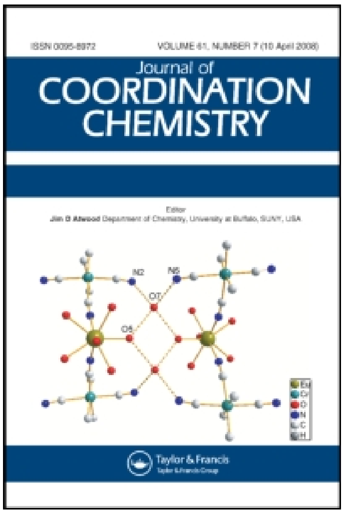

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COPPER(II) COMPLEXES OF 1-[*O*-ALLYLPHENOXY]-3-[ISOPROPYLAMINO]-2-PROPANOL (ALPRENOLOL)

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COPPER(II) COMPLEXES OF 1-[*O*-ALLYLPHENOXY]-3-[ISOPROPYLAMINO]-2-PROPANOL (ALPRENOLOL)

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Complexation of Cu(II) with the antihypertension drug Alprenolol (HAlp) under different conditions (metal/ligand ratios and solvents) results in the formation of two complexes – a binuclear green one, $Cu_2Alp_2Cl_2$ (1), and a mononuclear violet species $CuAlp_2 \cdot 2H_2O$ (2). Single crystals of (1) were isolated and its structure determined by X-ray diffraction. In the complex Alprenolol molecules are bidentately coordinated and each Cu atom is bound with NH, and bridged by the deprotonated OH group of the ligand to the second Cu centre. The chloride ions are coordinated to copper as terminal ligands. The mononuclear complex (2) was characterized using electronic and IR spectra, EPR, magnetochemical, calorimetric, thermogravimetric methods and elemental analysis. Copper is coordinated through O^- and N of OH and NH groups of the ligands in a distorted tetrahedral structure. The structure includes also two solvent molecules per $CuAlp_2$ unit.

Keywords: Copper complexes; Alprenolol; X-ray structure

INTRODUCTION

The essential metalloelements bound with proper bioligands like proteins, peptides *etc.*, are active participants and regulators of basic biological processes. For this reason any effect on their homeostasis, realized for

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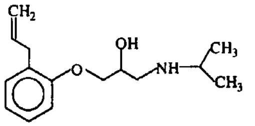
*Corresponding author.

example through complexation with other ligands, could result in physiological disturbances of different kinds. Thus in the last 10–15 years it was found that many widespread diseases such as gastric and duodenal ulcers, diabetes mellitus, arterial hypertension, collagenoses *etc.*, are copper and zinc dependent and are sensitive to factors that can affect the concentration levels of the two biometals (stress, hunger, changes in the concentration of metallothioneins and other bioligands, *etc.*) [1–7]. On the other hand most of the drugs used in the treatment of these diseases are mono, or most often, polydentate ligands, capable of strong bonding to these two metals. Recently it was hypothesized and proved in many cases that the effect of such drugs can be related (at least partially) to complexation with Cu and Zn [3, 6–9]. On that ground we initiated a systematic study on the complexation activity of antihypertensives of different kind (β-blockers, vasodilators, ACE-inhibitors, diuretics *etc.*) towards copper and zinc [9–17]. The next step of this study will be a comparison between the physiological effects of the complexes with that of the clean non-complexed drugs, a parallel for which at the moment we have preliminary, but quite stimulating, data.

The present work is dedicated to complexation of the β-blocker Alprenolol (I) with copper(II), isolation and characterization of the species formed and investigation of their basic properties and structures.



(I)

Alprenolol, 1-[*o*-allylphenoxy]-3-[isopropylamino]-2-propanol, like most of the β-blockers, is a phenoxyaminoalcohol, capable of forming a five-membered chelate ring with metal ions. Up to now no data are known for its capacity as a potential ligand, except for a very short note from 1983 in a Ukrainian pharmaceutical journal, mentioning that together with some other drugs it can form complexes with Mg^{2+}, Cu^{2+} and ATP [18].

EXPERIMENTAL

Materials and Syntheses

The ligand was obtained from Sopharma, Bulgaria, and used without any further purification, $CuCl_2 \cdot 2H_2O$ and CH_3OH, both of analytical grade, were supplied by Riedel E. de Haën AG.

