

# A New Copper(II) Complex with the N,N'-Bis(antipyryl-4-methyl)-piperazine (BAMP) Ligand: [Cu(BAMP)](ClO<sub>4</sub>)<sub>2</sub>

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The synthesis of the Mannich base N,N'-bis(antipyryl-4-methyl)-piperazine (BAMP) (**1**), its crystal structure as well as the synthesis and the crystal structure of the copper complex Cu(BAMP)(ClO<sub>4</sub>)<sub>2</sub> (**2**) are reported. C<sub>28</sub>H<sub>34</sub>N<sub>6</sub>O<sub>2</sub> · 4H<sub>2</sub>O (BAMP · 4H<sub>2</sub>O) crystallizes with triclinic symmetry, space group *P*1̄, lattice parameters: *a* = 704,9(2), *b* = 983,4(2), *c* = 1198,9(3) pm,  $\alpha = 68,72^\circ$ ,  $\beta = 73,62^\circ$ ,  $\gamma = 78,49^\circ$ . The copper-complex Cu(BAMP)(ClO<sub>4</sub>)<sub>2</sub> crystallizes with tetragonal symmetry, space group *P*4<sub>2</sub>/*n*, lattice parameters: *a* = 2295,1(3), *c* = 1412,2(2) pm. The copper(II) atom is five-coordinate by the two nitrogen atoms belonging to the piperazine ring and the oxygen atoms of the antipyryne moieties. The geometry of the copper(II) atom can be described as a square-based pyramid with the N<sub>2</sub>O<sub>2</sub> donor atoms of BAMP forming the basal plane and an oxygen atom of the neighbouring complex molecule occupying the apical position. BAMP acts as a tetradentate ligand, which incorporates a piperazine-fused ring. The structural parameters illustrate well the reinforcing effect exerted by the double "straps" of the piperazine molecule.

## Introduction

In 1912, Mannich and Krösche [1] discovered the property of formaldehyde to bind an amine with a carbon acid via a methylene bridge. The method has since been extended and is increasingly used in preparative chemistry providing an enormous pool of information for synthetic chemists [2, 3]. The molecules obtained, Mannich bases, are primary, secondary or tertiary amines, depending on the nature of the starting amine. The carbon acids contain an  $\alpha$  hydrogen atom activated by a carbonyl or a hydroxyl group so that except for the amine, the Mannich base contains another potential donor atom close to a chelate ring with a metal ion. The preorganising ability is increased if the Mannich base is obtained from a diamine or a diacid. In these cases a potential dinucleating ligand can be obtained.

Mannich type reactions in the presence [4, 5] or absence [6] of metal ions are well developed. These kinds of ligands have been designed with the aim to obtain binuclear metal complexes with special mag-

netic and redox properties [6]. Some complexes can be considered as models of iron or copper biosites [7], and Mannich bases with a polymeric structure have been used as selective ion exchangers [8].

Mannich bases obtained from antipyryne and its derivatives have been prepared with the aim to obtain antipyretic and analgesic compounds [9]. Their complexes with certain metal ions, including Pt(II) and Co(II) ions, have been shown to act as antitumor agents [10 - 14]; the formation of these complexes with some oligoelements may explain their pharmaceutical activity. In this respect, complexes of some first row metal ions with ligands containing the antipyryne moiety N,N'-bis(4-antipyrylmethyl)-piperazine (BAMP) have been studied [15 - 18], and some of them have been demonstrated to exhibit antitumor activity *in vitro* [19].

As a continuation of the work in this field, we report here on the synthesis of a new complex of copper(II) with BAMP, and on its structure and its spectroscopic characterisation. The structure of the ligand BAMP is also discussed.

