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The Synthesis and Crystal Structures of 7-Bromo-1,3-dihydro-1-methyl-3(*S*)-methyl-5-(2'-pyridyl)--2*H*-1,4-benzodiazepin-2-one and Its Cu^{II} Complex

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By reaction of the enantiomerically pure 7-bromo-1,3-dihydro-1-methyl-3(*S*)-methyl-5-(2'-pyridyl)-2*H*-1,4-benzodiazepin-2-one, (+)-**1**, with $CuCl_2 \cdot 2H_2O$ in a mixture of absolute ethanol and dichloromethane, dichloro-[7-bromo-1,3-dihydro-1,3-dimethyl-5-(2'-pyridyl)-2*H*-1,4-benzodiazepin-2-on-*N*,*N*,*O*]copper(II), (±)-**2**, was obtained. In both structures, the characteristic *boat* conformation of the seven-membered benzodiazepine ring was observed. Complex **2**, which was isolated as a racemic compound, revealed a slightly distorted trigonal bipyramid. Copper(II) was coordinated by two azometine nitrogen atoms, two chlorine atoms and the lactam oxygen of a neighbouring molecule. In this way, an infinite chain of complex molecules was formed in the crystal. The chemical behaviour of ligand **1** upon Cu^{II} coordination was compared with its 3-hydroxymethyl and 3-acetoxymethyl analogues.

Key words
chiral 1,4-benzodiazepine
copper complex
synthesis
crystal structure

INTRODUCTION

1,4-Benzodiazepines were discovered by chance in the early fifties,[1] and since then they have become the mostly prescribed psychotherapeutic drugs worldwide.[2,3] After the discovery of benzodiazepine receptors, in the CNS and peripheral tissue, in the mid seventies[4,5] it became quite clear that the molecular structure and biological activity of these compounds are closely correlated.[6] In the attempts to prepare even more potent drugs, chemists investigated the ability of these compounds to coordinate various transition metals.[7,8] In spite of an obvious interest in this subject, very few metal complexes of benzodiazepines, especially those with unambiguously determined structure, have been reported so far.[9,10] On the other hand, chiral 3-substituted benzodiazepine derivatives are the key intermediates in the synthesis of other enantiomerically pure biologically important compounds, like α-amino acids.[11] Therefore, it is of practical interest to study the effect of metal bonding on the absolute configuration at the ligand stereogenic centre. We have recently reported on the structural investigation of the series of chiral 3-substituted 5-phenyl-1,4-benzodiazepin-2-one derivatives.[12,13,14,15] In addition, the configurational, conformational and chemical stability of the 3-hydroxymethyl- and 3-acetoxymethyl-5-pyridyl-1,4-benzodiazepin-2-ones upon complexation with Cu^{II}, Zn^{II} and Pd^{II} were investigated.[16,17] Here, we report the synthesis and crystal structure determination of their 3-methyl analogue and its Cu^{II} complex. The results obtained are discussed with

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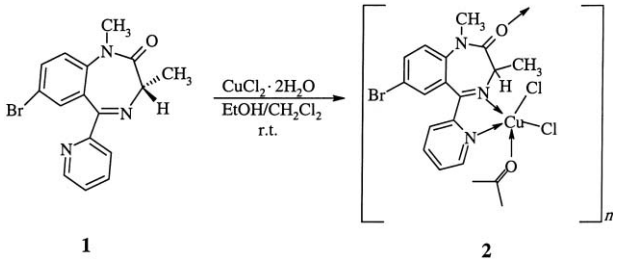
respect to the different chemical behaviour of various 3-substituted 1,4-benzodiazepine ligands upon Cu^{II} complexation.

Chemical diagrams of ligand 7-bromo-1,3-dihydro-1-methyl-3(*S*)-methyl-5-(2'-pyridyl)-2*H*-1,4-benzodiazepin-2-one (**1**) and complex dichloro-[7-bromo-1,3-dihydro-1,3-dimethyl-5-(2'-pyridyl)-2*H*-1,4-benzodiazepin-2-on-*N*,*N*,*O*]copper(II) (**2**) are given in Scheme 1.



1 **2**

Scheme 1.