The binuclear complex (1) was obtained at ambient temperature from a methanolic solution of the ligand (0.0714 g Alprenolol·HCl in 10 cm^3 of MeOH). Addition of Cu(II) (0.0426 g $CuCl_2 \cdot 2H_2O$ in 10 cm^3 of MeOH) and NaOH (0.0100 g in 10 cm^3 of MeOH) at a molar ratio of Cu: HAlp·HCl: NaOH = 1 : 1 : 1 resulted in the formation of a green solution from which after 20 days green microcrystals were formed. These were filtered off, washed with methanol and dried over P_2O_5 (yield ca. 23%). Found(%): C, 51.67;H, 6.23; N, 4.01; Cl, 10.11; Cu, 18.32%. Calc. for Cu_2 Alp_2Cl_2: C, 51.83; H, 6.38; N, 4.03; Cl, 10.21; Cu, 18.29.

The mononuclear complex (2) was obtained in the presence of a larger amount of the ligand in aqueous medium. An aqueous solution of Alprenolol.HCl (0.0714 g in 10 cm^3 of H_2O) was mixed with a solution of $CuCl_2 \cdot 2H_2O$ (0.0043 g in 1 cm^3 of H_2O) at molar ratio Cu: HAlp.HCl = 1 : 10. Dilute NaOH was added dropwise to pH ≈ 9. The violet precipitate which formed was filtered off, washed with water and dried first in air and then over P_2O_5 (yield ca. 18%). Found %:C, 59.77; H, 7.92; N, 4.58; Cu, 10.70%.Calc. for $CuAlp_2 \cdot 2H_2O$: C, 60.38; H, 8.11; N, 4.69; Cu, 10.66.

Apparatus and Analysis

IR spectra in the 4000–100 cm^{-1} range were recorded on a Perkin-Elmer model 893 spectrometer both in nujol and Csl, and the EPR spectra in the X-band on a Bruker ER 420 spectrometer. Electronic spectra were obtained on a Specord UV-VIS (Carl-Zeiss, Jena) instrument. The thermogravimetric study was performed using a Perkin-Elmer TGS-2 apparatus. Magnetic measurements were carried out in argon with a Faraday balance. Elemental analysis was performed according to classical methods: C, H were determined as CO_2 and H_2O, N through the Duma's method, chlorine by titration with $Hg(NO_3)_2$ after wet digestion of the sample, copper(II) after ignition of a sample, dissolution of the residue in dilute HNO_3 and titration with standard solution of EDTA using Murexide at pH 8 (ammonia buffer). X-ray diffraction was studied by an Enraf-Nonius CAD-4 diffractometer using MoKα radiation ($\lambda = 1.71073$ Å). A transparent green crystal of (1) was selected and mounted on the diffractometer. A hemisphere of 5873 reflections of which 1820 were independent was collected at room temperature using graphite-monochromated MoKα radiation. The structure was solved by direct methods and refined by least squares on F^2 (SHELXTL) [19]. First the Cu, Cl, N and O atoms were located and their positions refined isotropically. Next the C atoms were found and all atoms

TABLE I Crystal data and refinement details for the binuclear complex $Cu_2Alp_2Cl_2$

Empirical formula	$Cu_2C_{30}H_{44}N_2O_4Cl_2$	
Formula weight	694.68	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 7.5198(4)$ Å	
	$b = 26.1631(14)$ Å	$\beta = 95.84°(1)$
	$c = 8.6704(5)$ Å	
Volume, Z	1697.0(2) Å^3, 3	
Density (calculated)	1.359 g/cm^3	
Absorption coefficient	1.445 mm^{-1}	
$F(000)$	724	
Crystal size	0.25 × 0.20 × 0.18 mm	
Theta range for data collection	1.56 to 21.00 deg.	
Index ranges	$-9 <= h <= 10$ $-34 <= k <= 21$	$-11 <= l <= 11$
Reflections collected	5873	
Independent reflections	1820 [R (*int*) = 0.0232]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1820 / 0 /183	
Goodness-of-fit on F^2	1.067	
Final R indices [$I > 2\text{sigma}(I)$]	$R1 = 0.0334$	$wR2 = 0.0962$
R indices (all data)	$R1 = 0.0369$	$wR2 = 0.0984$
Extinction coefficient	0.0004(7)	
Largest diff. peak and hole	0.529 and -0.353 e Å^{-3}	

