PERGAMON

www.elsevier.nl/locate/poly

Polyhedron 19 (2000) 1843–1848

POLYHEDRON

Complexes of Cu(II) with α-[(ethylamino)methyl]-3-hydroxy, benzenemethanol (Effortil). Crystal structure of the mononuclear Cu(II) complex with Effortil

P.R. Bontchev [a,*], B.B. Ivanova [a], R.P. Bontchev [b], D.R. Mehandjiev [c], D.S. Ivanov [d]

[a] *Faculty of Chemistry, Sofia University, 1, J. Bourchier Boulevard, Sofia 1164, Bulgaria*
[b] *Department of Chemistry, University of Houston, Houston, TX 77204-5641, USA*
[c] *Institute of Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria*
[d] *Faculty of Pharmacy, Medical University-Sofia, Sofia, Bulgaria*

Received 22 February 2000; accepted 15 June 2000

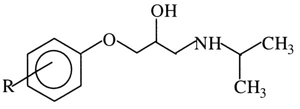
Abstract

The complexation processes between Cu(II) and the antihypotension drug Effortil (HEff) at different reaction conditions lead to the formation of two types of complex — a mononuclear violet one, $CuEff_2 \cdot 2CH_3OH$, and the binuclear green $Cu_2Eff_2Cl_2$. Monocrystals of the mononuclear $CuEff_2 \cdot 2CH_3OH$ complex were isolated and their structure determined by X-ray diffraction. Copper is coordinated through O^- and N of OH and NH groups from the ligands in a perfectly flat tetragon. The crystal structure also includes two solvent CH_3OH molecules per $CuEff_2$ unit. The $CuEff_2$ fragments are linked by hydrogen bonds. The binuclear $Cu_2Eff_2Cl_2$ complex was characterized using electronic and IR spectra, EPR, magnetochemical, calorimetric, thermogravimetric methods and elemental analysis. The complex contains bidentately bound monoanionic ligands and chloride ions. Each Cu atom is coordinated with NH, and bridged by the deprotonated OH group of Effortil with the second Cu center. The chloride ions are coordinated with copper as terminal ligands. © 2000 Elsevier Science Ltd. All rights reserved.

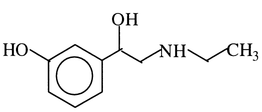
Keywords: Effortil; Cu(II) complexes; Structures; Stability constants; EPR; Magnetochemical data

1. Introduction

Recently it was assumed and found that arterial blood pressure is a process regulated by the biometals copper and zinc [1–4]. On the other hand, the drugs for treatment of arterial hypertension are effective ligands and it could be presumed that their action is at least partially related to complexation with the two metals, causing a shift in their homeostasis. From this point of view, we have already studied the complex formation between Cu(II) and different anti-hypertensives such as ACE-inhibitors [5], vasodilators [6] and diuretics [7,8]. Special attention was paid to the β-blockers [8–13], the drugs most widely used for this purpose, which represent aminoalcohols of type **I**, and differ by the substituent R in the phenyl ring.



(I)



(II)

It seems worth noting however, that one of the most efficient drugs used against arterial hypotension, Effortil, **II** also represents an aminoalcohol of the same type. It was interesting therefore, to study whether its behavior towards copper is analogous and why its effect on the blood pressure is just the opposite.

Hence, the aim of the present study was investigation of the complexation processes between copper(II) and Effortil.

---

* Corresponding author. Tel.: +35-92-628-323; fax: +35-92-962-5438.

E-mail address: prbontchev@chem.uni-sofia.bg (P.R. Bontchev).

