# New Copper(II) and Cobalt(II) Complexes with the N,N'-Bis(antipyryl-4methyl)-piperazine (BAMP) Ligand: Co<sub>2</sub>(BAMP)Cl<sub>4</sub> and [Cu(BAMP)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub>

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**Abstract.** The syntheses and the crystal structures of the complexes  $Co_2(BAMP)Cl_4$  (1) and  $[Cu(BAMP)(H_2O)](ClO_4)_2$  (2) are reported. 1 crystallizes in the monoclinic space group C2/c with the unit cell dimensions a = 3129.7(4), b = 772.9(1), c = 1503.4(2) pm,  $\beta = 112.47(1)^{\circ}$  and Z = 4. Cobalt(II) is surrounded in the fashion of a distorted tetrahedron built from the NO donor atoms of the BAMP ligand and two chloride anions. The copper compound 2 crystallizes in the monoclinic space group I2/a with unit cell dimen-

sions of a = 2539.0(3), b = 1448.1(1), c = 1887.0(2) pm,  $\beta$  = 93.40(1)° and Z = 8. Copper(II) coordination can be described as a square-based pyramid with the N<sub>2</sub>O<sub>2</sub> donor atoms of the BAMP molecule forming the basal plane completed by a water molecule in the apical position. Spectroscopic (IR and UV-Vis) and conductivity data of the new complex compounds are presented.

Keywords: Copper; Cobalt; Mannich base

# Neue Kupfer(II)- und Cobalt(II)-Komplexe mit dem BAMP-Liganden (N,N'-Bis(antipyryl-4-methyl)-piperazin). Kristallstrukturen von $Co_2(BAMP)Cl_4$ und $[Cu(BAMP)(H_2O)](ClO_4)_2$

**Inhaltsübersicht.** Die Verbindungen Co<sub>2</sub>(BAMP)Cl<sub>4</sub> (1) und [Cu-(BAMP)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> (2) wurden synthetisiert und durch Einkristallröntgenstrukturanalyse charakterisiert. Der Co-Komplex kristallisiert monoklin (C2/c, a = 3129.7(4), b = 772.9(1), c = 1503.4(2) pm,  $\beta$  = 112.47(1)° und Z = 4). Das Co<sup>2+</sup>-Ion ist verzerrt tetraedrisch von den NO-Atomen des BAMP-Liganden und den Chlorid-Ionen koordiniert. Die Cu-Verbindung 2 kristallisiert in

# der monoklinen Raumgruppe I2/a mit acht Formeleinheiten in der Elementarzelle (a = 2539.0(3), b = 1448.1(1), c = 1887.0(2) pm, $\beta$ = 93.40(1)°). Die N<sub>2</sub>O<sub>2</sub>-Donor-Atome des BAMP-Liganden bilden gemeinsam mit einem H<sub>2</sub>O-Molekül einen quadratisch-pyramidablen Koordinationspolyeder um das Cu-Kation. An beiden Verbindungen wurden spektroskopische (IR und UV-Vis) und Leitfähigkeits-Messungen durchgeführt.

### Introduction

Mannich type reactions in the presence [1] or absence [2] of metal ions are well developed. These kinds of ligands have been designed with the aim to obtain binuclear metal complexes with special magnetic and redox properties. Some complexes can be considered as models of iron or copper biosites [3]. Mannich bases with a polymeric structure have been used as selective ion exchangers [4].

Mannich bases obtained from antipyrine and its derivatives have been prepared with the aim to obtain antipyretic and analgesic compounds [5]. Their complexes with certain metal ions, including Pt<sup>II</sup> and Co<sup>II</sup>, have been shown to act as antitumor agents [6]. The formation of these complexes with some oligo-elements may explain their pharmaceutical activity. In this respect, complexes of some first row metal ions with ligands containing the antipyrine moiety N,N'bis(4-antipyrylmethyl)-piperazine (BAMP) have been studied in our group [7], and some of them have been demonstrated to exhibit antitumor activity *in vitro* [8].