TABLE II Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3). $U(eq)$ is defined as one third of the trace of the orthogonalized Uij tensor

	x/a	y/b	z/c	$U(eq)$
Cu(1)	4489(1)	4996(1)	8300(1)	41(1)
Cl(1)	3420(2)	4465(1)	6455(1)	58(1)
O(1)	3824(4)	4685(1)	171(3)	56(1)
O(2)	808(4)	3630(1)	0471(3)	57(1)
N(1)	4891(4)	5609(1)	6986(3)	42(1)
C(1)	1683(7)	5760(2)	6428(9)	112(2)
C(2)	3208(5)	4197(2)	617(4)	50(1)
C(3)	6677(5)	5794(2)	7619(4)	47(1)
C(4)	1311(6)	4114(2)	9906(4)	55(1)
C(5)	5865(5)	2986(2)	9210(5)	60(1)
C(6)	7066(5)	2771(2)	316(5)	51(1)
C(7)	3424(5)	5997(2)	7014(5)	55(1)
C(8)	8727(5)	2984(1)	733(4)	42(1)
C(9)	6303(5)	3428(2)	8507(5)	59(1)
C(10)	7942(5)	3661(2)	8900(4)	53(1)
C(11)	9242(5)	3434(1)	2(4)	42(1)
C(12)	3755(8)	6468(2)	6076(6)	92(2)
C(13)	33(5)	2731(2)	1928(4)	54(1)
C(14)	1430(7)	2442(2)	1223(6)	80(2)
C(15)	1671(8)	1948(3)	1333(7)	104(2)

refined anisotropically. Finally the H atoms were refined using a riding model. Crystal data and refinement details are summarized in Table I, and the atomic coordinates of non-hydrogen atoms are given in Table II.

RESULTS AND DISCUSSION

Binuclear $Cu_2Alp_2Cl_2$ Complex (1)

X-ray Data and Structure

The asymmetric unit in (1), with 50% therminal ellipsoids, and with the atom numbering scheme is shown in Figure 1. In the structure all atoms occupy general positions. Each Cu atom is coordinated by two bridging O atoms of the deprotonated OH groups of two Alprenolol molecules, by one Cl and one N atom in a distorted tetrahedron. The Cu—O and Cu—N distances 1.926(2) and 2.007(3) Å, respectively, compare well with analogous distances reported for other similar copper complexes [9]. The distorted tetrahedral structure is supported also by the values 79.22(11) and 100.78(11)° for the angles O—Cu—O and Cu—O—Cu, respectively, in the Cu_2O_2 unit (Tab. III). The closest Cu—Cu separation between two adjacent dimers is 5.85Å along *c*, 7.52Å along *a* and 13.19Å along *b*, respectively.

Electronic Spectra

Methanolic solutions of (1) show absorbance at 700 nm ($\varepsilon = 971 \cdot mol^{-1} cm^{-1}$) and 377 nm ($\varepsilon = 1681 \cdot mol^{-1} cm^{-1}$). The first band is associated

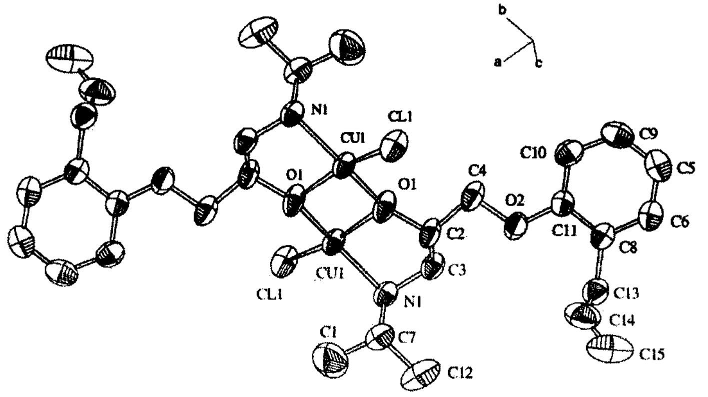


FIGURE 1 Structure of the asymetric unit of the binuclear complex $Cu_2Alp_2Cl_2$.

Table III Selected interatomic distances (Å) and bond angles (deg.)