0277-5387/00/$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.
PII: S0277-5387(00)00468-X

2. Experimental

2.1. Apparatus and analysis

The IR spectra in the 4000–100 cm^{-1} range were recorded on a Perkin–Elmer 893 spectrometer both in Nujol and CsI, the X-band EPR spectra on a Bruker ER 420 spectrometer and the electronic spectra were obtained on a Specord UV–Vis (Carl–Zeiss, Jena). The calorimetric and gravimetric studies were performed on DSC-2C and TGS-2 Perkin–Elmer equipment in argon. The magnetic measurements were carried out in argon atmosphere by the Faraday balance. The elemental analysis was performed according to the standard methods: C and 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) was determined after ignition of a sample, dissolution of the residue in diluted HNO_3 and titration with standard solution of EDTA using indicator Murexide at pH 8 (ammonia buffer). The potentiometric measurements were provided with aqueous solutions of ($Cu(ClO_4)_2 \cdot 6H_2O$) containing 5×10^{-4} Cu(II) and 1×10^{-3} mol dm^{-3} of Effortil base (HEff). Aliquots of these solutions with Cu–HEff molar ratio 1:2 were titrated with 9.95×10^{-3} mol dm^{-3} $HClO_4$ to obtain the stability constants. The ionic strength was adjusted to 0.1 mol dm^{-3} with $NaClO_4 \cdot H_2O$. Argon was bubbled through the samples to remove O_2 and CO_2 and for stirring the solution. Measurements were performed on a Radiometer PHM84 pH-meter with accuracy of ±0.001 pH units, equipped with a GK240C combined electrode and an ABU80 automatic burette for potentiometric titration. The stability constants were calculated by means of a general computation program (PSEQUAD) [14]. X-ray diffraction was studied on a monocrystal using an Enraf–Nonius CAD-4 diffractometer. A transparent violet crystal of $CuEff_2 \cdot 2CH_3OH$ was selected and mounted on an Enraf–Nonius CAD-4 diffractometer. A hemisphere of 1743 independent reflections, of which 1620 with $I > 2\sigma(I)$, was collected at r.t. using graphite monochromated Mo Kα radiation ($\lambda = 1.71073$ Å). The structure was solved by direct methods (SHELXTL) [15] and refined by least squares on F^2 (SHELX-96) [16]. First the Cu, N and O atoms were located according to the difference Fourier map and their positions refined isotropically. Next the C atoms were found and all the atoms refined anisotropically. Finally the H atoms were refined using a riding model. The main crystal and refinement data are listed in Table 1.

Table 1
Crystal data and structure refinement for the mononuclear complex $CuEff_2 \cdot 2CH_3OH$

Empirical formula	$Cu(C_{10}NO_2H_{14})_2 \cdot 2CH_3OH$
Formula weight	488.08
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$ (no. 14)
Unit cell dimensions	
a (Å)	7.7373(6)
b (Å)	13.5607(10)
c (Å)	11.7331(9)
α (°)	90
β (°)	99.1470(10)
γ (°)	90
Volume (Å^3)	1215.4(2)
Z	2
D_{calc} (g cm^{-3})	1.295
Absorption coefficient (mm^{-1})	0.935
$F(000)$	518
Crystal size (mm)	$0.20 \times 0.15 \times 0.10$
θ Range for data collection (°)	2.31–23.26
Index ranges	$-8 \le h \le 8$, $0 \le k \le 15$, $0 \le l \le 13$
Reflections collected	1743
Independent reflections	1743 [$R_{int} = 0.052$]
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	1743/0/143
Goodness-of-fit on F^2	1.139
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0442$, $wR_2 = 0.1267$
R indices (all data)	$R_1 = 0.0470$, $wR_2 = 0.1290$
Largest difference peak and hole (e Å^{-3})	0.634 and −0.269

2.2. Synthesis

The ligand was obtained from Sopharma, Bulgaria, $CuCl_2 \cdot 2H_2O$ and CH_3OH (both of analytical grade) were supplied by Riedel E. de Haën AG.