As a continuation of the work in this field, we report here on the synthesis, the structure, spectral and room temperature magnetic properties of binuclear  $Co_2(BAMP)Cl_4$  (1) and mononuclear [Cu(BAMP)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> (2) which contain the BAMP molecule as a bis-bidentate and tetradentate ligand, respectively.

# **Experimental Section**

All chemicals have been purchased from commercial sources and were used without further purification. Analytical data were obtained by a Perkin-Elmer Model 240C elemental analyzer. Electronic spectra were recorded on a Perkin Elmer Lambda 12 spectrophotometer, IR spectra by using KBr pellets on a BIO-RAD FTS 135 spectrometer. The magnetic susceptibilities were measured at T = 300 K with a Faraday balance using CuSO<sub>4</sub>·5H<sub>2</sub>O as the calibrant. The molar magnetic susceptibility values were corrected for the diamagnetism of the constituent atoms.

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 $Cu(BAMP)(ClO_4)_2$  was synthesized according to the published procedure [9]. BAMP has been obtained according to the Mannich synthesis under the experimental conditions as reported previously [9].

**Co<sub>2</sub>(BAMP)Cl<sub>4</sub> (1):** 0.46 g (2 mmol) of  $CoCl_2 \cdot 6H_2O$  dissolved in 5 ml of EtOH was poured dropwise into a solution containing 0.486 g (1 mmol) of BAMP dissolved in 10 ml EtOH at 55 °C under vigorous stirring. The blue reaction mixture was stirred for 120 min at room temperature. The light blue microcrystalline precipitate of the complex was collected by filtration, washed with ethanol and dried over CaCl<sub>2</sub>. The product was recrystallysed from DMSO. Light blue crystals suitable for X-ray analysis were thus obtained. Yield: 0.7 g (93 %).  $-C_{28}H_{34}N_6Cl_{14}Co_2O_2$  (746.27): calcd. C 45.06, H 4.59, N 11.26, Cl 19.00, Co 15.79; found C 45.17, H 4.62, N 11.25, Cl 19.31, Co 15.73 %.

UV/vis (DMSO)  $\lambda_{max}$  (lg $\epsilon$ ) = 615 nm (176), 670 nm (281), UV/vis (DMF):  $\lambda_{max}$  (lg $\epsilon$ ) = 609 nm (389), 674 nm (618);  $\Lambda_{M}$  (DMSO) = 75  $\Omega^{-1}$  mol<sup>-1</sup> cm<sup>2</sup>,  $\Lambda_{M}$  (DMF) = 55  $\Omega^{-1}$  mol<sup>-1</sup> cm<sup>2</sup>. – IR (KBr): 1600, 1588, 1568, 1508, 1498, 1474, 1434, 1354, 1324, 1296, 1283, 1268, 1208, 1074, 972, 932, 868, 832, 764, 738, 694, 674, 646, 616, 608, 596 cm<sup>-1</sup>. – Far IR (polyethylene): 584, 564, 536, 520, 516, 504, 496, 472, 394, 380, 342 cm<sup>-1</sup>. –  $\mu$  = 4.65  $\mu_{B}$ .

[Cu(BAMP)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> (2): 0.04 g (0.2 mmol) of MnCl<sub>2</sub> · 4H<sub>2</sub>O dissolved in 5 ml of a mixture of CH<sub>3</sub>OH : H<sub>2</sub>O = 3 : 1 was poured dropwise into a solution containing 0.15 g (0.2 mmol) of Cu-(BAMP)(ClO<sub>4</sub>)<sub>2</sub> dissolved in a 20 ml mixture of CH<sub>3</sub>OH : H<sub>2</sub>O = 3 : 1 at 35 °C under vigorous stirring. The green reaction mixture was stirred for 60 min at room temperature and after filtration, light green crystals suitable for X-ray analysis were collected. Yield: 0.65 g (85 %).  $- C_{28}H_{36}N_6Cl_2CuO_{11}$  (767.07): calcd. C 43.84, H 4.73, N 10.96, Cl 9.24, Cu 8.28; found C 43.75, H 4.78, N 10.95, Cl 9.31, Cu 8.31 %.

