihydro-1,3-dioxepin-2-yl)-1,3-dioxepin [**1**, bis-(1,3-dioxepin), or C₁₀H₁₄O₄] have been investigated. The crystal and molecular structures of bis-(1,3-dioxepin) (**1**), bis-(1,3-dioxepin) lithium-perchlorate (2:1) (**2**) and bis-(1,3-dioxepin) sodium-perchlorate (1:1) (**3**) complexes, as well as bis-(1,3-dioxepin) hexaaquamagnesium-perchlorate (3:1) chlatrate (**4**), have been determined by X-ray diffraction. The molecule of bis-(1,3-dioxepin) is a bidentate ligand in mononuclear lithium complex **2**, in contrast to its bridging mode in 2D polymeric sodium complex **3**. The coordination environment around lithium in **2** is distorted octahedral with C₂ symmetry, while around sodium in **3** it is quasi-pentagonal bipyramidal. Out of four possible conformations of bis-(1,3-dioxepin) molecule, twist-boat-twist-boat centrosymmetric (*tb-tb-c*), twist-boat-twist-boat non-centrosymmetric (*tb-tb*), twist-boat-chair (*tb-ch*) and chair-chair (*ch-ch*), three have been found in the investigated crystal structures: *ch-ch* in **1**, *tb-tb* in **2** and *tb-tb-c* in **3** and **4**.

Key words: X-ray, 1,3-dioxepin, conformation.

* Dedicated to Professor Boris Kamenar on the occasion of his 70th birthday.

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INTRODUCTION

4,7-Dihydro-1,3-dioxepins are the dienophiles of choice in the Diels-Alder syntheses of pyridoxine (vitamin B6).²⁻⁷ Recently, in the context of our investigations in the same field,⁸ we reported bis-(4,7-dihydro-1,3-dioxepin) approach to pyridoxine⁹ and the application of nitro-bis-(4,7-dihydro-1,3-dioxepin) as pyridoxine precursor.¹⁰ Furthermore, 1,3-dioxepin moiety is contained in sulfonyldioxepinoazirines, a new class of antihyperglycemics,¹¹ as well as in many other molecules of biological interest or intermediates for their synthesis.

We are interested in the structure of metal complexes of 1,3-dioxepino- and bis-(1,3-dioxepino)-derivatives in order to understand their ligation properties, which are important in chemical catalysis as well as in interaction with metals in biological systems. This type of complexes was not known in the bis-(1,3-dioxepin) series, although those of bis-(1,3-dioxolanes) and bis-(1,3-dioxanes) with metal perchlorates and thiocyanates, as well as mercury and zinc halogenides, were reported.¹² However, there was no data about their spatial structure.

Now, we would like to describe structural investigations of alkaline and earth alkaline perchlorate complexes of bis-(1,3-dioxepin) and correlate them with the structure of **1** as model compound. Special attention is paid to coordination properties of **1** and its conformational changes.

EXPERIMENTAL

Preparations and Crystallizations

A single crystal of **1** suitable for X-ray analysis was obtained by slow evaporation of ethyl acetate solution.

Complexes with metal-perchlorates **2** and **3** as well as chlorate **4** were prepared by mixing ethyl acetate solutions of corresponding perchlorates and bis-(1,3-dioxepin) **1** in the ratio 1:1 (compounds **3** and **4**) or 1:2 (compound **2**) in analogy with previously described bis-(1,3-dioxolanes) and bis-(1,3-dioxanes).¹² Single crystals of **2**, **3** and **4** suitable for X-ray analysis were obtained by slow evaporation of such mixtures at room temperature.