EXPERIMENTAL

Materials and Instrumentation

7-Bromo-1,3-dihydro-1-methyl-3(*S*)-methyl-5-(2'-pyridyl)-2*H*-1,4-benzodiazepin-2-one (**1**) was prepared by methylation of 7-bromo-1,3-dihydro-3-(*S*)-methyl-5-(2'-pyridyl)-2*H*-1,4-benzodiazepin-2-one[18] with dimethyl sulphate and sodium methoxide as the base. Analytical grade $CuCl_2$ dihydrate and solvents were used without purification. FTIR spectra were recorded on a Perkin Elmer 2000 spectrophotometer using KBr (4000–400 cm^{-1}) and polyethylene (400–200 cm^{-1}) pellets. Elemental analyses (CHN) were performed with a Perkin-Elmer Elemental Analyser E-2400 Series 2.

*Preparation of Ligand **1***

Reaction was performed under a dry argon atmosphere. The reaction temperature ought to be below 0 °C in order to avoid racemisation. Starting compound 7-bromo-1,3-dihydro-3(*S*)-methyl-5-(2'-pyridyl)-2*H*-1,4-benzodiazepin-2-one (0.2 g, 0.6 mmol) was suspended in dry MeOH (1.5 mL). During 15 min, under stirring and cooling at –5 °C, a solution of sodium (0.054 g, 2.3 mmol) in MeOH (2 mL) was added dropwise. After stirring at –5 °C for 30 min, the reaction mixture was cooled at –10 °C and Me_2SO_4 (0.230 g, 1.82 mmol) was added dropwise during 15 min. The reaction was terminated after 30 min and the solvent was evaporated at ambient temperature. The crude product was dissolved in water (3 mL) and extracted with CH_2Cl_2 (3 × 2 mL). The organic extracts were dried (Na_2SO_4) and evaporated to dryness. The crude product was purified by flash chromatography (10 g silicagel) with the solvent mixture CH_2Cl_2/*i*-Pr_2O/MeOH/Net_3 (3 : 3 : 0.1 : 2 drops). The pure product (0.53 g, 85 %) was crystallised from Me_2CO solution. IR (KBr) ν_{max}/cm^{-1}: 1680 vs, [ν(C=O)], 1465 m, 1320 w-m, 1230 w, 1110 s, 840 w, 800 m, 750 w-m; ^{1}H NMR ($CDCl_3$) δ/ppm: 1.72 (d, CH**CH$_3$**, J = 6.4 Hz), 3.37 (s, NCH_3), 3.77 (q, CH), 7.19–8.60 (m, 7H); ^{13}C NMR ($CDCl_3$) δ/ppm: 17.10 (CH**CH$_3$**), 34.95 (N**CH$_3$**), 58.88 (C*H), 116.45, 122.83, 123.68, 124.56, 129.75, 133.08, 134.09, 136.72, 142.66, 148.70, 155.50, 165.58, 170.80 (CO).

*Preparation of Complex **2***

A solution of **1** (0.061 g, 0.18 mmol) in a 1:1 mixture of absolute EtOH and CH_2Cl_2 (5 mL) was added dropwise to a stirred solution of $CuCl_2 \cdot 2H_2O$ (0.030 g, 0.18 mmol) in the same mixture of solvents (5 mL). After complete addition, the reaction mixture was continuously stirred for 1 h at ambient temperature. The green precipitate formed was filtered off, washed with cold absolute EtOH and dried under vacuum. Yield 0.076 g (88 %); IR (KBr) ν_{max}/cm^{-1}: 1686 vs, 1676 vs [ν(C=O)], 1593 m, 1580 w, 1553 w [ν(C=N), ν(C=C)], 1487 m, 1470 m-s, 1443 w-m, 1399 m, 1380 w, 1335 m-s, 1322 w-m, 1299 w, 1252 m, 1234 w-m, 1190 w, 1148 w, 1115 m, 1105 s, 1052 w, 1021 m, 992 w, 930 w, 890 w, 819 m-s, 809 m, 799 m, 760 w-m, 712 w, 617 m, 646 w, 625; IR (polyethylene) ν_{max}/cm^{-1}: 368 w, 334 sh, 318 sh, 309 m-s br, 274 w.

Anal. Calcd. for $C_{16}H_{14}N_3OBrCl_2Cu$ (M_r = 478.66): C 40.14, H 2.95, N 8.78 %; found C 39.71, H 3.12, N 8.54 %.