UV/vis (DMSO):  $\lambda_{max}$  (lg $\epsilon$ ) = 374 nm (561), 709 nm (199), UV/vis (DMF):  $\lambda_{max}$  (lg $\epsilon$ ) = 374 nm (625), 709 nm (224);  $\Lambda_{M}$  (DMSO) = 14  $\Omega^{-1}$  mol<sup>-1</sup> cm<sup>2</sup>,  $\Lambda_{M}$  (DMF) = 28  $\Omega^{-1}$  mol<sup>-1</sup> cm<sup>2</sup>. – IR (KBr): 3521, 1598, 1578, 1556, 1495, 1457, 1440, 1405, 1379, 1326, 1284, 1273, 1179, 1108, 1088, 1013, 965, 951, 847, 808, 766, 741, 698, 659, 624 cm<sup>-1</sup>. – Far IR (polyethylene): 598, 552m, 512, 495, 454, 376, 334 cm<sup>-1</sup>. –  $\mu$  = 1.92  $\mu_{B}$ .

#### **Results and Discussion**

The BAMP molecule has two kinds of donor atoms situated on each side of the piperazine bridge, i.e. a carbonyl oxygen and a piperazine nitrogen atom. Subject to their donor properties, their relatively flexible or rigid structure and the symmetry of the BAMP molecule mono- and binuclear complexes may be formed. Their actual structure depends on the conformation of the piperazine moiety. Most stable is the distorted chair conformation of the piperazine molecule. As a result, most BAMP complexes are homo- and heterobinuclear of the general type MM'(BAMP) [7].

The binuclear complex  $Co_2(BAMP)Cl_4$  (1) has been obtained as suitable crystals for X-ray analysis for the first time by the reaction of cobalt(II) chloride hexahydrate with BAMP in a metal to ligand ratio of either 1 : 1 or 2 : 1 in methanol followed by recrystallization of the crude product.

Only two mononuclear copper(II) complexes with the BAMP ligand were reported so far [9, 10]. They contain the BAMP unit as a tetradentate ligand through the  $N_2O_2$  donor atom set and the boat conformation of the piperazine bridge. One of these complexes, Cu(BAMP)(ClO<sub>4</sub>)<sub>2</sub>, shows a square-based pyramidal coordination geometry of the



Figure 1 Mesomeric forms of the antipyrine fragment

copper(II) ion, created by the  $N_2O_2$  donor atoms of a BAMP molecule and by an oxygen atom of the neighboring complex molecule in the apical position. In these terms, the complex can be better described as a dimer. Surprisingly, in the presence of MnCl<sub>2</sub>, the mononuclear species [Cu(BAMP)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> (2) crystallizes. The role of the manganese(II) salt remains unclear.

Both complexes are stable in air, insoluble in most common organic solvents like alcohols, acetone, chloromethane, or benzene, and soluble in DMSO, DMF or acetonitrile. The molar conductivity values in these solvents indicate the non-electrolytic nature of (1) while the value of 234  $\Omega^{-1}$ mol<sup>-1</sup>cm<sup>2</sup> for (2) in acetonitrile agrees well with those expected for 1 : 2 electrolytes [11].

# Spectral Characteristics

The absorption spectrum of (1) displays a single broad band centered at 670 nm with a shoulder on the high energy side. According to the literature this band is assigned to the  ${}^{4}T_{1}$  (P)  $\leftarrow {}^{4}A_{2}$  (F) transition characteristic for Co<sup>II</sup> in a C<sub>2v</sub> environment [12]. The magnetic moment of 4.65  $\mu_{B}$  at ambient temperature supports the distorted tetrahedral coordination sphere in the Co<sup>II</sup> complex [13]. The electronic spectra of the copper(II) complex (2) recorded on 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 709 nm with a shoulder on the low energy side is typical for a square-planar CuN<sub>2</sub>O<sub>2</sub> coordination geometry with one more weakly bound axial ligand, supported also by the magnetic moment of 1.92  $\mu_{B}$ .