2.2.1. The mononuclear complex

HEff·HCl (0.0541 g) was dissolved in 10 ml methanol. The addition of 1 ml methanolic Cu(II) solution containing 0.0043 g $CuCl_2 \cdot 2H_2O$ and NaOH (0.0200 g in 20 ml methanol) at molar ratio Cu–HEff·HCl–NaOH = 1:10:20 leads to the formation of a violet solution from which a crystalline violet mononuclear complex was obtained after four months. It was filtered, washed with methanol and dried over P_2O_5. *Anal.* Found: C, 54.21; H, 6.97; N, 5.63; Cu, 12.01. Calc. for $CuEff_2 \cdot 2CH_3OH$: C, 54.36; H, 7.05; N, 5.76; Cu, 12.07%. The mononuclear complex was also obtained in aqueous solution, at excess of the ligand, Cu–HEff·HCl = 1:2–1:10 and pH 10.5.

The synthesis of the binuclear complex was realized using 0.0541 g HEff·HCl in 10 ml methanol, Cu(II) salt (0.0213 g $CuCl_2 \cdot 2H_2O$ in 5 ml methanol) and NaOH (0.0100 g in 10 ml methanol). The molar ratio was Cu–HEff·HCl–NaOH = 1:2:2. After three days a green precipitate was formed and it was filtered, washed with methanol and dried over P_2O_5. *Anal.* Found: C, 42.94; H, 5.00; N, 5.04; Cu, 22.61. Calc. for $Cu_2Eff_2Cl_2$: C, 43.02; H, 5.05; N, 5.02; Cu, 22.76%.

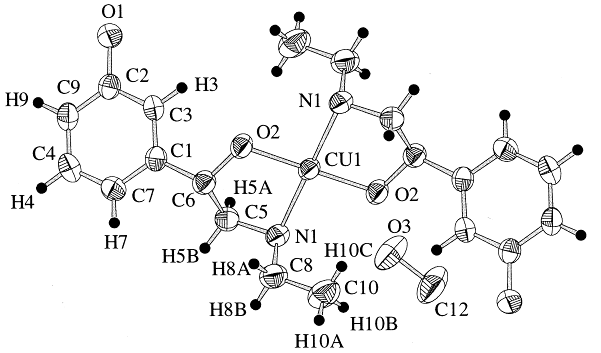


Fig. 1. The asymmetric unit and coordination of the copper atoms in $CuEff_2 \cdot 2CH_3OH$, 50% thermal ellipsoids.

Table 2
Selected bond lengths (Å) and angles (°) for $CuEff_2 \cdot 2CH_3OH$ [a]

Cu coordination		Effortil	
Cu(1)–O(2)	1.905(2)	C(8)–N(1)	1.489(5)
Cu(1)–O(2)	1.905(2)	C(5)–N(1)	1.484(4)
Cu(1)–N(1)	2.042(3)	C(2)–O(1)	1.370(4)
Cu(1)–N(1)	2.042(3)	C(6)–O(2)	1.412(4)
C–C range within 1.375(5)–1.528(5) Å			
O(2)–Cu(1)–O(2)	180.0		
O(2)–Cu(1)–N(1)	85.65(10)		
O(2)–Cu(1)–N(1)	94.35(10)		
O(2)–Cu(1)–N(1)	94.35(10)		
O(2)–Cu(1)–N(1)	85.65(10)		
N(1)–Cu(1)–N(1)	180.0		

[a] Symmetry transformation used to generate equivalent atoms: $1-x$, $-y+1$, $-z$.

3. Results and discussion

3.1. Mononuclear $CuEff_2 \cdot 2CH_3OH$ complex

3.1.1. X-ray data and crystal structure

The structure is shown in Fig. 1, and selected bond lengths and angles in Table 2.

