



# Synthesis, magnetism and X-ray structures of [Cu(2-aminopyrimidine)<sub>2</sub>(μ-OH)(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(2-aminopyrimidine)<sub>2</sub>, a new hydroxo-bridged dinuclear Cu(II) compound generating extremely small antiferromagnetism

Gerard A. van Albada<sup>a</sup>, Iipo Mutikainen<sup>c</sup>, Wilberth J.J. Smeets<sup>b</sup>, Anthony L. Spek<sup>b</sup>,  
Urho Turpeinen<sup>c</sup>, Jan Reedijk<sup>a,\*</sup>

<sup>a</sup> Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, Netherlands

<sup>b</sup> Bijvoet Center for Biomolecular Research, Sectie Kristal- en Structuurchemie, Utrecht University, Padualaan 8, 3584 CH Utrecht, Netherlands

<sup>c</sup> Laboratory of Inorganic Chemistry, Department of Chemistry, PO Box 55 (A.I. Virtasen aukio 1), University of Helsinki, 00014 Helsinki, Finland

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In honour of the scientific career of Professor Kees Vrieze, who recently retired from the University of Amsterdam

## Abstract

The synthesis, optical and magnetic properties and X-ray crystal structure of [Cu(2-aminopyrimidine)<sub>2</sub>(OH)(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(2-aminopyrimidine)<sub>2</sub>, a new dinuclear hydroxo-bridged copper(II) compound with a Cu–O–Cu angle of 97.96° and a very small antiferromagnetic interaction for which the singlet–triplet exchange parameter  $J$ , is described. The magnetic exchange coupling is almost negligible and, depending on the actual sample, varies from  $-1.8$  to  $-7.2$  cm<sup>-1</sup>. © 2002 Published by Elsevier Science B.V.

**Keywords:** Magnetism; Copper complexes; Hydroxo-bridged complexes; Crystal structures

## 1. Introduction

Hydroxo- and alkoxo-bridged dinuclear compounds of first-row transition metals have received much attention because of their interesting magnetic properties [1,2]. Some decades ago it was reported that certain planar di-μ-hydroxo-bridged copper(II) dinuclear compounds exhibit an antiferromagnetic interaction, while others exhibit a ferromagnetic interaction [3]. A detailed study has resulted in the linear correlation between the Cu–O–Cu angle and singlet–triplet exchange parameter  $J$ , established by Hodgson and Hatfield [4], and was proposed as:  $J = -74.53\varphi + 7270$  cm<sup>-1</sup> (in which  $\varphi$  is the Cu–O–Cu angle).

From this correlation it is concluded that when the Cu–O–Cu angle is larger than 97.55°, the overall magnetic behaviour is antiferromagnetic and for smaller values a ferromagnetic coupling would be observed. At a Cu–O–Cu angle of about 97.55° the singlet–triplet splitting energy would be very close to zero.

Analogous correlations have been reported for dinuclear di-μ-alkoxide-bridged copper(II) complexes [5] and for dinuclear μ-hydroxo/μ-carboxylato-copper(II) systems [6].

Several theoretical calculations were performed to better understand this correlation [7,8]; most recently different density functional methods were used to extend the study on the magnetic behaviour and introduced some new parameters concerning the non-planarity of the Cu<sub>2</sub>O<sub>2</sub> core and the out-of-plane displacement angle of the hydroxo hydrogen atom [9–11]. Very recently additional theoretical approaches

\* Corresponding author. Tel.: +31-71-527 4459; fax: +31-71-527 4671.

E-mail address: reedijk@chem.leidenuniv.nl (J. Reedijk).

were applied to understand the nature of the ferromagnetic/antiferromagnetic interactions [12].