The infrared spectra of the complexes show the characteristic bands of the ligand. They support the involvement of the antipyrine oxygen atom in the coordination in accord with the mesomeric structures II and III in Figure 1. Thus, the strong v(C=O) stretching vibration at 1669 in the spectrum of the free ligand disappears and a new band at 1208 for (1) and 1179 cm<sup>-1</sup> for (2) appears as a result of the reduction of the C-O bond order. The new band at 1568 cm<sup>-1</sup> for (1) and 1556 cm<sup>-1</sup> in the spectrum of (2) can be assigned to a combination of the v(C=O) and v(C=N) stretching modes [14] and is also in accord with the mesomeric forms II and III (Fig. 1). Differences in the characteristic frequencies of the piperazine bridge in the two complexes can be noticed. For example, the bands at 1296, 1283 and 1268 cm<sup>-1</sup> in the spectrum of (1), assigned to the wag-

	1	2	
empirical formula	$\begin{array}{c} C_{28}H_{34}N_6O_2Cl_4Co_2\\ Co_2(C_{28}H_{34}N_6O_2)Cl_4 \end{array}$	$\frac{C_{28}H_{36}N_6O_{11}Cl_2Cu}{[Cu(C_{28}H_{34}N_6O_2)(H_2O)](ClO_4)_2}$	
formula mass	746.27	767.07	
data collection			
diffractometer	STOE IPDS II		
radiation	Mo-K $\alpha$ (graphite monochromated, $\lambda = 71.073$ pm)		
temperature /K	293(2)	293(2)	
index range	$-40 \le h \le 40$	$-30 \le h \le 30$	
c	$-9 \le k \le 9$	$-17 \le k \le 17$	
	$-19 \le 1 \le 19$	$-22 \le 1 \le 22$	
rotation angle range	$0^{\circ} \leq \omega \leq 180^{\circ}; \psi = 0^{\circ}$	$0^{\circ} \leq \omega \leq 180^{\circ}; \psi = 0^{\circ}$	
6 6	$0^{\circ} \leq \omega \leq 180^{\circ}; \psi = 90^{\circ}$	$0^{\circ} \leq \omega \leq 180^{\circ}; \psi = 90^{\circ}$	
	$0^{\circ} \le \omega \le 180^{\circ}$ , $\psi = 135^{\circ}$	$0^{\circ} \le \omega \le 18^{\circ} \cdot \psi = 135^{\circ}$	
increment	$\Delta \omega = 2^{\circ}$	$\Delta \omega = 2^{\circ}$	
no of images	270	189	
exposure time /min	5	3	
detector distance /mm	120	100	
2.0 range /deg	10 54.9	2 2 50 5	
total data collected	20201	2.5 - 59.5	
unique dete	2761	43343	
unique data	3/01	0103	
Deserved data	1930	3113	
K <sub>merg</sub>	0.0923	0.08/1	
absorption correction	numerical, after crystal snape optimiz	ation [24, 25]	
transmission min / max	0.78357 0.9513	0.6681 / 0.8486	
crystallographic data			
crystal size /mm	$0.3 \cdot 0.3 \cdot 0.2$	$0.2 \cdot 0.2 \cdot 0.1$	
colour, habit	blue, column	blue, polyhedron	
crystal system	monoclinic	monoclinic	
space group	C2/c (no. 15)	I2/a (no. 15)	
a /pm	3129.7(4)	2539.0(3)	
b /pm	772.9(1)	1448.1(1)	
c /pm	1503.4(2)	1887.0(2)	
β /°	112.47(1)	93.40(1)	
volume /nm <sup>3</sup>	3.3606(7)	6.9255(12)	
Z	4	8	
$\rho_{calc} / (g \text{ cm}^{-3})$	1.475	1.471	
$\mu / \text{mm}^{-1}$	1.340	0.850	
F(000)	1528	3176	
structure analysis and refinement			
refinement method	Full-matrix least-squares on $F^2$		
structure determination	SHELXS-97 [26] and SHELXL-93 [27]		
no, of variables	259	438	
R indexes $[I > 2\sigma I]$	$R_1 = 0.0308$	$R_1 = 0.0753$	
re indexes [1. 201]	$wR_{2} = 0.0507$	$wR_2 = 0.2007$	
R indexes (all data)	$R_{1} = 0.0821$	$R_{1} = 0.1270$	
te maeries (un autu)	$wB_{2} = 0.0577$	$wR_{2} = 0.2231$	
goodness of fit $(S_{\pm})$	0.761	0.886	
goodness of fit $(S_{u})$	0.761	0.886	
largest difference man	0.701	0.000	
hole / neak [e $10^{-6}$ nm <sup>-3</sup> ]	-0.693/0.278	-0.390 / 1.628	
	0.0757 0.270	0.3707 1.020	