In the structure the Cu atoms occupy one crystallographically independent special position. Each Cu atom is coordinated by two OH groups and two N atoms from two ligand molecules in a perfectly flat tetragon. The Cu–O and Cu–N distances (1.905 and 2.042 Å) and O–Cu–N angles (85.60 and 94.40°) are typical for a four-fold square coordination and compare well with the distances reported for similar copper complexes [17]. The $CuEff_2$ and the solvent methanol molecules are arranged in layers parallel to the *b*-axis. A complex network of hydrogen bonds links these layers in a 3D structure (Fig. 2). The closest Cu–Cu separation corresponds to the *a*-axis (7.737 Å) which clearly indicates that there is no direct magnetic interaction between the Cu centers in the structure. The C–C, C–N and C–O distances in the Effortil and methanol molecules range from 1.375 to 1.528 Å and the C–H distances are of the order 0.8–1.1 Å.

3.1.2. Electronic spectra

In methanolic solution the mononuclear complex shows an absorbence at 519 nm ($\varepsilon = 92$ l mol^{-1} cm^{-1}) and 626 nm ($\varepsilon = 75$ l mol^{-1} cm^{-1}). These data are in accordance with the assumption for the formation of Cu–N and Cu–O bonds. As a rule the first ones are

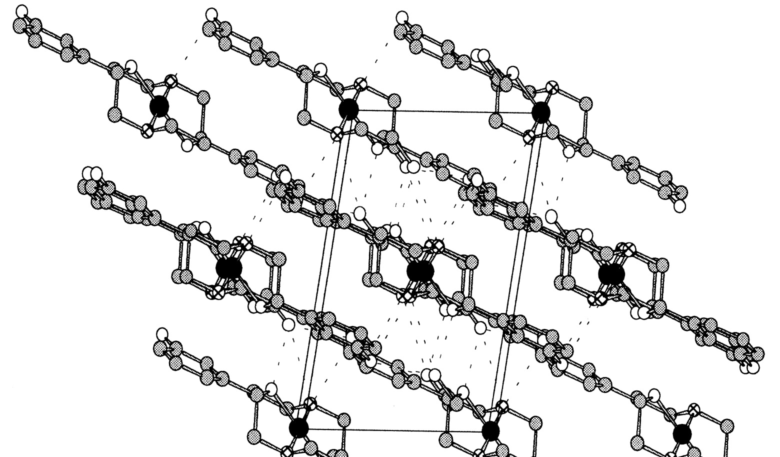


Fig. 2. The 3D structure of $CuEff_2 \cdot 2CH_3OH$, view along the *b*-axis. Copper, nitrogen, carbon and oxygen atoms are depicted as black, hatched, filled and open circles, respectively, hydrogen atoms are omitted for clarity. The hydrogen bonds are shown as dotted lines.

connected with absorbencies at wavelengths below 600 nm and the second type in the range 600–750 nm, but quite often these regions are not so strictly localized and separated. The position and the intensity of the bands observed are characteristic for Cu(II) complexes with a tetragonal geometry [18,19].

3.1.3. Magnetic measurements

The temperature dependence of the magnetic susceptibility is typical for a normal mononuclear paramagnetic complex (Fig. 3(a)), without any measurable exchange interaction between the Cu(II) centers. The Curie–Weiss law is not obeyed in the temperature range studied and in such conditions the magnetic moment was calculated using the equation $\mu_{\mathrm{eff}} = 2.828(\kappa_{\mathrm{M}}T - \theta)^{1/2}$; $\theta = -80$. At low temperatures, the magnetic moment μ is temperature dependent and corresponds to a tetrahedral coordination of copper(II) (Fig. 4) but at higher temperatures (>253 K), the μ-value differs from the theoretical one. Most probably the deviation observed is due to a deformation of the tetrahedral structure to a nearly square-planar one, a fact supported by the obtained EPR data, is also observed in other similar complexes [10,11] and is directly confirmed in the present work by X-ray diffraction data.