X-ray Crystal Structure Determinations

Most of the relevant details concerning general crystal data and intensity collections are listed in Table I. The cell parameters and intensities were collected with the Philips PW1100 diffractometer (Stoe upgrade) using graphite monochromatised Mo-K α radiation ($\lambda = 0.71069 \text{ \AA}$) at room temperature. The intensity data were corrected for Lorentz and polarisation effects¹³ but not for absorption. The structures were solved by direct methods incorporated in SIR88 programme¹⁴ and refined on F^2

TABLE I
Crystal data

	1	2	3	4
Formula	$C_{10}H_{14}O_4$	$Li[(C_{10}H_{14}O_4)_2(ClO_4)]$	$Na[(C_{10}H_{14}O_4)(ClO_4)]$	$[Mg(H_2O)_6][ClO_4]_2(C_{10}H_{14}O_4)_3$
Molecular mass	198.22	502.83	320.66	925.95
Crystal system	triclinic	monoclinic	monoclinic	trigonic
Space group	$P\bar{1}$	$C2/c$	$P2_1/c$	$R\bar{3}$
$a/\text{\AA}$	4.348(2)	16.641(7)	9.418(3)	13.826(2)
$b/\text{\AA}$	6.014(2)	7.857(1)	16.738(5)	13.826(2)
$c/\text{\AA}$	9.552(6)	17.789(4)	9.793(4)	19.255(1)
$\alpha/^\circ$	91.50(4)	90.00	90.00	90.00
$\beta/^\circ$	93.64(3)	94.98(4)	115.68(2)	90.00
$\gamma/^\circ$	103.74(3)	90.00	90.00	120.00
$V/\text{\AA}^3$	241.9(2)	2317(1)	1 391.3(8)	3188(2)
$D_x / \text{Mg m}^{-3}$	1.36	1.44	1.53	1.45
Z	1	4	4	3
μ / mm^{-1}	0.105	0.227	0.339	0.258
F_{000}	106	1056	664	1464
$\theta_{\text{max}}/^\circ$	30	30	27	30
No. unique refl.	1408	3251	3031	2084
$R_{\text{int}}[F^2]$	0.112	0.105	0.040	0.057
No. obs. refl. ^a	983	2087	1640	1361
No. parameters	64	155	182	91
R_F	0.0879	0.0551	0.0790	0.0514
wR_F^2	0.2120	0.1496	0.2157	0.1518
S	1.081	1.132	1.154	1.162

by SHELXL93 programme.¹⁵ For all structures, H atoms were let to ride on their carrier C atoms at calculated positions. All non-hydrogen atoms were refined anisotropically.

Thermogravimetry

Water of chlatrate **4** was determined thermogravimetrically. The measurement was made using the instrument Mettler TA4000. The heating rate was controlled at 10 K/min.

RESULTS AND DISCUSSION

Description of Structures

Compound **1** crystallises in the centrosymmetric triclinic space group $P\bar{1}$. Its solid state conformation is centrosymmetric and the centre of symmetry lies between atoms C1 and C1'. Therefore, both 1,3-dioxepin rings adopt the same, chair conformation *ch-ch* (see Figure 5 for all possible conformations of **1**). A view of the molecule is shown in Figure 1. Bond distances and angels for **1** in comparison with compounds **2–4** are listed in Tables II and III, respectively.

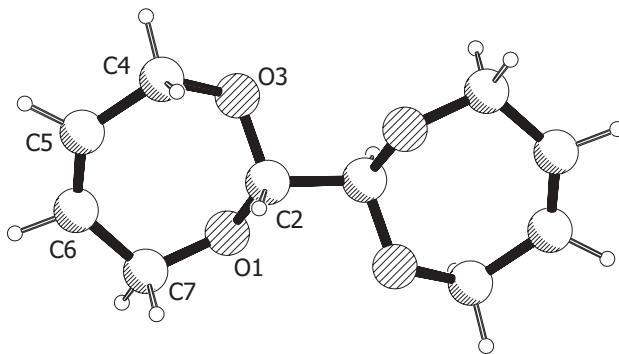


Figure 1. View of the bis-(1,3-dioxepin) molecule (**1**).