# Table 1 Crystal Data and Structure Refinement Parameters for Co<sub>2</sub>(BAMP)Cl<sub>4</sub> (1), and [Cu(BAMP)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> (2)

 $\mathbf{R}_{1} = \Sigma \|\mathbf{F}_{0}| - |\mathbf{F}_{c}\| / \Sigma |\mathbf{F}_{0}|, \ \mathbf{w}\mathbf{R}_{2} = [\Sigma \ \mathbf{w} \ (|\mathbf{F}_{0}|^{2} - |\mathbf{F}_{c}|^{2})^{2} / \Sigma \ \mathbf{w} \ (|\mathbf{F}_{0}|^{2})^{2}]^{1/2}, \ \mathbf{S}_{2} = [\Sigma \ \mathbf{w} \ (|\mathbf{F}_{0}|^{2} - |\mathbf{F}_{c}|^{2})^{2} / (\mathbf{n} - \mathbf{p})]^{1/2}, \ \text{with} \ \mathbf{w} = 1 / [\sigma^{2} \ (\mathbf{F}_{0})^{2} + (0.0246 \cdot \mathbf{P})^{2}] \text{ for (1) and } \mathbf{w} = 1 / [\sigma^{2} \ (\mathbf{F}_{0})^{2} + (0.1436 \cdot \mathbf{P})^{2}] \text{ for (2), were } \mathbf{P} = (\mathbf{F}_{0}^{-2} + 2\mathbf{F}_{c}^{-2}) / 3. \ \mathbf{F}_{c}^{*} = \mathbf{k} \ \mathbf{F}_{c} \ [1 + 0.001 \cdot |\mathbf{F}_{c}|^{2} \ \lambda^{3} / \sin(2\theta)]^{-1/4}.$ 

The H atoms for (1) were derived from the difference Fourier map. Hydrogen atoms for (2) were generated geometrically and allowed to ride on their parent carbon atoms. The water molecule in (2) was refined without H atoms.

ing modes of the piperazine  $CH_2$  groups, occupy the same positions as in the free ligand whereas the spectrum of (2) shows a very weak shoulder at 1284 cm<sup>-1</sup> and a well resolved band at 1273 cm<sup>-1</sup>. The band assigned to the piperazine skeleton appears at 832 cm<sup>-1</sup> for (1) and at 847 cm<sup>-1</sup> for (2) compared with 830 cm<sup>-1</sup> for the free ligand. The stretching modes v<sub>3</sub> (1108 cm<sup>-1</sup>) and v<sub>4</sub> (624 cm<sup>-1</sup>) characteristic for the uncoordinated perchlorate ion of T<sub>d</sub> symmetry can be observed in the IR spectrum of (2) [15]. In the FIR spectra, the bands at 516 for (1) and 512 cm<sup>-1</sup> for (2) may be associated with the Cu–O bonds. The Cu–N vibrations were identified at 394 for (1) and  $454 \text{ cm}^{-1}$  for (2) [16].