X-ray Structure Analysis

Colourless prisms of **1** were obtained by slow evaporation of MeCN solution at room temperature, whereas green single crystals of low quality of **2** were obtained from a mixture of MeCN, CH_2Cl_2 and MeOH by cooling at 4 °C. Experimental details of data collection, as well as the data on structure solution and refinement are given in Table I. Data were collected on an Enraf Nonius CAD4 diffractometer using CAD4 Express software.[19] Data were corrected for Lorentz and polarisation effects,[20] as well as for the absorption effect.[21] Structures were solved using the SIR97 package[22] and refined using SHELXL97.[23] Molecular geometry calculations and illustrations were prepared with PLATON.[24] Atomic scattering factors were those included in SHELXL97. The H-atom coordinates were calculated geometrically and refined using the SHELXL97 riding model. In the structure of **2**, not all non-hydrogen atoms were refined anisotropically due to the low quality of the data set obtained.

RESULTS AND DISCUSSION

By reaction of the enantiomerically pure 7-bromo-1,3-dihydro-1-methyl-3(*S*)-methyl-5-(2'-pyridyl)-2*H*-1,4-benzodiazepin-2-one, (+)-**1**, with $CuCl_2 \cdot 2H_2O$ in a 1:1 mixture of absolute ethanol and dichloromethane, dichloro-[7-bromo-1,3-dihydro-1,3-dimethyl-5-(2'-pyridyl)-2*H*-1,4-benzodiazepin-2-on-*N*,*N*,*O*]copper(II), (±)-**2** was obtained as a racemic mixture. The same ligand racemisation upon Cu^{II} complexation was observed in chiral 3-hydroxymethyl- and 3-acetoxymethyl-1,4-benzodiazepin-2-ones.[16] The configurational stability of the stereogenic centre C3 is lowered upon complexation, presum-

TABLE I. Crystal data, data collection and refinement of compounds **1** and **2**

	1	**2**
Formula	$C_{16}H_{14}N_3OBr$	$C_{16}H_{14}N_3OBrCuCl_2 \cdot 0.5\ CH_3OH \cdot 0.5\ H_2O$
M_r	344.21	478.66
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
a / Å	7.3835(3)	11.030(5)
b / Å	10.9427(2)	9.548(4)
c / Å	18.5384(3)	19.79(1)
β / °	–	97.21(3)
V / Å^3	1497.82(7)	2068(1)
Z	4	4
D_x / Mg m^{-3}	1.526	1.608
Temperature / K	293(2)	293(2)
Wavelength / Å	1.54183	0.71069
Absorption correction	Y-scan	Y-scan
Total data collected	1795	4678
Unique data	1771	4180
Observed data [$I > 2\sigma(I)$]	1677	842
Θ_{max} / °	74.33	26.32
Range of h, k, l	0, 9; –13, 0; –23, 0	0, 13; 0, 11; –24, 24
R_1 [$F_o > 4\sigma\ (F_o)$]	0.0299	0.0900
wR_2 (F^2)	0.0921	0.2682
S	1.023	0.882
No. of parameters	247	231
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.40, –0.46	0.79,-1.02
Weighting scheme[(a)]	$w = 1 / [\sigma^2(F_o^2) + (0.0722P)^2 + 0.2793P]$	$w = 1 / [\sigma^2(F_o^2) + (0.0773P)^2]$

[(a)] $P = (F_o^2 + 2F_c^2) / 3$.

ably by the Cu^{II} promoted enolisation. The Cu^{II} ion enhances the acidity of C3, and promotes the enolisation, which results in the racemisation of the optically active structures.[16] This phenomenon was, however, not observed by complexation of Zn^{II} and Pd^{II} with the same ligands.[17] Furthermore, in the case of the 3-hydroxymethyl derivative, racemisation at room temeprature was followed by the catalytic oxygenation at the stereogenic centre, and finally by the ring contraction to a new quinazoline complex. A similar reaction occurred in the case of 3-acetoxymethyl derivative, but at 80 °C. The study presented in this paper shows that the 3-methyl derivative was not subjected to any of the above mentioned chemical changes upon complexation to Cu^{II}, not even after extensive heating. This study suggests the key role of 3-substituent for the chemical behaviour of the chiral 1,4-benzodiazepin-2-one derivatives when complexing copper(II).