Complex **2** crystallises in the centrosymmetric monoclinic space group $C2/c$ with four lithium cations in the unit cell. It is a monomeric complex with a distorted octahedral coordination of lithium. Lithium atom is coordinated with two crystallographically equivalent bidentate molecules of **1** and one bidentate perchlorate anion. Lithium and chlorine atoms are in special position, on the two-fold axis. One bis-(1,3-dioxepin) molecule, half of

Table II
Selected bond lengths / Å

	1	2(A) ^a	2(B) ^b	3(A) ^c	3(B) ^d	4
O1–C2	1.403(2)	1.4071(18)	1.4022(18)	1.400(4)	1.406(4)	1.401(2)
O3–C2	1.402(2)	1.3974(19)	1.3977(19)	1.408(4)	1.425(4)	1.412(2)
O1–C7	1.428(2)	1.4530(19)	1.4485(19)	1.452(5)	1.435(4)	1.438(3)
O3–C4	1.423(2)	1.438(2)	1.430(3)	1.425(5)	1.428(5)	1.444(3)
C4–C5	1.496(3)	1.497(3)	1.495(3)	1.499(6)	1.507(6)	1.489(4)
C5–C6	1.323(3)	1.311(3)	1.308(3)	1.286(7)	1.289(7)	1.315(4)
C6–C7	1.489(3)	1.490(3)	1.488(3)	1.491(7)	1.495(7)	1.497(4)
C2–C2'	1.516(3)	1.528(2)		1.509(7)	1.497(8)	1.518(4)
O1–M	–	2.015(2)	2.0439(13)	2.487(3)	2.430(3)	–
O3–M	–	–	–	2.418(3)	2.397(3)	–

^a First ring of the bis-(1,3-dioxepin) molecule in **2**.

^b Second ring of the bis-(1,3-dioxepin) molecule in **2**.

^c Crystallographically independent molecule A of the bis-(1,3-dioxepin) in complex **3**.

^d Crystallographically independent molecule B of the bis-(1,3-dioxepin) in complex **3**.

Table III
Selected bond angles / °

	1	2(A) ^a	2(B) ^b	3(A) ^c	3(B) ^d	4
C2–O1–C7	115.42(15)	113.26(12)	114.19(12)	113.8(3)	113.5(3)	113.18(16)
C2–O3–C4	114.61(15)	115.48(13)	115.92(15)	116.8(3)	117.7(3)	115.66(15)
O1–C2–O3	110.57(14)	112.14(12)	112.26(13)	111.9(3)	111.5(3)	111.81(16)
O1–C2–C2'	107.16(17)	107.89(12)	107.40(12)	105.7(3)	107.3(4)	106.56(18)
O3–C2–C2'	107.21(18)	111.67(12)	111.48(13)	112.4(4)	111.6(4)	111.0(2)
O3–C4–C5	116.24(17)	111.73(16)	112.55(17)	112.5(4)	112.6(4)	110.8(2)
C4–C5–C6	129.7(2)	125.40(18)	125.19(19)	125.4(4)	126.1(4)	124.3(2)
C5–C6–C7	130.6(2)	124.57(18)	125.04(17)	125.9(4)	125.2(4)	125.9(3)
O1–C7–C6	116.72(19)	111.45(15)	111.67(15)	111.1(4)	111.2(4)	111.7(2)
C2–O1–M	–	116.66(9)	112.29(9)	116.6(2)	115.1(2)	–
C7–O1–M	–	126.39(10)	119.46(12)	121.1(2)	119.9(2)	–
C2–O3–M	–	–	–	110.5(2)	110.1(2)	–
C4–O3–M	–	–	–	114.5(2)	114.6(2)	–

lithium atom and half of perchlorate anion are present in asymmetric unit. Molecules of **1** adopt *tb-tb* non-centrosymmetric conformation. A view of the complex and crystal packing diagram are given in Figure 2.