	BAMP · 4H <sub>2</sub> O (1)	Cu(BAMP)(ClO <sub>4</sub> ) <sub>2</sub> (2)
Empirical formula	C <sub>28</sub> H <sub>42</sub> N <sub>6</sub> O <sub>6</sub>	C <sub>28</sub> H <sub>34</sub> N <sub>6</sub> O <sub>10</sub> Cl <sub>2</sub> Cu
Crystal system	triclinic	tetragonal
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> 4 <sub>2</sub> / <i>n</i> (no. 86)
<i>a</i> [pm]	704.9(2)	2295.1(3)
<i>b</i> [pm]	983.4(2)	
<i>c</i> [pm]	1198.9(3)	1412.2(2)
$\alpha$ [deg]	68.72(2)	
$\beta$ [deg]	73.62(2)	
$\gamma$ [deg]	78.49(2)	
Volume [nm <sup>3</sup> ]	0.7386(3)	7.4390(14)
<i>Z</i>	1	8
Formula mass [g mol <sup>-1</sup> ]	558.68	749.05
$\rho_{\text{calc}}$ [g cm <sup>-3</sup> ]	1.256	1.338
$\mu$ [mm <sup>-1</sup> ]	0.089	0.787
Absorption correction	numerical	numerical
Transmission max / min	0.7455 / 0.9279	0.8217 / 0.9580
$\theta$ Range [°]	2.24 - 24.99	1.69 - 24.00
Collected reflections	11953	58001
Index range	-10 ≤ <i>h</i> ≤ 9, -14 ≤ <i>k</i> ≤ 14, -17 ≤ <i>l</i> ≤ 17	-26 ≤ <i>h</i> ≤ 26, -26 ≤ <i>k</i> ≤ 26, -15 ≤ <i>l</i> ≤ 15
Unique reflections	2609	5714
Observed data [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	1127	2505
Diffractometer	STOE Image Plate Diffraction System	
Radiation	Mo-K $\alpha$ (Graphit-Monochromator, $\lambda$ = 71.073 pm)	
Temperature [K]	293	170
<i>R</i> <sub>merg</sub>	0.1251	0.2100
<i>R</i> Indexes [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0463 <i>wR</i> <sub>2</sub> = 0.0412	<i>R</i> <sub>1</sub> = 0.1015 <i>wR</i> <sub>2</sub> = 0.2366
<i>R</i> Indexes (all data)	<i>R</i> <sub>1</sub> = 0.1390 <i>wR</i> <sub>2</sub> = 0.0535	<i>R</i> <sub>1</sub> = 0.1858 <i>wR</i> <sub>2</sub> = 0.2526
Goodness of fit ( <i>S</i> <sub>obs</sub> )	0.946	2.484
Goodness of fit ( <i>S</i> <sub>all</sub> )	0.740	1.673
No. of variables	266	419
<i>F</i> (000)	300	3096
Largest difference map Hole / peak [e 10 <sup>-6</sup> pm <sup>-3</sup> ]	-0.136 / 0.128	-0.479 / 1.804

Table 1. Crystal data and structure refinement parameters for BAMP · 4H<sub>2</sub>O (1) and Cu(BAMP)(ClO<sub>4</sub>)<sub>2</sub> (2).

## Experimental Section

All chemicals have been purchased from commercial sources and used without further purification. Analytical data were obtained by a Perkin-Elmer Model 240C elemental analyser. Electronic spectra were recorded on a Perkin Elmer Lambda 12 spectrophotometer, IR spectra by using KBr pellets on a BIO-RAD FTS 135 spectrometer.

C<sub>28</sub>H<sub>34</sub>N<sub>6</sub>O<sub>2</sub> · 4H<sub>2</sub>O (BAMP) (1) has been obtained according to the Mannich synthesis under the experimental conditions published earlier [9]. Crystals suitable for structural analysis were obtained by slow evaporation of the solvent. Yield: 87%. – UV/vis (C<sub>2</sub>H<sub>5</sub>OH):  $\lambda_{\text{max}}$  ( $\lg \epsilon$ ) = 240 nm (14 000), 257 nm (20 513). – IR (KBr): 2950, 2910, 2805, 2766, 1669, 1620, 1595, 1492, 1454, 1429, 1371, 1346, 1315, 1298, 1284, 1271, 1172, 1153,

1129, 1098, 1006, 995, 945, 800, 764, 703, 655, 640 cm<sup>-1</sup>. – Far IR (polyethylene): 587, 505, 499, 458, 431, 401, 360, 340, 292, 283, 269, 175, 155 cm<sup>-1</sup>. – Raman : 2952, 2927, 2806, 2765, 1668, 1620, 1604, 1589, 1491, 1456, 1445, 1411, 1352, 1312, 1296, 1288, 1271, 1172, 1153, 1129, 1101, 1089, 1003, 994, 949, 798, 773, 756, 704, 640, 607, 590, 507 cm<sup>-1</sup>. – C<sub>28</sub>H<sub>42</sub>N<sub>6</sub>O<sub>6</sub> (558.68): calcd. C 60.20, H 7.58, N 15.04; found C 60.13, H 7.77, N 14.96.