To our knowledge, so far only one dinuclear Cu(II) compound with a Cu<sub>2</sub>O<sub>2</sub> chromophore is published, having a Cu–O–Cu angle of nearly 98°, i.e. the compound  $\alpha$ -[Cu(dmaep)OH]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (in which dmaep = 2-(2-dimethylaminoethyl)pyridine) [13,14] with a Cu–O–Cu angle of 98.35(9)° and an experimental *J* value of  $-4.7\text{ cm}^{-1}$ . Unfortunately this compound is not pure and crystallizes together with a monoclinic  $\beta$  form [15]. This  $\beta$  form has a larger Cu–O–Cu angle (100.4°) and also a smaller *J* value ( $J = -105\text{ cm}^{-1}$ ).

In an effort to prepare a unique and stable compound with the desired angle, we now used the ligand 2-aminopyrimidine (hereafter abbreviated as ampym) and investigated the structural and magnetical behaviour of some Cu complexes. With this ligand Cu(II), X-ray structures are known in which ampym acts as a mono-chelating ligand [16–22], or as a bis-chelating ligand in polymeric structures [23,24]. With strong anions like Cl and Br chains are formed with either hydronated or dihydronated (H<sub>2</sub>ampym)<sup>2+</sup> as cations [21,25,26].

In this paper we present the synthesis, optical and magnetic properties and also the X-ray crystal structure of [Cu(ampym)<sub>2</sub>(OH)(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>](ampym)<sub>2</sub>, a new dinuclear hydroxo-bridged copper(II) compound with a Cu–O–Cu angle of 97.96° and a very small antiferromagnetic interaction.

## 2. Experimental

### 2.1. Syntheses

2-Aminopyrimidine was purchased from Acros Organics, Belgium and used without further purification. The metal salts and solvents were commercially available and used without further purification.

The compound was prepared according to the following procedure: 1.2 mmol of copper(II) triflate and 1.2 mmol of ampym was each dissolved in 10 ml of ethanol. The Cu(II) salt solution was then added slowly to the ligand solution preventing precipitation, filtered to remove any solids and after a few days to some weeks the blue crystals separated. The synthesis was reproduced several times and from two different batches the X-ray crystal structures were determined, also by using different crystallographic equipment (see Section 2.3).

*Anal.* Found (typical sample): Cu, 12.1; C, 30.1; N, 24.1; H, 3.0; S, 6.0. Calc. for C<sub>26</sub>H<sub>32</sub>Cu<sub>2</sub>F<sub>6</sub>N<sub>18</sub>O<sub>8</sub>S<sub>2</sub>: Cu, 12.3; C, 30.3; N, 24.5; H, 3.1; S, 6.2%.

### 2.2. Physical measurements

C, H, N and Cu determinations were performed by the Microanalytical Laboratory of University College, Dublin, Ireland.

Ligand-field spectra were obtained on a Perkin–Elmer Lambda900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. X-band powder EPR spectra were obtained on a JEOL RE2x electron spin resonance spectrometer using DPPH (*g* = 2.0036) as a standard. FTIR spectra were performed on a Perkin–Elmer Paragon 1000 FTIR spectrophotometer, equipped with a Golden Gate ATR device, using the reflectance technique (4000–300 cm<sup>-1</sup>, res. 4 cm<sup>-1</sup>).

Magnetic susceptibility measurements (5–280 K) were carried out using a Quantum Design MPMS-5 5T SQUID magnetometer (measurements carried out at 1000 Gauss). Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

### 2.3. Crystallographic data collection and refinement of the structure

#### 2.3.1. Structure 1

A crystal suitable for X-ray structure determination was covered by an inert oil, glued to the tip of a glass fibre and immediately placed in the cold dinitrogen stream (150 K) on an Enraf–Nonius CAD4-T diffractometer with rotating anode. Data were collected in the  $\omega$ -scan mode. Unit-cell dimensions and standard deviations were obtained by least-squares fit (SET4) [27]. Reduced-cell calculations did not indicate higher lattice symmetry (Lepage) [28]. The structure was solved by automated direct methods (SHELXS86) [29]. Refinement on *F*<sup>2</sup> was carried out by full-matrix least-squares techniques (SHELXL-93) [30]. Anisotropic displacement parameters were used for all non-hydrogen atoms. The hydrogen atoms of the bridging O–H and amino nitrogen were located from a difference Fourier map; all other hydrogen atoms were included in the refinement cycle at calculated positions, riding on their carrier atoms. All geometrical calculations and the ORTEP illustrations were performed with PLATON [31]. Crystal data and details of the refinement are collected in Table 1.