3.1.4. EPR spectra

The methanolic solution of the complex at room temperature shows an isotropic spectrum with a resolved hyperfine structure from ^{63,65}Cu and parameters $g_{\mathrm{iso}} = 2.103$, $A_{\mathrm{iso}} = 86$ at $H_{\mathrm{iso}} = 3300$ G. The spectrum of the same solution at 77 K exhibits an anisotropic signal with an additional resolved SHFS from ^{14}N in the perpendicular region of the magnetic field due to the formation of Cu–N bonds. The EPR parameters ($g_{//} = 2.23$, $g_{\perp} = 2.07$, $A_{//} = 204$, $A_{\perp} = 24$, $A_{\mathrm{N}} = 14$ G) are typical for Cu(II) complexes with a nearly square-planar symmetry. The EPR data for the solid state complex at ambient temperature are analogous to those for frozen solutions at 77 K as in other similar cases [10,11,13].

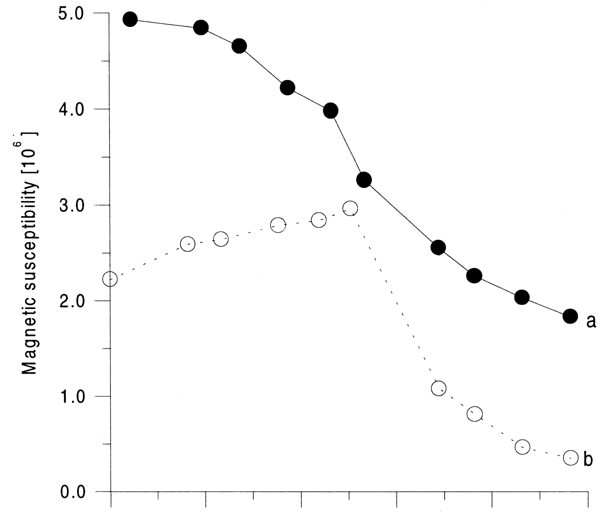


Fig. 3. Magnetic susceptibility vs. T for (a) mononuclear complex CuEff$_2$·2CH$_3$OH and (b) binuclear Cu$_2$Eff$_2$Cl$_2$ complex.

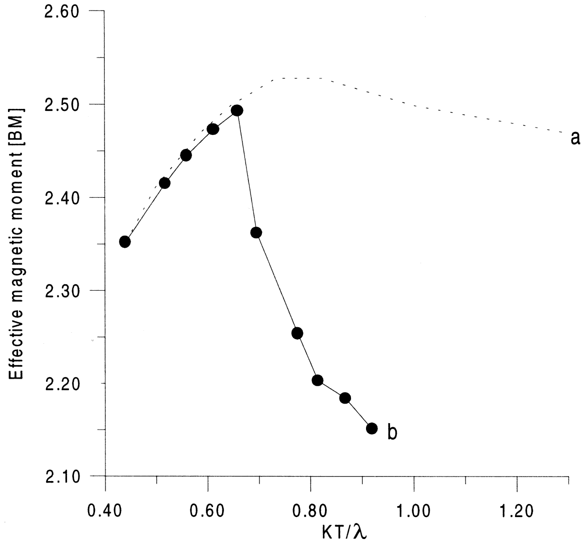


Fig. 4. Graphs μ_{eff} vs. T for the monouclear complex (a) theoretical dependence for a tetrahedral Cu(II) complex; (b) experimental data ($\theta = -80$).

3.1.5. IR spectra

The Effortil base shows absorption bands at 3450 and 3200 cm^{-1} corresponding to ν(OH) and ν(NH), a broad band in the 2600–2800 cm^{-1} range, that can be attributed to $\nu(\mathrm{NH}_2^+)$ and a band at 1600 cm^{-1} assigned to δ(NH). In the complex the band at 3450 cm^{-1} is observed with a low intensity, as a result of OH group deprotonation in the aminoalcohol fragment and the presence of CH$_3$OH. The coordination of NH follows from the shift of the bands of the complex to 3180 and 1650 cm^{-1}. The absorbence in the 2600–2800 cm^{-1} range practically disappears in the complex, which is also an indication for coordination of NH. In the far IR spectrum of the complex, new bands at 475 and 370 cm^{-1} are observed, corresponding to ν(Cu–N) and ν(Cu–O) respectively [20].