Cu(BAMP)(ClO<sub>4</sub>)<sub>2</sub> (2): 0.5 g (1 mmol) of BAMP dissolved in 20 ml of ethanol was poured dropwise into a solution containing 0.37 g (1 mmol) of Cu(ClO<sub>4</sub>)<sub>2</sub> · 6 H<sub>2</sub>O in 10 ml of ethanol under vigorous stirring at 40 °C. The reaction mixture was stirred for an additional 30 min at 60 °C. After cooling to room temperature, a light blue microcrystalline precipitate of the complex was collected by filtration, washed with ethanol and dried over CaCl<sub>2</sub>

Table 2. Selected interatomic distances [Å] and angles [deg] for the compounds BAMP · 4 H<sub>2</sub>O (**1**) and Cu(BAMP)(ClO<sub>4</sub>)<sub>2</sub> (**2**)

<i>BAMP · 4H<sub>2</sub>O</i> :			
O1-C14	1.250(3)	N1-C3	1.480(3)
C3-C4	1.498(4)	C4-C14	1.430(4)
C4-C5	1.356(4)	C5-N2	1.374(3)
N2-N3	1.412(3)	N3-C14	1.390(3)
N1-C1-C2	110.9(2)	N1-C2-C1	109.5(2)
C1-N1-C2	108.8(2)	C1-N1-C3	110.8(2)
C2-N1-C3	108.4(2)	O1-C14-C4	131.0(2)
C3-C4-C14	124.9(3)		
<i>Cu(BAMP)(ClO<sub>4</sub>)<sub>2</sub></i> :			
Cu1-O1	2.005(8)	Cu1-O2	1.933(8)
Cu1-N1	2.036(10)	Cu1-N2	2.040(10)
Cu1-O1'	2.372(8)	O1-C28	1.309(14)
N1-C5	1.483(14)	C5-C6	1.500(20)
C6-C28	1.410(20)	C6-C7	1.370(20)
C7-N3	1.340(20)	N3-N4	1.363(13)
N4-C28	1.355(14)	O2-C27	1.263(14)
N2-C16	1.480(20)	C16-C17	1.470(20)
C17-C27	1.440(20)	C17-C18	1.350(20)
C18-N6	1.380(20)	N6-N7	1.340(14)
N7-C27	1.364(15)		
O2-Cu1-O1	90.0(3)	O2-Cu1-N1	165.2(4)
O1-Cu1-N1	96.9(4)	O2-Cu1-N2	97.0(4)
O1-Cu1-N2	168.0(4)	N1-Cu1-N2	74.2(4)
N2-C3-C4	108.9(10)	N1-C4-C3	107.0(10)
C2-N2-C3	106.6(10)	C2-N2-C16	112.2(10)
O1-C28-C6	130.2(10)	C28-C6-C5	122.9(10)
O2-C27-C17	131.9(10)	C27-C17-C16	122.2(10)

in air. The product was recrystallised from ethanol : acetonitrile (1 : 1) as light blue crystals suitable for X-ray analysis. Yield: 0.57 g (76.1 %). – UV/vis (CH<sub>3</sub>CN): λ<sub>max</sub> (lg ε) = 378 nm (656), 670 nm (225). – UV/vis (solid): λ<sub>max</sub> = 660 nm. – A<sub>M</sub> (CH<sub>3</sub>CN): 234 Ω<sup>-1</sup>mol<sup>-1</sup>cm<sup>2</sup>. – IR (KBr): 1599, 1561, 1495, 1457, 1438, 1384, 1347, 1324, 1274, 1174, 1120, 1106, 1088, 768, 701, 660, 636, 624, 596 cm<sup>-1</sup>. – Far IR (polyethylene): 596, 551, 534, 509, 474, 431, 419, 400, 361, 338, 292, 288, 268, 173 cm<sup>-1</sup>. – C<sub>28</sub>H<sub>34</sub>N<sub>6</sub>Cl<sub>2</sub>CuO<sub>10</sub> (749.06): calcd. C 44.90, H 4.58, N 11.22, Cl 9.47, Cu 8.48; found C 44.63, H 4.77, N 10.98, Cl 9.24, Cu 8.34.