#### 2.3.2. Structure 1A

A crystal was selected and mounted to a glass fibre using the oil-drop method. Data were collected on a Rigaku AFC-7S diffractometer (graphite-monochromated Mo K $\alpha$  radiation,  $\omega$ -2 $\theta$  scans). The intensity data were corrected for Lorentz and polarization effects, for absorption (psi-scan absorption correction) and extinction. All non-H atoms were refined anisotropically. H atoms were introduced in calculated

positions and refined with fixed geometry with respect to their carrier atoms. The structure was solved by direct methods. The programs TEXSAN [32], SHELXS-97 [33], and SHELXL-97 [34] were used for data reduction, structure solution and structure refinement, respectively. Refinement of  $F^2$  was done against all reflections. The weighted  $R$  factor,  $wR$ , and goodness of fit  $S$  are based on  $F^2$ . Conventional  $R$  factors,  $R$ , are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . Crystal data and details of the refinement are collected in Table 1.

### 3. Results and discussion

#### 3.1. Crystal structure of

#### $[Cu(ampym)_2(OH)(CF_3SO_3)]_2(ampym)_2$

The structure of the compound is depicted in Fig. 1, with relevant bond-length and bond-angle information given in Table 2. The unit cell contains four dinuclear hydroxo-bridged copper(II) units and eight ligand

Table 1  
Crystal data and details of the structure determination

	Structure 1	Structure 1A
<i>(a) Crystal data</i>		
Empirical formula	$C_{26}H_{32}Cu_2F_6N_{18}O_8S_2$	$C_{26}H_{32}Cu_2F_6N_{18}O_8S_2$
Molecular weight	1029.9	1029.9
Crystal system	monoclinic	monoclinic
Space group	$C2/c$ (No. 15)	$C2/c$ (No. 15)
$a$ (Å)	15.1767(14)	15.189(3)
$b$ (Å)	18.288(2)	18.370(4)
$c$ (Å)	14.8021(11)	14.844(3)
$\beta$ (°)	95.172(6)	95.02(3)
$V$ (Å <sup>3</sup> )	4091.6(7)	4125.9(14)
$Z$	4	4
$D_{calc}$ (g cm <sup>-3</sup> )	1.672	1.658
$F(000)$	2088	2088
$\mu$ (mm <sup>-1</sup> )	1.24	1.24
Crystal size (mm), colour	0.20 × 0.30 × 0.50, blue	0.40 × 0.20 × 0.15, blue
<i>(b) Data collection/refinement</i>		
Temperature (K)	150	193
$\theta_{min}$ , $\theta_{max}$ (°)	1.38–26.48	2.61–25.03
Radiation	Mo K $\alpha$ , 0.71073 Å	Mo K $\alpha$ , 0.71073 Å
Total data collected	8316	3236
Unique reflections ( $R_{int}$ )	4067 (0.0455)	3125 (0.0699)
Observed reflections ( $I > 2\sigma(I)$ )	3482	2099
Number of refined reflections, parameters	4067, 293	3125, 283
Weighting scheme	$w = 1.0/[\sigma^2(F_o^2) + (0.0550P)^2 + 2.39P]$	$w = 1.0/[\sigma^2(F_o^2) + (0.0927P)^2 + 51.00P]$
Final $R_1$ , $wR_2$ , $S$	0.037, 0.099, 1.069	0.070, 0.164, 0.932
Min/max resd.dens. (e Å <sup>-3</sup> )	−0.53, +0.72	−0.649, +0.644