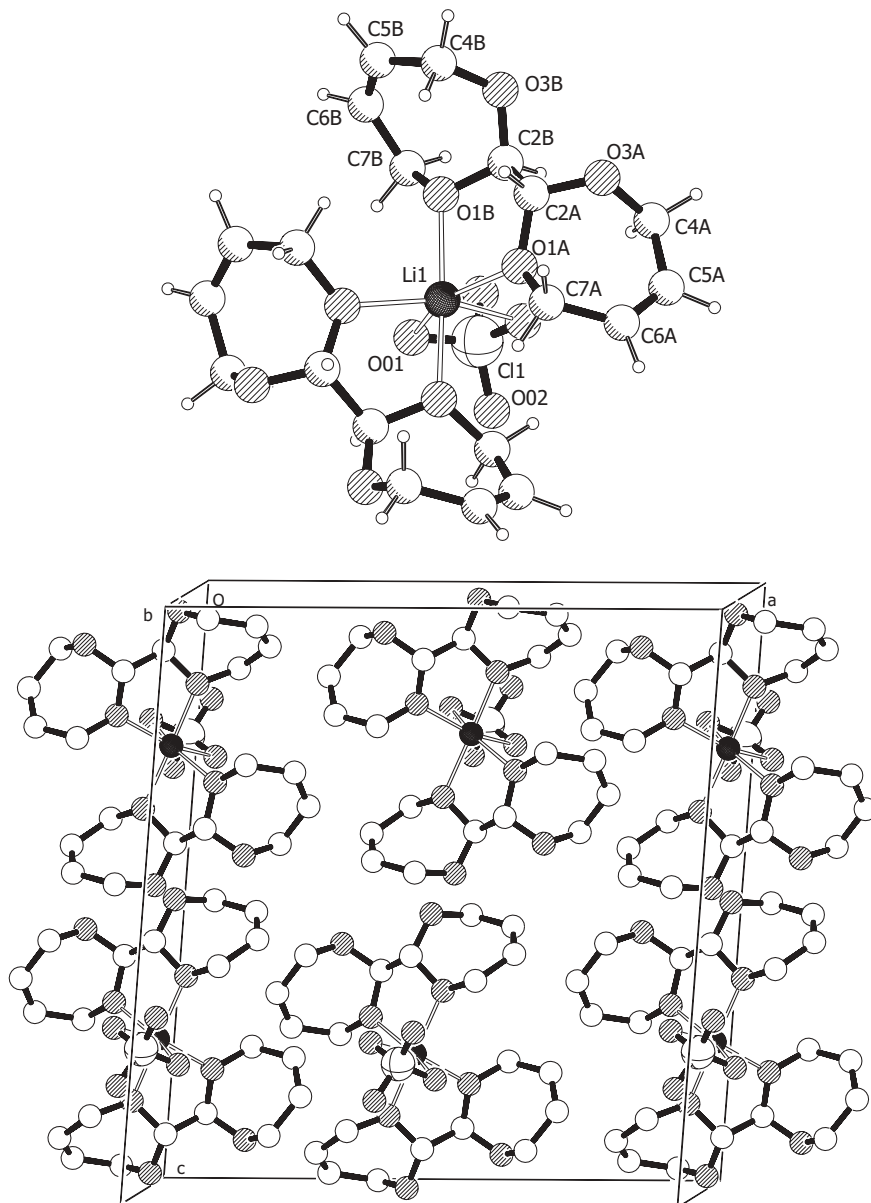


Figure 2. View of complex **2** (a) and its packing diagram (b).

Complex **3** crystallises in the centrosymmetric monoclinic space group $P2_1/c$ with four sodium cations in the unit cell. It is polymeric and forms layers perpendicular to the crystallographic b axis. The sodium atom is hepta-