Cu coordination			
Cu(1)—O(1)	1.926(2)	O(1)—Cu(1)—O(1)#1	79.22(11)
Cu(1)—O(1)#1	1.928(2)	O(1)—Cu(1)—N(1)	151.99(12)
Cu(1)#1—O(1)	1.928(2)	O(1)#1—Cu(1)—N(1)	85.33(11)
Cu(1)—Cl(1)	2.2085(10)	O(1)—Cu(1)—Cl(2)	103.73(8)
Cu(1)—Cu(1)#1	2.9694(8)	O(1)#1—Cu(1)—Cl(1)	159.30(10)
Cu(1)—N(1)	2.007(3)	N(1)—Cu(1)—Cl(2)	98.98(9)
		O(1)—Cu(1)—Cu(1)#1	39.64(7)
Alprenolol		O(1)#1—Cu(1)—Cu(1)#1	39.58(7)
O(1)—C(2)	1.425(4)	N(1)—Cu(1)—Cu(1)#1	121.32(8)
O(2)—C(11)	1.377(5)	Cl(1)—Cu(1)—Cu(1)#1	139.59(3)
O(2)—C(4)	1.422(4)	C(2)—O(1)—Cu(1)	136.6(2)
N(1)—C(3)	1.479(5)	C(2)—O(1)—Cu(1)#1	114.2(2)
N(1)—C(7)	1.501(5)	Cu(1)—O(1)—Cu(1)#1	100.78(11)

C—C, C—N and C—O range with in 1.305(7) – 1.523(5) Å C—H ranges within 0.9 – 1.1 Å.

with *d*–*d* transitions in Cu(II), while the second one at 377 nm is attributed to a ligand-to-metal charge-transfer when polynuclear copper(II) complexes with oxygen-bridged ligands are formed [15–17, 22, 23].

Magnetic Data

The temperature dependence of the magnetic susceptibility of (1) (Fig. 2a) is characteristic for a paramagnetic Cu(II) complex. The magnetic moment, calculated through $\mu_{eff} = 2.828\,(\text{æ}_M \cdot T - \Theta)\exp x\ 1/2$ for $\Theta = 100$ depends on temperature and corresponds to the theoretical values of μ_{eff} for tetrahedral coordination of Cu(II) (Fig. 3a). This is in accordance with results obtained

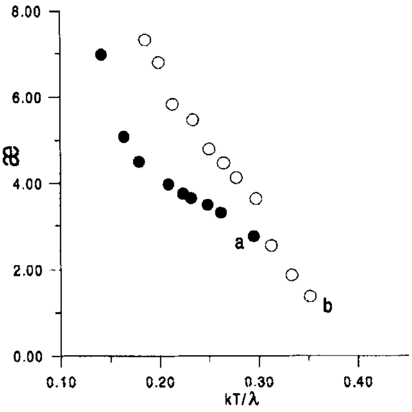


FIGURE 2 Temperature dependence of the magnetic susceptibility (a) for the binuclear complex (1) and (b) for the mononuclear complex (2).

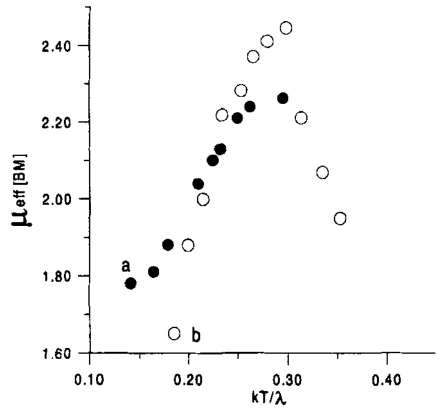


FIGURE 3 Temperature dependence of μ_{eff} (a) for the binuclear complex (1) and (b) for the mononuclear complex (2).

by other methods used. The magnetochemical data thus obtained clearly indicate the absence of any magnetic interaction between the Cu(II) paramagnetic centres both of intramolecular type in the framework of the Cu_2O_2 fragment or of intermolecular type between Cu dimers in the structure. The last possibility could be eliminated also by taking into account the large distances between the dimers found by the X-ray diffraction study.

EPR Spectra

In methanolic solution both at ambient temperature and at 110 K complex (1) shows only a weak signal at 3300 G with $g_{\|} = 2.20$ and $g_{\perp} = 2.03$, parameters typical for a normal paramagnetic copper(II) complex. Here again there is no indication of a measurable magnetic interaction between the Cu(II) centres.

IR Spectra

Alprenolol base shows absorption bands at 3250 cm^{-1} and 3050 cm^{-1} corresponding to ν(NH), a broad band in the 2600–2800 cm^{-1} range, attributed to (ν(NH_2^+)) and to intramolecular hydrogen bonds between OH and NH, and a band at 1580 cm^{-1} assigned to δ(NH). The coordination of NH in (1) is reflected by the shift of the corresponding bands in the complex to 3090 and 1600 cm^{-1} and by the disappearence of the band at 3250 cm^{-1}. Absorbance in the 2600–2800 cm^{-1} range practically disappears in the complex, an indication of coordination of NH. In the far-IR spectrum of the complex new bands at 520, 410 cm^{-1} and 250 cm^{-1} are observed, assigned to ν(Cu—N), ν(Cu—O) and ν(Cu—Cl), respectively [20].