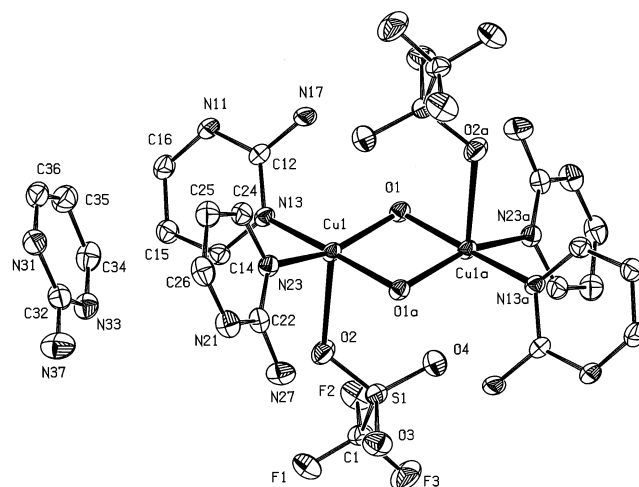


Fig. 1. ORTEP 50% probability plot of  $[Cu(ampym)_2(OH)(CF_3SO_3)]_2(ampym)_2$  (1). Hydrogen atoms are omitted for clarity. Atoms with an 'a' are generated by inversion symmetry ( $a = 1/2 - x, 1/2 - y, 1 - z$ ).

molecules. The dinuclear unit has a centre of symmetry located in the  $Cu_2O_2$  plane. The Cu atom has a square-pyramidal coordination with the basal plane comprised of two nitrogens from two ampym ligands (Cu(1)–N(13) 2.022(2) Å, Cu(1)–N(23) 2.028(2) Å) and the oxygens of two hydroxo molecules (Cu(1)–O(1) 1.9289(17) Å). The apical position is occupied by the oxygen of the triflate anion (Cu(1)–O(2) 2.5039(19) Å). The Cu atom lies 0.1517(3) Å above the basal plane towards the oxygen of the triflate anion. The second oxygen of the triflate anion is at a much larger distance of the other Cu atom (Cu(1)–O(4)a 3.0469(19) Å), and also forms intramolecular hydrogen bonds with the amino nitrogen of the ligand (N(17)–H(172)⋯O(4)a 3.132(3) Å).

The Cu–Cu distance within the dinuclear unit is 2.9015(5) Å, while the Cu–O–Cu angle is 97.96(8)°.

A special feature of the structure appears to be an uncoordinated ampym molecule, which lies in a stacked way above one of the coordinated ampym molecules with a ring–ring distance, which varies from 3.715(4) to 3.759(4) Å. A few other structures containing the ampym ligand, i.e. *catena*-[Ni(SO<sub>4</sub>)(ampym)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](ampym), [Ni(ampym)(H<sub>2</sub>O)<sub>5</sub>](SO<sub>4</sub>)(ampym) and  $[Cu(ampym)_2(H_2O)_2(CF_3SO_3)_2](ampym)_2(ampym)_2$  also contain uncoordinated ampym molecules in the lattice [16,22] and have the same way of stacking. The stabilization of the lattice is furthermore enhanced by hydrogen bonding of the amine-nitrogen of the uncoordinated ampym molecule and the ring-nitrogen of the coordinated ampym molecules (N37⋯N21 3.048(4) Å), from the hydroxo oxygen to the ring-nitrogen of the uncoordinated ampym molecule (O1⋯N31 2.876(3) Å) and from the amine-nitrogen of the coordinated ampym molecules to the ring-nitrogens of neigh-

bouring ampym molecules (distances vary from 2.944(3) to 2.952(3) Å). Details of the hydrogen contacts are included in Table 2.

As the Cu–O–Cu angle of the compound was found so close to 97.5° (see Section 1), it was decided to perform another X-ray crystal structure of a second completely freshly prepared batch (compound **1A**) and using different crystallographic equipment (see Table 1). In fact the two structures appear to be the same within the experimental error. The Cu–Cu distance for compound **1A** refined to 2.8971(19) Å and the Cu–O–Cu angle is 97.5(2)°. Further structural details of compound **1A** are given as supplementary material.