Infrared Spectra

The IR spectra of the benzodiazepine ligand **1** and its Cu^{II} complex **2** are very complicated, with significant vibrational coupling and overlapping of absorption bands. When comparing the results obtained for the complex with those of the free ligand, the most significant differences may be noticed between 1690 and 1550 cm^{-1}. In this region, bands arising from the stretching modes of the donor groups involved in bonding to copper, the lactam C=O as well as the azomethine and pyridine C=N groups, are present.[16,25,26] A very strong band of ν(C=O) vibration in the ligand is found at 1682 cm^{-1}, while its complex in this frequency region shows a split band with maxima at 1686 and 1676 cm^{-1}. The variation in position and intensity of the ν(C=N) and ν(C=C) absorption bands, occurring between 1610 and 1550 cm^{-1}, could be assigned to π-electronic redistribution in the benzodiazepine molecule caused by coordination of both nitrogen atoms to Cu^{II}. There are also marked changes in intensity and frequency on the bands in the range from 1500 to 1000 cm^{-1}, where some stretching ring vibrations are expected to occur along with various modes of C–N and C–O stretching, and CH bending vibrations. The far-IR spectrum of the complex shows a few bands between 400 and 200 cm^{-1}, in the frequency region associated with

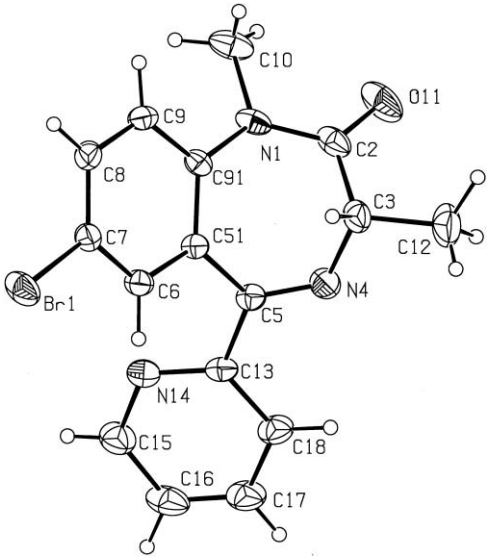


Figure 1. ORTEP drawing of **1**. Thermal ellipsoids are scaled at 30 % probability level.

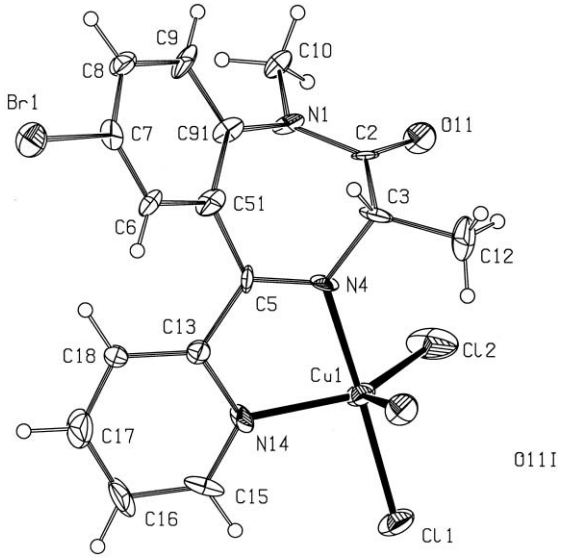


Figure 2. ORTEP drawing of **2**. Thermal ellipsoids are scaled at 30 % probability level.

the metal-ligand stretching vibrations. These bands, mostly weak, are coupled and difficult to assign. The low symmetry of the complex does not allow one to expect highly characterised copper-specific vibrations.

Crystal Structures

ORTEP[27] drawings of the molecular structures of **1** and **2** are given in Figure 1 and Figure 2, respectively. The crystal structure of **2** is depicted by a PLUTON[24] drawing in Figure 3. Selected geometry for both structures is summarised in Tables II and III.