#### X-ray crystallography

A suitable single crystal of each compound was carefully selected under a polarizing microscope and mounted in a glass capillary. The scattering intensities were collected with an imaging plate diffractometer (IPDS - I / IPDS - II, STOE & CIE) equipped with a normal focus, 1.75 kW, sealed tube X-ray source (Mo-K<sub>α</sub>, λ = 0.71073 Å) operating at 50 kV and 35 mA. Intensity data

for **1** were collected at room temperature by ω-scans in 230 frames (0 ≤ ω ≤ 180°, ψ = 0°; 0 ≤ ω ≤ 180°, ψ = 90°; 0 ≤ ω ≤ 100°, ψ = 135°; Δω = 2°, exposure time 4 min).

Intensity data for **2** were collected at 170 K by ψ-scans in 125 frames (0 ≤ ψ ≤ 250°, Δψ = 2°, exposure time 4 min). Structure solution and refinement were carried out using the programs SHELXS-97 [20] and SHELXL-93 [21]. The H atom positions for **1** were taken from the difference Fourier card at the end of the refinement. The hydrogen atoms in **2** were placed geometrically and held in the riding mode. The perchlorate anions and one of the aromatic rings (C21 to C26) in **2** show high atomic displacement parameters due to a severe disorder. A numerical absorption correction was applied after an optimisation of the crystal shape (X-RED [22] and X-SHAPE [23]). The last cycles of refinement included atomic positions for all atoms, anisotropic displacement parameters for all non-hydrogen atoms and isotropic displacement parameters for all hydrogen atoms. Details of the refinements are given in Table 1. Selected bond distances and angles are presented in Table 2. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-184326 (**1**) and CCDC-184327 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

#### Results and Discussion

The tetradentate ligand BAMP (**1**) was obtained by condensation of antipyrine with formaldehyde and piperazine following a Mannich procedure. BAMP has two groups of donor atoms situated on each side of the piperazine bridge consisting of a carbonyl oxygen and a piperazine nitrogen atom. The donor properties, the relatively flexible / rigid structure and the symmetry of BAMP offer the opportunity to prepare mono- and dinuclear complexes, the nature of its metal complexes depending on the conformation of the piperazine molecule. Thus, homo- and hetero-dinuclear complexes of the general type MM'(BAMP) can be obtained if the piperazine bridge adopts a distorted “chair” conformation. BAMP will act as a tetradentate ligand through its N<sub>2</sub>O<sub>2</sub> donor atom set if the piperazine bridge adopts the “boat” conformation, thus generating mononuclear complexes. The most stable

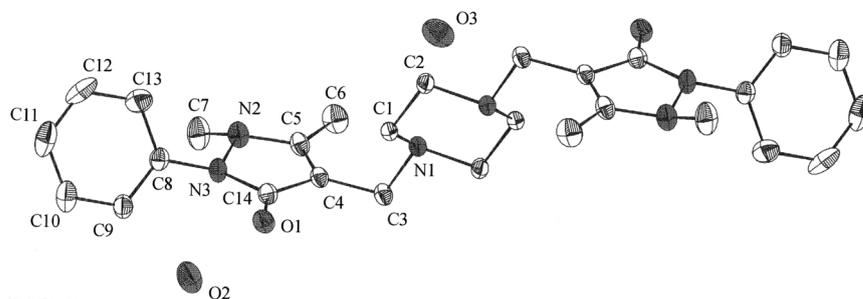


Fig. 1. Molecular structure and atomic labeling scheme of BAMP ( $C_{28}H_{34}N_6O_2 \cdot 4 H_2O$ ). The displacement ellipsoids enclose a probability density of 50%. Hydrogen atoms are omitted for the sake of clarity.

conformation contains the “chair” form of the piperazine; as a result, most of the BAMP complexes are dinuclear. Only two mononuclear complexes were reported. [18, 24]

The complex [Cu(BAMP)](ClO<sub>4</sub>)<sub>2</sub> (**2**) has been obtained by the reaction of copper(II) perchlorate hexahydrate with BAMP with a metal to ligand ratio of 1 : 1 or 2 : 1 in methanol. The compound is stable in air, insoluble in most common organic solvents like alcohols, acetone, chloromethane, or benzene, and soluble in DMSO and DMF. The molar conductivity of  $234 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$  in acetonitrile, a value in the expected range for 1 : 2 electrolytes, indicates that the anion does not coordinate to the copper(II) ions [25].