3.1.6. Calorimetric and thermogravimetric data

The thermogravimetric study of the complex shows a reduction of the sample weight with about 13.20% in the temperature range 350–430 K. This fact correlates well with the expected value of 13.17% that corresponds to the elimination of two methanol molecules. It is also supported by the DSC data obtained (Fig. 5) showing an endothermic effect at about 400 K, with an enthalpy change of 13.3 cal g^{-1}. The value is higher than the expected one, probably due to another endothermic process at the same temperature interval, indications for which are observed in the DSC curve in Fig. 5.

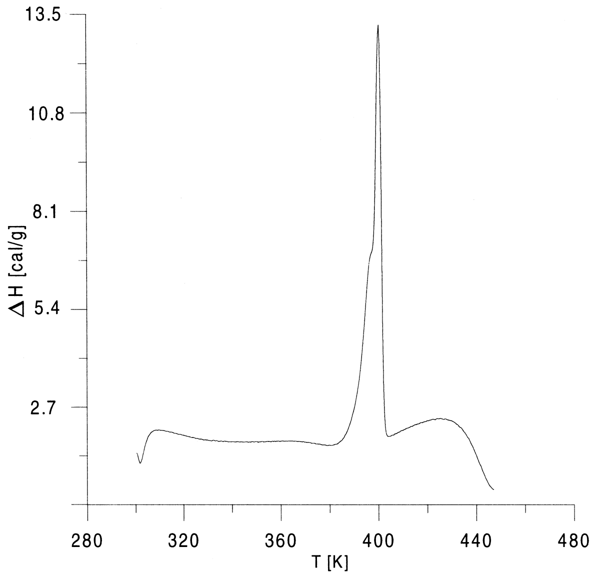


Fig. 5. DSC data for the mononuclear complex CuEff$_2$·2CH$_3$OH.

3.1.7. Dissociation and stability constant

The dissociation (acidity) constant of Effortil using a free base was determined as p$K_a = 8.83 \pm 0.09$. For a molar ratio Cu–HEff = 1:2, two stability constants were calculated: $lg\beta_1[\mathrm{Cu(Eff)}]^+ = 5.52 \pm 0.05$; $lg\beta_2[\mathrm{Cu(Eff)_2}] = 10.55 \pm 0.04$.

Two Effortil molecules are coordinated to Cu(II), consequently forming the complexes $[\mathrm{Cu(Eff)}]^+$ and $[\mathrm{Cu(Eff)_2}]$.

3.2. Binuclear complex — Cu$_2$Eff$_2$Cl$_2$

3.2.1. Electronic spectra

The methanolic solution of the green complex shows absorbance at 700 nm ($\varepsilon = 96$ l mol^{-1} cm^{-1}) and 385 nm ($\varepsilon = 106$ l mol^{-1} cm^{-1}). The first band is associated with d–d transitions in Cu(II), engaged in Cu–O bonds. The second band at 385 nm is attributed to a ligand-to-metal charge-transfer when a polynuclear copper(II) complex with oxygen-bridge ligand is formed [10,11,13]. It is interesting to notice that in such binuclear complexes, with both Cu–N and Cu–O bonds there is usually no separate bond at $\lambda < 600$ nm, typical for Cu–N bond, but only one broad complex band at 600–700 nm [9–13,22].

3.2.2. Magnetic data

The temperature dependence of the magnetic susceptibility (Fig. 3(b)) is typical for cases of antiferromagnetic exchange interaction between copper(II) centers (see for example [21]). In complexes of that type, the intramolecular antiferromagnetism leads first to an increase of the magnetic susceptibility to a maximum (at the Neel's temperature) and then it decreases as a result of disturbance of the exchange interaction. At high temperatures the complex exhibits a normal paramagnetic character.

These results are in accordance with the other spectral and EPR data indicating the formation of binuclear species in this case, namely the EPR signals at lower and higher fields (1350 and 5470 G, respectively) and the absorbence at 385 nm in the electronic spectra as well.