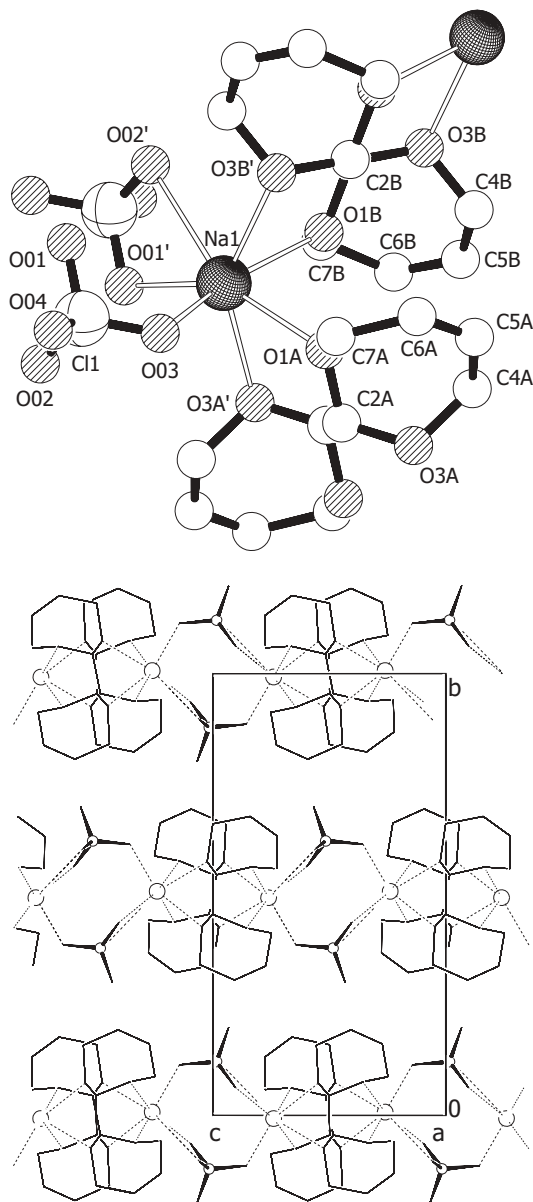


Figure 3. View of complex **3** (a) and its crystal packing diagram (b).

coordinated (quasi-pentagonal bipyramide) with four oxygen atoms from two molecules of **1** and three oxygen atoms from two crystallographically equivalent perchlorate anions. Each of two bis-(1,3-dioxepin) ligands is centrosymmetric with very similar twist-boat conformations but they are crystallographically independent. A view of the complex and molecular packing diagram is given in Figure 3.

Chlatriate **4** crystallises in the centrosymmetric trigonic space group $R\bar{3}$. It consists of isolated molecules of **1** in *tb-tb-c* conformation, octahedral hexaaquamagnesium(II) ions and perchlorate anions in the ratio 3:1:2. The molecules of **1** utilise crystallographic three-fold axes in constructing channels, which are filled with alternating hexaaqua-coordinated magnesium cations and perchlorate anions. Asymmetric unit consists of 1/2 bis-dioxepine molecule, 1/6 hexaaquamagnesium cation and 1/3 perchlorate anion. A view of the crystal packing diagram of chlatriate **4** is given in Figure 4. Water molecules in chlatriate **4** are also identified by thermogravimetry analysis. Loss

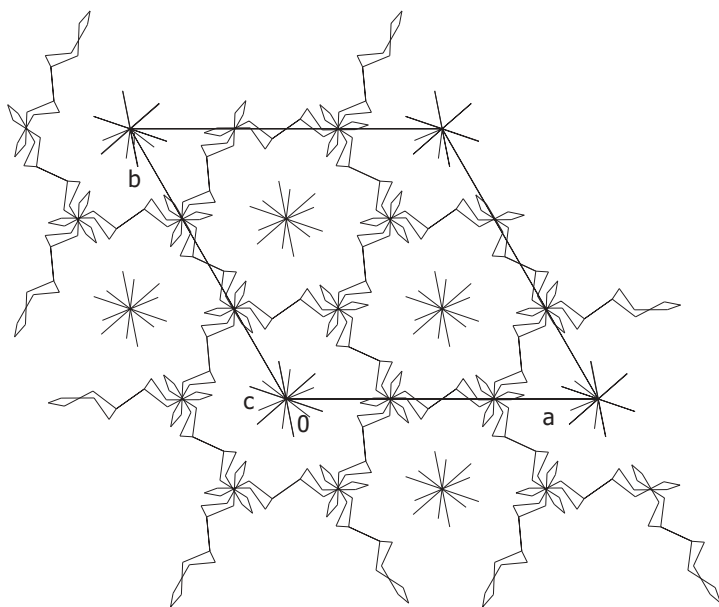


Figure 4. Packing diagram of chlatriate **4**.

of water proceeds in two-steps, at 110 and 150 °C, and continues with compound decomposition. Mass-loss accompanying loss of water is 11.9% and corresponds to the loss of six mol of water per mol of salt (calculated mass-loss is 11.7%).