#### Description of the structure

**BAMP (1)**: appears as discrete molecules in the crystalline state with no interactions stronger than those arising from van der Waals forces. Fig. 1 shows a view of the molecule and gives the numbering scheme of the atoms. Examples of the positioning of the molecules in the unit cell can be seen in Fig. 2. As shown in Fig. 1, the geometry of the molecule is characterized by the “chair” conformation of the piperazine molecule. As a result, the two antipyrine moieties are pointing away from the bridge in opposite directions, suggesting the ability of BAMP to coordinate two metal centers. The interatomic distances C–C and C–N of the piperazine bridge are within the range expected for these types of bonds. The piperazine nitrogen atoms are definitely pyramidal as shown by the valence angles around each of these atoms. The pyrazolonic fragment contains two nitrogen atoms in an unsaturated five-membered ring and a carbonyl function at C(14). The C(4)–C(14) and C(4)–C(5) bond distances of 1.430(4) and 1.356(4) Å are in the range of

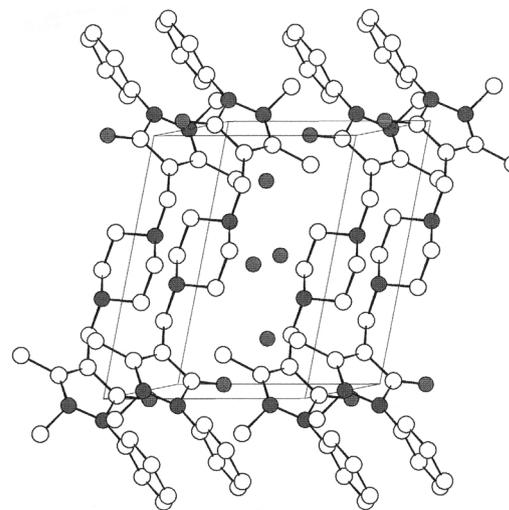


Fig. 2. Perspective view of the crystal structure of BAMP ( $C_{28}H_{34}N_6O_2 \cdot 4H_2O$ ).

values found for the sum of the covalent radii for a single bond (1.464 Å) and a double bond (1.334 Å). Also the carbon-nitrogen distances of 1.374(3) and 1.390(3), respectively, are shorter than the average value for heterocyclic C–N bonds of 1.472 Å, cited by Sutton [26], whereas the N(2)–N(3) distance is slightly longer than the sum of the covalent radii of 1.40 Å, but similar to that reported for other hydrazides [27, 28] or for the saturated pyrazole rings [29]. The angles around the pyrazolonic ring atoms suggest  $sp^2$  hybridization. However, the endocyclic angles are compressed so that they range from 105.8(2) to 119.6(2)°.

The pyrazole and phenyl rings are planar with the dihedral angle between their mean planes of 41°. The spatial arrangement of BAMP molecules is shown in a view down the *c* axis in Fig. 2. Layer-like arrangements of the molecules in the plane (001) can be clearly seen in this view. Between the layers there are channels parallel to *c* which are occupied

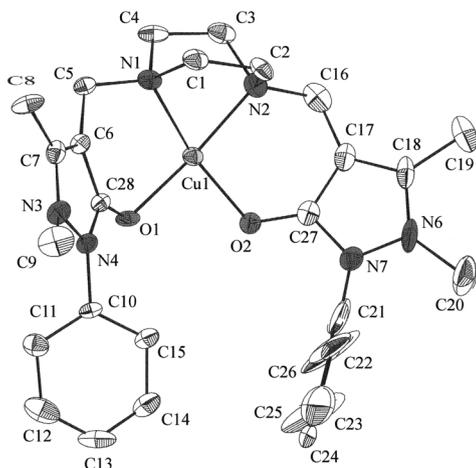


Fig. 3. Molecular structure and atomic labeling scheme of  $\text{Cu}(\text{BAMP})(\text{ClO}_4)_2$ . The displacement ellipsoids enclose a probability density of 50%. Hydrogen atoms and perchlorate anions are omitted for the sake of clarity.

by the water molecules anchored in the structure through hydrogen bonds to the carbonyl oxygen atoms ( $\text{O2}-\text{O1}$  2.82(0) and  $\text{O2}'-\text{O1}'$  3.00(5) Å, respectively) and the piperazine nitrogen atoms ( $\text{O3}-\text{N1}$  2.97(8) Å). The view is interesting because it indicates that the crystal structure owes much of its stability to these hydrogen bonds.