Thermogravimetric Data

A thermogravimetric study over the 300 – 500 K range, showed no solvent molecules are present in the solid binuclear complex.

Mononuclear $CuAlp_2 \cdot 2H_2O$ Complex (2)

Electronic Spectra

In solution complex (**2**) shows absorption bands at 519 nm ($\varepsilon = 491 \cdot mol^{-1} cm^{-1}$) and 626 nm ($\varepsilon = 401 \cdot mol^{-1} cm^{-1}$) assigned to *d–d* transitions in Cu(II) engaged in Cu—N and Cu—O bonds. The position and the intensity of the bands observed are in accordance with known data for Cu(II) complexes of tetragonal symmetry [21, 22].

Magnetic Measurements

The temperature dependence of the magnetic susceptibility is typical of a mononuclear paramagnetic complex (Fig. 2b), but the Curie-Weiss law is not followed over the temperature range studied. At low temperatures the magnetic moment μ is temperature dependent and corresponds to tetrahedral coordination of copper(II) (Fig. 3b) but at higher temperatures (> 300 K) the μ-values differ markedly from theoretical. Most probably the deviation observed is due to a deformation of the tetrahedral structure to a nearly square-planar one, for which additional support was found also in the electronic and EPR spectra.

EPR Spectra

The solution of (**2**) at room temperature shows an isotropic spectrum with a resolved hyperfine structure from $^{63,65}Cu$ and parameters $g_{iso} = 2.101$, $A_{iso} = 82$ G at $H_{iso} = 3300$ G. The spectrum of the complex in the solid state at ambient temperatures exhibits an anisotropic signal with resolved SHFS from ^{14}N in the perpendicular region of the magnetic field due to the formation of Cu—N bonds. The EPR parameters ($g_{\parallel} = 2.22$, $g_{\perp} = 2.02$, $A_{\parallel} = 201$ G, $A_{\perp} = 23.8$ G, $A_N = 14$ G) provide additional evidence for the (assumed) nearly square-planar structure of (**2**). It is noted that an analogous change in structure was obtained in the case of the copper(II) complex of oxprenolol, another β-blocker with the same substituent in the *o*-position of the main aminoalcohol chain, responsible for complexation of Cu(II) [23]. The spectrum of (**2**) in frozen solution at 77 K is analogous to that of the solid complex described above.

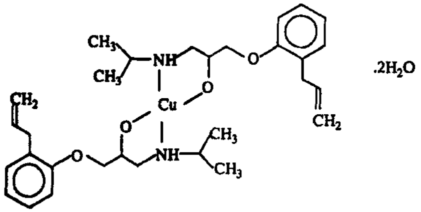
IR Spectra

Absorption bands at 3250 and 3050 cm^{-1} (ν(NH)) of the Alprenolol base are substituted by only one at 3090 cm^{-1} in the spectrum of (**2**). The band at 1580 cm^{-1} (δ(NH)) shifts to 1610 cm^{-1} in the complex and absorbance in the 2600–2800 cm^{-1} range (ν(NH_2^+)) practically disappears. The far-IR spectrum of the complex shows two new bands at 470 and 370 cm^{-1}, assigned to ν(Cu—N) and ν(Cu—O), respectively [20].

Thermogravimetric Data

Thermogravimetric study of the complex shows a reduction of sample weight by 6.00% in the temperature range 375–400 K. This correlates well with the expected value of 6.04%, corresponding to the elimination of two water molecules.

All experimental data obtained for (**2**) indicate bidentate coordination of two ligand molecules with copper(II), bound through NH and the deprotonated hydroxy group of the aminoalcohol fragment, shown in (II).



(II)

Two water molecules per mol of complex are also incorporated in the solid phase, as follows from the thermogravimetric investigation. It must be emphasized that an analogous mononuclear Cu(II) complex was synthesized with Effortil, another aminoalcohol of the same type [24]. The magnetochemical, EPR and spectroscopic parameters of the two complexes are practically identical and the Cu(II)-Effortil solid complex also contains two molecules of solvent (either H_2O or MeOH). The structure in this case (including the two solvent molecules) was firmly proven by X-ray diffraction. The analogy between all other experimental results in both cases gives additional support to the proposed structure (II).

Acknowledgements

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Supplementary data

Full lists of crystallographic data are available from the authors upon request.

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