Enantiomerically pure (*S*) ligand **1** was used for preparation of complex **2**. In a separate experiment we proved that enantiomerically pure compounds undergo fast racemisation in an ethanol solution in the presence of Cu^{II} ions.[28] This phenomenon was also observed during the formation of complex **2**, which crystallised in the centrosymmetric space group $P2_1/n$. In the crystal structure of **1**, the seven-membered benzodiazepine ring appears in a *boat* conformation [ϕ_1 = 60.2(1)°, ϕ_2 =36.0(1)°],[29] which is retained in its Cu^{II} complex **2** [ϕ_1 = 60(2)°, ϕ_2 = 37(1)°]. The metal complexation did not greatly affect the conformation of the benzodiazepine ring (Table II). The intramolecular contact C6-H···N14 (D-H···A, 3.02 Å, 101°; H···A, 2.71 Å) stabilises the orientation of the phenyl ring in the crystal structure of ligand **1**. Rupture of this contact, however, allows a free rotation of the pyridyl moiety about the bond C5–C13 (Figure 1), which brings the two azomethine nitrogens (N4 and N14) into a sterically favourable position to be coordinated by Cu^{II}. In addition to this intramolecular contact, the N14 atom takes

TABLE II. Selected bond lengths /Å, angles /° and torsion angles /° in **1** and **2**

Bond	**1**	**2**	Angle	**1**	**2**	Torsion angle	**1**	**2**
Br1–C7	1.891(3)	1.93(2)	N1–C2–C3	115.7(3)	115.2(16)	C2–N1–C91–C51	–47.4(5)	–46(3)
N1–C2	1.391(5)	1.38(3)	C2–C3–N4	106.4(4)	105.1(16)	N4–C5–C51–C91	44.0(5)	47(3)
C2–C3	1.511(5)	1.53(3)	C3–N4–C5	118.1(3)	119.7(15)	C91–N1–C2–C3	6.7(5)	13(3)
C3–N4	1.463(5)	1.47(3)	N4–C5–C51	123.0(3)	119.6(19)	C3–N4–C5–C51	2.2(5)	8(3)
N4–C5	1.271(5)	1.31(2)	C5–C51–C91	121.9(3)	121.0(19)	N1–C2 –C3–N4	70.7(4)	64(2)
C5–C51	1.488(3)	1.47(3)	C51–C91–N1	122.3(2)	122.7(17)	C5–N4–C3–C2	–76.4(4)	–81(2)
C51–C91	1.403(3)	1.41(3)	C91–N1–C2	122.2(3)	124.6(15)	C2–N1–C91–C51	–47.4(5)	–46(3)
N1–C10	1.465(5)	1.47(2)				C5–C51–C91–N1	8.1(5)	9(2)
C2–O11	1.216(5)	1.21(2)						
C3–C12	1.520(7)	1.53(3)						
C5–C13	1.490(4)	1.48(3)						

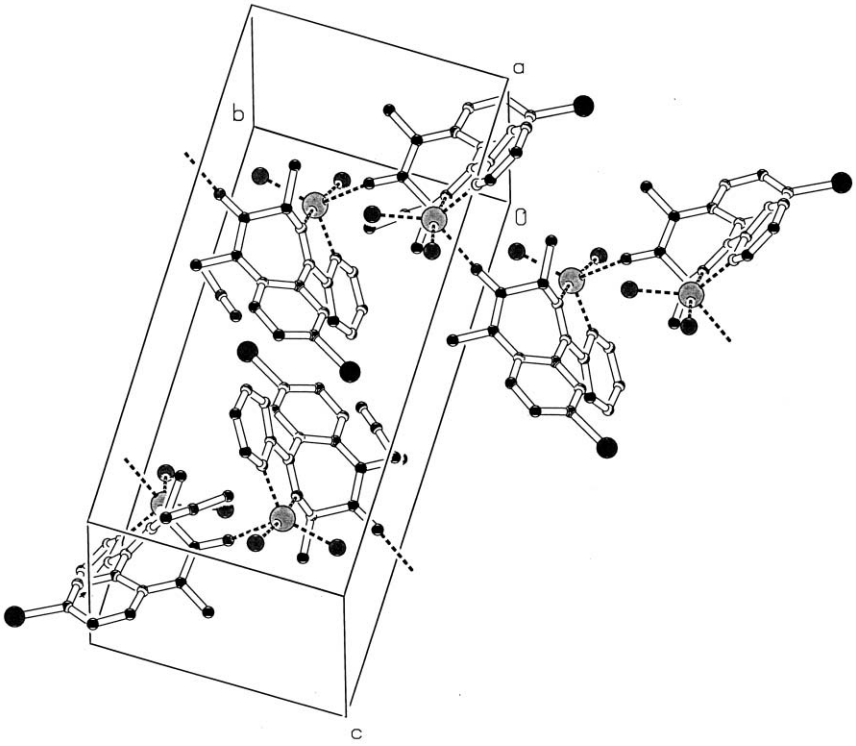


Figure 3. The crystal structure of **2**. Hydrogen atoms are omitted for clarity.