# Crystal structures

 $Co_2(BAMP)Cl_4$  (1). The X-ray study reveals a binuclear unit with the structure described by the basic configuration of the BAMP molecule. Figure 2 shows a perspective view of the complex unit and gives the numbering scheme of the atoms. The molecule is centrosymmetric with the center of inversion in the center of the piperazine bridge.

Co <sub>2</sub> (BAMP)Cl <sub>4</sub>			
Col - O7	196.5(2)	O7 - Co1 - N3	97.5(1)
Co1 - N3	212.0(2)	Cl1 – Co1 – Cl2	113.2(1)
Col – Cll	224.0(1)	O7 - Co1 - Cl1	113.2(1)
Col – Cl2	222.7(1)	Cl1 - Co1 - N3	104.8(1)
N3 - C1	149.0(3)	Cl2 - Co1 - N3	116.3(1)
N3 – C2	148.5(3)	N3 - C2 - C1	111.5(2)
C1 – C2	150.6(3)	C2 - C1 - N3	111.5(2
		C1 - N3 - C2	108.6(2))
[Cu(BAMP)(H <sub>2</sub>	O](ClO <sub>4</sub> ) <sub>2</sub>		
Cu1 - O1	195.5(4)	N2 - Cu1 - O1	163.8(2)
Cu1 - O2	194.2(4)	O2 - Cu1 - N1	164.2(2)
Cu1 - N1	202.8(5)	O2 - Cu1 - O1	91.0(2)
Cu1 - N2	206.5(6)	N2 - Cu1 - N1	72.7(2)
Cu1 - O3	229.8(6)	N2 - C3 - C4	107.4(6)
N2 - C1	146.2(9)	N2 - C1 - C2	107.9(5)
N2 - C3	147.7(8)	C3 - N2 - C1	108.1(5)
N1 - C2	148.3(8)	C2 - N2 - C4	107.3(5)
N1 - C4	148.7(8)		
C1 – C2	152.5(9)		
C3 – C4	151.2(9)		

Table 2 Selected internuclear distances /pm and angles /deg for  $Co_2(BAMP)Cl_4$  (1), and  $[Cu(BAMP)(H_2O)](ClO_4)_2$  (2)



Figure 2 Perspective view of the molecule  $Co_2(BAMP)Cl_4$  (1) with the atomic labeling sheme according to Table 2. The displacement ellipsoids enclose a probability of 50 %. Symmetry-related atoms are drawn as empty ellipsoids. H atoms have been omitted for clarity.

Each cobalt atom is four-coordinate by NO atoms belonging to the BAMP molecule and two chloride anions building, in total, a distorted tertrahedral surrounding. The interatomic Co-Cl distances of 222.7 and 224.0 pm are shorter than those found in the polymeric compound Co(Ppz)Cl<sub>2</sub> (Ppz = piperazine) with 224.7(8) and 224.7 pm [17]. Also, the bond length of 212.0 pm for the Co-N distance is longer than found in the same polymeric compound (204.2 - 206.4 pm). The Co-O distance is 196.5 pm. The angles around the cobalt(II) ion are spread over the range 97.5° (O7-Co1-N3) and 116.3 (N3-Co1-Cl2). They deviate from the standard values and show a distorted tetrahedral environment. This may be caused by the repulsion between the electronegative donor atoms.

The two cobalt atoms in one molecule are separated by 592.1 pm by a piperazine bridge which adopts a distorted chair conformation. The structural data compare very well with those found for the free ligand [9]. 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 molecule. Thus, the C6–O7 (127.6 pm) dis-



Figure 3 The unit cell of  $Co_2(BAMP)Cl_4$  (1) in a view along the crystallographic b axis.