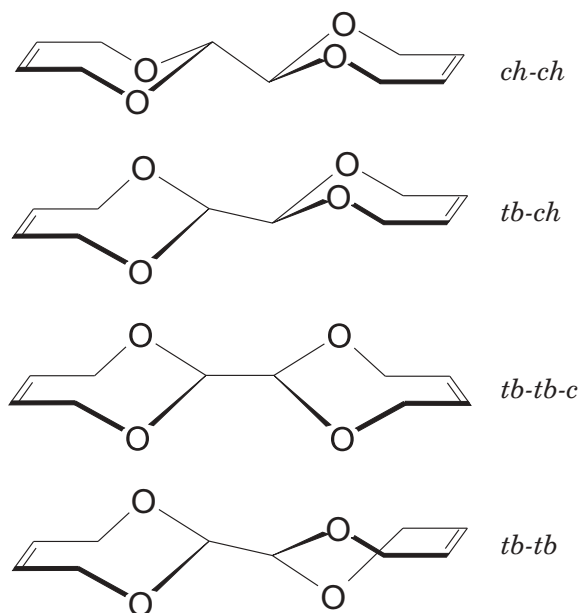


Figure 5. All possible conformations of **1**.

Conformation of Bis-(1,3-dioxepin) Molecules in the Presented Structures

1,3-Dioxepin moiety may adopt chair (*ch*) conformation of C_S symmetry or any of two mirror related twist-boat (*tb*) conformations of C_2 symmetry. Connecting two 1,3-dioxepin moieties in bis-(1,3-dioxepin) molecule (**1**) generates the four possible conformations shown in Figure 5: twist-boat-twist-boat centrosymmetric (*tb-tb-c*), twist-boat-twist-boat non-centrosymmetric (*tb-tb*), twist-boat-chair (*tb-ch*) and chair-chair (*ch-ch*). Three of them are found in the presented crystal structures: *ch-ch* in **1**, *tb-tb* in **2** and *tb-tb-c* in **3** and **4**.

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SAŽETAK

Kemija 1,3 dioksepina. XIV. Strukturne studije 4,7-dihidro-(4,7-dihidro-1,3-dioksepin-2-il)-1,3-dioksepina i njegovih metalnih kompleksa

Dijana Matak-Vinković, Mladen Vinković i Miljenko Dumić

Istraživana su koordinacijska svojstva i konformacijsko ponašanje 4,7-dihidro-(4,7-dihidro-1,3-dioksepin-2-il)-1,3-dioksepina [**1**, bis-(1,3-dioksepin), C₁₀H₁₀O₄]. Difrakcijom rentgenskih zraka na monokristalu određene su kristalne i molekulske strukture bis-(1,3-dioksepina) (**1**), kompleksnih spojeva bis-(1,3-dioksepin)litijeva perklorata (2:1) (**2**) i bis-(1,3-dioksepin)natrijeva perklorata (1:1) (**3**), kao i klatrata bis-(1,3-dioksepin)-heksaakvماغnezijeva perklorata (3:1) (**4**). Molekula bis-(1,3-dioksepina) bidentatan je ligand u mononuklearnom litijevu kompleksu **2**, za razliku od premosne uloge u 2D polimernom natrijevu kompleksu **3**. Koordinacijsko okruženje litijeva atoma u **2** jest deformirani oktaedar simetrije C₂, a za natrijev atom u **3** to je pseudopentagonska bipiramida. Od četiri moguće konformacije molekule bis-(1,3-dioksepina): centrosimetrična izvijena kolijevka-izvijena kolijevka (*tb-tb-c*), necentrosimetrična izvijena kolijevka-izvijena kolijevka (*tb-tb*), izvijena kolijevka-stolica (*tb-ch*) i stolica-stolica (*ch-ch*), u istraživanim kristalnim strukturama nađene su tri: *ch-ch* u **1**, *tb-tb* u **2** i *tb-tb-c* u **3** i **4**.