3.2.3. EPR spectra

In methanolic solution at room temperature, the complex is EPR silent. The spectrum of the same solution at 77 K shows a weak signal at 3300 G and two signals at 1350 and 5470 G. The last two signals are connected with an antiferomagnetic coupling between Cu(II) centers in bi- and polynuclear structures [22]. The spectrum of the solid phase complex shows the same signals as the frozen solution. Similar EPR spectra for Cu(II) complexes with a nearly square-planar geometry were already reported [10,13].

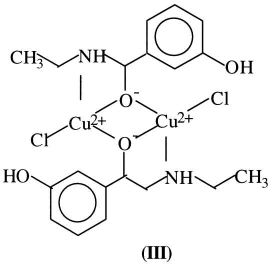
3.2.4. IR spectra

The absorption bands at 3450 and 3200 cm^{-1} (ν(OH) and ν(NH)) of the Effortil base are transformed into one broad band at 3400–3250 cm^{-1} in the spectrum of the complex. The band at 1600 cm^{-1} (δ(NH)) shifts to 1620 cm^{-1} in the complex and the absorbance in the 2600–2800 cm^{-1} range ($\nu(\mathrm{NH}_2^+)$) practically disappears. The far IR spectrum of the complex shows three new bands at 538, 420 and 251 cm^{-1} assigned to ν(Cu–N), ν(Cu–O) and ν(Cu–Cl), respectively [20].

3.2.5. Calorimetric and thermogravimetric data

The calorimetric and thermogravimetric studies were provided in the 300–500 K range. The results obtained have shown that no solvent molecules are present in the structure of the solid binuclear green complex.

All data obtained for the Cu$_2$Eff$_2$Cl$_2$ complex indicate that they are similar to those for the analogous binuclear Cu(II) complexes of pindolol and oxprenolol, studied by X-ray diffraction [12,13,23]. On the grounds of all these considerations, structure **III** was suggested for the Cu$_2$Eff$_2$Cl$_2$ binuclear complex **III**.



(III)

4. Discussion

Effortil forms two types of complex, depending on the solvent and the metal-to-ligand molar ratio. At excess of the ligand, the mononuclear soluble violet complex $Cu(Eff)_2 \cdot 2CH_3OH$ was formed in alkaline methanolic solution, from which the neutral complex very slowly spontaneously precipitated.

The violet complex, however, was obtained in aqueous alkaline solution in a soluble form only, a fact indicating that most probably in such conditions it includes hydroxyl ions instead of solvent molecules and the charged complex thus formed remains in solution. The negative charge of this complex was confirmed by its sorption on anionite (Amberlite IRA-400, Merck). That was the reason for isolating the mononuclear complex in a solid phase only from methanol.

On the other hand the binuclear complex is formed at compatible amounts of the metal and the ligand (1:1–1:2) and only in alkaline methanolic media. In this case, the deprotonated oxygens of the two coordinated ligands act as bridges between the two copper atoms in the framework of the binuclear complex. Each Cu atom is bound also with NH from one ligand, thus forming a chelate ring with one Cl^- present as a terminal ligand. This configuration of the binuclear complex was already proved by us with different methods, including X-ray diffraction for Cu(II) complexes of some β-blockers with similar chemical composition and structure [23]. Unfortunately, in the present case we were unable to obtain crystals of proper size for X-ray study.

The mononuclear violet complex precipitated from methanolic solution can be transformed slowly in excess of the ligand into the green binuclear one after addition of proper amount of Cu(II) in the solution. The reciprocal process, however, is much slower and occurs only partially when excess of Heff is added to the solvent containing the green precipitate. These experiments show that the two complexes can be transformed into each other by changing the reaction conditions in an appropriate way.

5. Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Centre, CCDC No. 140618. Copies of this information may be obtained free of charge from The Director, CCDC 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors greatly acknowledge the financial support given by the National Research Fund of Bulgaria.