**Figure 4** Ellipsoid presentation of the  $[Cu(BAMP)(H_2O)]^{2+}$  cation in **2**. Thermal ellipsoids represent 50 % probability. The labelling of the atoms is as given in Table 2. All H atoms were omitted for clarity.

tances are longer than those found for the free ligand (125.0 pm). Furthermore, the distances between the atoms in the pyrazolonic rings generally become shorter due to coordination except for the C5-C17 (136.6 pm) bond length which becomes longer. Comparing the torsion angles of the pyrazolonic rings [18], we notice an increase of the tendency to planarity on going from free BAMP to the coordinated molecule. The observed differences support an important contribution of the mesomeric structures II and III (Fig. 1) which is also suggested by the IR spectra. The aromatic rings of the ligands are planar within experimental error and, as the view of the molecular packing along the ac plane (Fig. 3) shows, the phenyl rings of the neighboring molecules are arranged in a parallel manner with the distances between their ring centroids of 501.3 pm [19].

**[Cu(BAMP)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> (2).** The crystal structure of the copper(II) complex (2) includes the mononuclear cation  $[Cu(BAMP)(H_2O)]^{2+}$  and two perchlorate anions. A view of the molecule is shown in Figure 4 and the packing in the crystallographic unit cell is given in Figure 5. The copper(II) ion is fivefold coordinated by the N<sub>2</sub>O<sub>2</sub> donor set of the BAMP ligand forming a rather regular plane and the oxygen atom of a water molecule in the apical position thus



Figure 5 A projection of the non-hydrogen atoms of the salt [Cu- $(BAMP)(H_2O)$ ](ClO<sub>4</sub>)<sub>2</sub> along the *ab* plane.

describing a square pyramidal environment. The metal ion is disposed 22.6 pm above the basal plane [19] and the two Cu-O (194.2 pm, 195.5 pm) distances as well as the two Cu-N distances (202.8 pm, 206.5 pm) fall into the range common for such complexes. The bite angle N1-Cu-N2 of 72.7(2), smaller as usual, and the different values of the Cu-N distances account for the tension induced by the presence of the two straps between the two adjacent nitrogen donors of the piperazine fragment. The piperazine bridge adopts a distorted boat conformation with the bond pair distances N2-C3 (147.7 pm) and N2-C1 (146.2 pm) shorter than that of N1-C4 (148.7 pm) and N1-C2 (148.3 pm). Additionally, they are longer than the corresponding distances in the free ligand [9]. The angles C1-N2-C3 and C2-N1-C4 (108.1°, 107.3°) are compressed when compared to the corresponding angles in the free ligand  $(108.8^{\circ} - 110.3^{\circ})$ .

These changes along with structural data about the copper(II) coordination sphere mirror the so-called "reinforced" effect induced by the piperazine bridge [20].

The pyrazolonic rings of BAMP become more planar compared to the free ligand, as in complex (1). Further, in this case, the two phenyl rings of a BAMP molecule are planar and disposed in a point-to-face, T-shape conformation with the distances between atoms varying in the range of 387.8 pm to 489.3 pm. According to *Janiak* [21], this arrangement is a limiting form in aromatic interaction of the type C-H<sup>...</sup> $\pi$ .

A view of the unit cell (Fig. 5) shows a columnar arrangement of the molecules. The atom H22 bonded to C22 (CHaromatic) and H9B bonded to C9 (CH<sub>3</sub>-pyrazolone) forms a intramolecular hydrogen bond with atom O11 (ClO<sub>4</sub><sup>-</sup>) (259.7 pm) and atom O22 (ClO<sub>4</sub><sup>-</sup>) (277.9 pm), respectively [22]. The phenyl rings belonging to neighboring columns are stacked with distances between their atoms falling in the range between 387.5 pm and 390.5 pm. Thus, the forces responsible for this arrangement can be described as intermolecular  $\pi$ - $\pi$  interactions [23]. Acknowledgements. This work was financially supported by the Romanian Academy of Science and by the State of Nordrhein-Westfalen / Universität zu Köln.

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