part in an intermolecular C–H ··· N bond [C9–H ··· N14^{i}; D–H ··· A, 3.41 Å, 171°; H ··· A, 2.48 Å; *i*) -1/2+*x*, 1/2-*y*, -z] that connects molecules of **1** into infinite chains inside the crystal. The reaction of **1** with Cu^{II} ions did not result in chemical and structural changes in the ligand molecule observed with 3-hydroxymethyl and 3-acetoxymethyl analogues of **1**.[16] Complex **2** was formed instead, as unambiguously detected by the X-ray structure analysis. In **2**, Cu^{II} is coordinated to the ligand *via* two azomethine nitrogens, N4 and N14 and the five-fold coordination is completed by the lactam oxygen (O11) from the neighbouring molecule and two chlorine atoms. In this way, the complex molecules are connected into infinite chains in the crystal (Figure 2). The coordination sphere is a slightly distorted trigonal bipyramid, the base of which is formed by atoms N14, Cl2 and O11^{i}, whereas N4 and Cl1 are at the apical sites. Angle N4–Cu–Cl1 deviates from 180° [168.5(5)°], introducing a slight distortion of the polyhedron. The geometrical parameters defining the coordination sphere are summarised in Table III. The somewhat longer Cu–O distance [2.47(1) Å] is presumably a consequence of the steric effects, as well as of the Jahn-Teller distortion.

TABLE III. Selected geometry of the coordination sphere of the complex **2**; bond lengths / Å, angles / °

Bond		Angle	
Cu–Cl1	2.225(5)	Cl1–Cu–Cl2	96.4(2)
Cu–Cl2	2.215(7)	Cl1–Cu–N4	168.5(5)
Cu–N4	2.06(1)	Cl1–Cu–N14	95.3(5)
Cu–N14	2.04(2)	Cl1–Cu–O11^{i}	88.5(4)
Cu–O11^{i}	2.47(1)	Cl2–Cu–N4	93.6(5)
		Cl2–Cu–N14	136.4(5)
		Cl2–Cu–O11^{i}	127.3(4)
		N4–Cu–N14	81.1(6)
		N4–Cu–O11^{i}	81.0(5)
		N14–Cu–O11^{i}	94.8(6)

i) 0.5-*x*, 0.5+*y*, 0.5-*z*.

Supplementary Materials. – CCDC 182104 and CCDC 182105 contain supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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SAŽETAK

Sinteza i kristalne strukture 7-bromo-1,3-dihidro-1-metil-3(*S*)-metil-5-(2'-piridil)-2*H*-1,4-benzodiazepin-2-ona i njegova Cu^{II} kompleksa

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Miješanjem enantiomerno čistoga 7-bromo-1,3-dihidro-1-metil-3(*S*)-metil-5-(2'-piridil)-2*H*-1,4-benzodiazepin-2-ona, (+)-**1** s $CuCl_2 \cdot 2H_2O$ u smjesi apsolutnoga etanola i diklorometana pripravljen je kompleks dikloro-[7-bromo-1,3-dihidro-1,3-dimetil-5-(2'-piridil)-2*H*-1,4-benzodiazepin-2-on-*N*,*N*,*O*]bakar(II), (±)-**2**. U obje strukture, sedmeročlani benzodiazepinski prsten pojavljuje se u karakterističnoj konformaciji *čamca*. U kompleksu **2**, koji je izoliran kao racemični spoj, pojavljuje se lagano izobličena trigonska bipiramida. Bakar(II) je koordiniran s dva azometinska dušika, dva klorova atoma te s laktamskim kisikom iz susjedne molekule. Na taj način formira se beskonačni lanac međusobno povezanih poliedara. Kemijsko ponašanje liganda **1** nakon koordiniranja bakra uspoređeno je s ponašanjem njemu analognih 3-hidroksimetil- i 3-acetoksimetil-liganada.