The phenyl rings of neighboring molecules are arranged in a parallel manner with a distance of 7.05 Å between their mean plane, ruling out any  $\pi$ -stacking.

$[\text{Cu}(\text{BAMP})](\text{ClO}_4)_2$  (2): The structure of  $[\text{Cu}(\text{BAMP})](\text{ClO}_4)_2$  includes the mononuclear copper(II) cation  $[\text{Cu}(\text{BAMP})]^{2+}$  and two perchlorate anions. A view of the cation is shown in Fig. 3 and the packing in the crystallographic unit cell is given in Fig. 4. A view of the unit cell (Fig. 4) shows that the complex cations are stacked in columns leading to channels. One of the two phenyl groups and the two anions fill up these empty spaces in the structure. This lack of coordination leads to high displacement ellipsoids of the above-mentioned molecules. Relevant interatomic distances and angles with their estimated standard deviations are listed in Table 2. The coordination geometry around each copper(II) ion can be described as square-based pyramidal with the  $\text{N}_2\text{O}_2$  donor atoms of BAMP forming the basal plane and an oxygen atom of the neighboring complex molecule occupying the apical position. In the basal plane, the Cu–O

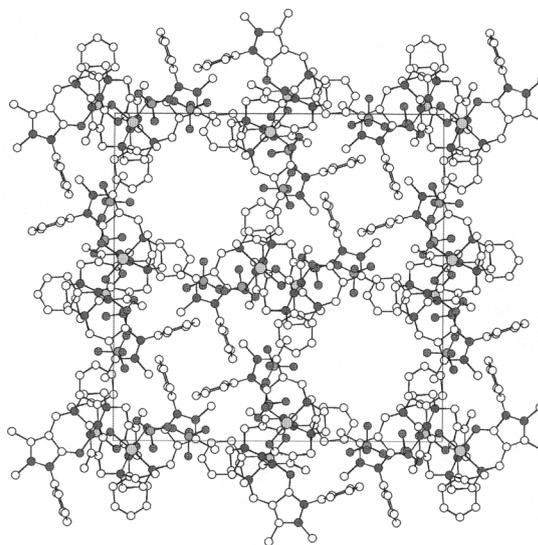


Fig. 4. Crystal structure for  $\text{Cu}(\text{BAMP})(\text{ClO}_4)_2$  viewed along [001].

bond distances are within the expected range. However, the two distances are different, as the nature of the two oxygen atoms is different: one of them acts as a terminal donor ( $\text{Cu1}-\text{O2}$  1.933(8) Å), whereas the second one acts as a bridge between two neighboring copper atoms ( $\text{Cu1}-\text{O1}$  2.005(8) Å).

The distance between Cu1 and O1' of a neighbouring complex molecule is 2.372(8) Å. A  $\text{Cu}_2\text{O}_2$  cycle is closed with  $\text{Cu1}-\text{O1}-\text{Cu1}$  and  $\text{O1}-\text{Cu1}-\text{O1}$  angles of  $95.1(3)^\circ$  and  $84.9(3)^\circ$ , respectively. The copper-copper distance is 3.233 Å and angles subtended at copper by the two bridging oxygen atoms are 86.1 and  $85.1^\circ$ , respectively. The Cu–N bond lengths of 2.036(10) and 2.040(10) Å are slightly longer than the average Cu–N distance (2.037 Å) in analogous structures without the additional “strap”, but within the expected range for a tertiary nitrogen atom. The basal plane  $\text{CuN}_2\text{O}_2$  deviates from a square geometry with  $\text{O1}-\text{Cu1}-\text{N2}$  and  $\text{O2}-\text{Cu1}-\text{N1}$  angles of  $168.0(4)^\circ$  and  $165.2(4)^\circ$ , and a compressed  $\text{N1}-\text{Cu1}-\text{N2}$  angle of  $74.2(4)^\circ$ . The “bite” angle at the Cu center of  $73.4(4)^\circ$  in the five-membered chelate ring, as well as the Cu–N distances, are the result of the “reinforcing” effect exerted by the piperazine ring. The piperazine ring is distorted so that the two  $-\text{CH}_2-\text{CH}_2-$  “straps” are not parallel. Thus, the C1 and C3 atoms are located slightly above a mean plane of carbon atoms, and the C2 and C4 atoms below the same plane. N1 is situated

above (0.720 Å) and N2 below (0.768 Å) the same plane.