References

[1] L.M. Klevay, Biol. Trace Elem. Res. 5 (1983) 245.

[2] D. Gantenand and E. Ritz (Eds.), Lehrbuch der Hypertonie: Pathophysiologie, Klinik, Therapie, Epidemiologie, Schattauer, Frankfurt, 1985, p. 628.

[3] Ch. Nachev, Dr. Sci. Diss., Medical Academy, Sofia, 1988.

[4] B. Sarkar, in: H.G. Seiler, H. Sigel (Eds.), Handbook on Toxicity of Inorganc Compounds, Marcel Dekker, New York, 1988.

[5] P.R. Bontchev, G. Gochev, B. Evtimova, H. Kadum, Ch. Nachev, J. Inorg. Biochem. 46 (1992) 23.

[6] P.R. Bontchev, Ch. Nachev, B. Evtimova, N.D. Yordanov, E. Zhecheva, D.R. Mehandjiev, Proceedings of the 12th Conference Coordinate Chemistry, Smolenice, CSSR, 1989, pp. 47–52.

[7] P.R. Bontchev, H. Kadum, G. Gochev, B. Evtimova, J. Macicek, Ch. Nachev, Polyhedron 11 (1992) 1973.

[8] P.R. Bontchev, B. Ivanova, K. Koicheva, Proceedings of the Fifth International Symposium on Applied Inorganic and Bioinorganic Chemistry, Corfu, Greece, 1999.

[9] P.R. Bontchev, H. Kadum, B. Evtimova, Ch. Nachev, E. Zecheva, D. Mehandjiev, D. Ivanov, J. Inorg. Biochem. 48 (1992) 153.

[10] I. Pantcheva, P.R. Bontchev, Ch. Nachev, in: G. Ondrejovic, A. Sirota (Eds.), Progress in Coordination and Organometallic Chemistry, Slovac Technical University Press, Bratislava, 1997, pp. 209–214.

[11] P.R. Bontchev, I. Pantcheva, B.B. Ivanova, D. Mehandjiev, Bulg. Chem. Commun. 31 (1999) 59.

[12] P.R. Bontchev, in: G. Ondrejovic, A. Sirota (Eds.), Coordination Chemistry at the Turn of the Century, Slovac Technical University Press, Bratislava, 1999, pp. 53–66.

[13] P.R. Bontchev, I. Pantcheva, B.B. Ivanova, Proceedings of the Fifth International Symposium on Applied Inorganic and Bioinorganic Chemistry, Corfu, Greece, 1999.

[14] D.J. Leggett, Computational Methods for the Determination of Formation Constants, Plenum, New York, 1985, p. 291.

[15] G.M. Sheldrick, SHELXTL, Version 5.03, Siemens Analytical X-ray Instruments, Madison, WI, 1995.

[16] G.M. Sheldrick, SHELX-96, Program for Crystal Structure Determination, University of Göttingen, Germany, 1996.

[17] M. Melnik, M. Kabesova, M. Dunaj-Jurco, C.E. Holloway, J. Coord. Chem. 41 (1997) 35.

[18] E.I. Solomon, W.P. Kevin, E.W. Dean, Structure and Bonding, Springer–Verlag, Berlin, 1983, p. 3.

[19] C. Oldham, in: G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, vol. 5, Pergamon, Oxford, 1987, p. 663.

[20] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th ed., Wiley, New York, 1997.

[21] F.E. Mabbs, D.J. Machin, Magnetism and Transition Metal Complexes, Chapman and Hall, London, 1973, p. 172.

[22] P.R. Bontchev, I. Pantcheva, G. Gochev, D. Mehandjiev, D. Ivanov, Trans. Met. Chem. 25 (2000) 196.

[23] P.R. Bontchev, Proceedings of the Fifth International Symposium on Applied Inorganic and Bioinorganic Chemistry, Corfu, Greece, 1999.