The two CuN<sub>2</sub>O<sub>2</sub> units of the two neighboring molecules are distorted in a different manner. In one of them, the copper(II) center and the nitrogen (N1 and N2) atoms lie slightly below (0.017, 0.245, and 0.1933 Å, respectively) whereas the oxygen atoms are located above the mean plane of CuN<sub>2</sub>O<sub>2</sub> (O1 0.1, O2 0.2 Å). The second chromophore is more distorted: O1 and N2 are situated below the mean plane and O2 and N1 above. The distance of the copper(II) atom to this plane is 0.2 Å.

The complex cation contains two six-membered chelate rings, and each of them adopts a distorted "boat" conformation. Due to the BAMP coordination, a charge density delocalization occurs at the antipyrine moieties. This fact is mirrored by changes in the bond lengths of these fragments compared with those in the free BAMP. Thus, the distances between the atoms in the pyrazolonic rings generally become shorter after coordination. However, the changes observed for the two antipyrine fragments A and B are different. For example, the C17–C27 distance in B is equal to that found in the free ligand but much longer than C6–C28 in A. Also, the bond distance O1–C28 (A) and the corresponding one O2–C27 (B) are different, respectively, but they are significantly longer than those of the free ligand (Table 2). Comparing the torsion angles of the pyrazolonic rings (see supplementary material), we notice an increase of the tendency to planarity on going from free BAMP to the A and, further, to the B rings of the coordinated BAMP. The observed differences are consequences of the different coordination numbers of the oxygen donor atoms O1 and O2, and they support an important contribution of mesomeric structures II and III (Fig. 5) which is also suggested by the IR spectra.

#### Spectral characteristics

The electronic spectra of the copper(II) complex (**2**) recorded with a freshly prepared acetonitrile solution and nujol mull are very similar, proving that its structure is preserved in solution. The single broad band centered at 667 nm with a shoulder on the low energy side is typical for a square-planar

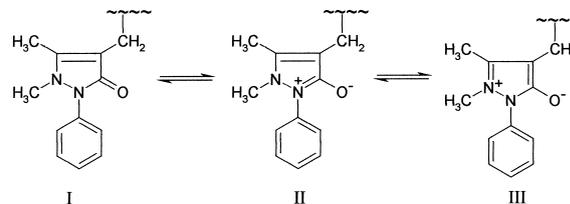


Fig. 5. Mesomeric forms of the antipyrine fragment.

CuN<sub>2</sub>O<sub>2</sub> coordination geometry with one more weakly bound axial ligand [30]. This agrees with the crystal structure. The IR and Raman spectra of BAMP are similar. Bands belonging to both antipyrine and piperazine moieties can be observed [11]. The band at 1429 cm<sup>-1</sup> in the IR spectrum appears as a doublet in the Raman spectrum (1445 and 1411 cm<sup>-1</sup>) and can be tentatively assigned to the antipyrine –C=C– group. The strong  $\nu(\text{C}=\text{O})$  stretching vibration at 1662 cm<sup>-1</sup> appears as a medium intensity band in the Raman spectrum. The bands at 1297 - 1240 and 764 cm<sup>-1</sup> assigned to the CH<sub>2</sub> groups of the piperazine bridge are also Raman active. In the infrared spectrum of the copper(II) complex, the characteristic bands of the coordinated ligand can be noticed. An examination of the IR data supports the involvement of the antipyrine oxygen atom in the coordination, which suggests structures II and III in Fig. 5. Indeed, the strong  $\nu(\text{C}=\text{O})$  stretching vibration at 1669 cm<sup>-1</sup> in the spectrum of the free ligand disappears, with a new band appearing in the region 1174 cm<sup>-1</sup> for the complex, as a result of the lowering of the C–O bond order. The new band at 1561 cm<sup>-1</sup> in the spectrum of **2**, which is assigned [31] to a combination of the  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}=\text{N})$  stretching modes, also suggests the mesomeric forms II and III.

In the far-IR spectra, the two types of Cu–O bonds may be associated with the bands at 550 and 534 cm<sup>-1</sup>. The Cu–N vibrations were identified at 419 cm<sup>-1</sup> [32]. The strong bands in the 1120 - 1088 cm<sup>-1</sup> region as well as that at 624 cm<sup>-1</sup> show the presence of the uncoordinated perchlorate ion.

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