### 3.2. Spectroscopy

The ligand-field spectrum measured as a solid with the diffuse-reflectance technique shows a band at  $16.2 \times 10^3 \text{ cm}^{-1}$ , which is a normal ligand-field transition for a  $\text{CuN}_2\text{O}_2$  or a  $\text{CuN}_2\text{O}_2(\text{O})_x$  chromophore [35–37].

In the infrared the N–H vibrations amino group of the ligands are observed at 3388 and 3478  $\text{cm}^{-1}$ . The characteristic vibrations of the triflate anion are observed at 1269–1239  $\text{cm}^{-1}$  ( $\nu_{\text{as}}(\text{S–O})$ ), 1224  $\text{cm}^{-1}$  ( $\nu_{\text{s}}(\text{C–F})$ ), 1153  $\text{cm}^{-1}$  ( $\nu_{\text{as}}(\text{C–F})$ ), 1022  $\text{cm}^{-1}$  ( $\nu_{\text{s}}(\text{S–O})$ ). The splitting of 30  $\text{cm}^{-1}$  for the  $\nu_{\text{as}}(\text{S–O})$  vibration is normal for a monodentate coordinating triflate anion [38,39].

### 3.3. Magnetic measurements

The X-band polycrystalline powder EPR spectra of this compound, up to 1000 mT at 77 K, exhibits four

features at 160, 320, 620 and 840 mT. The spectrum is qualitatively similar to that reported for other coupled copper(II) pairs with a  $D > hv$  [40–44]. The feature at 320 mT is most certainly from a monomeric Cu(II) impurity, which is always present in dinuclear species and the weak absorption at low field (160 mT) is the  $\Delta M_s = \pm 2$  transition. The presence of the other peaks at high field values is as expected for the case in which the value of the axial zero-field splitting parameter  $D$  is larger than the incident quantum (about 0.3  $\text{cm}^{-1}$ ). Although it is not the intention of this paper to perform a detailed EPR study, including variable frequencies, to determine the parameters  $D$  and  $E$ , a global analysis yields [45] a  $D$  of about 0.5  $\text{cm}^{-1}$ .

In a frozen solution (THF/MeOH 1:1) only a mononuclear  $S = 1/2$  signal is observed with a  $g_{\perp}$  value of 2.07, a  $g_{\parallel}$  of 2.34 and an  $A_{\parallel}$  value of about 13.3 mT, which indicates that the compound decomposes in this solution.

The magnetic susceptibility of a powdered sample was measured from 5 to 280 K. The magnetic properties of the complex are given in Fig. 2 in the form of  $\chi_{\text{M}}T$  versus  $T$  and show a very weak antiferromagnetic behaviour. The  $\chi_{\text{M}}T$  value of the compound stays at a constant value of about 0.80  $\text{cm}^3 \text{ mol}^{-1}$  ( $\mu_{\text{eff}}$  of 1.60 BM per Cu) down to about 40 K; below that temperature this value slowly decreases to 0.54  $\text{cm}^3 \text{ mol}^{-1}$  ( $\mu_{\text{eff}}$ : 1.45 BM per Cu), indicative for antiferromagnetism.

The theoretical expression for the magnetic susceptibility for two interacting  $S = 1/2$  centres, which is based on the general Hamiltonian [1]:  $H_{\text{ex}} = -JS_1S_2$ , in which the exchange parameter  $J$  is negative for antiferromagnetic and positive for ferromagnetic interaction.

Table 2  
Selected distances and angles of  $[\text{Cu}(\text{ampym})_2(\text{OH})(\text{CF}_3\text{SO}_3)]_2(\text{ampym})_2$  (**1**)

Cu(1)–O(1)	1.9289(17)	Cu(1)–Cu(1)a	2.9015(5)
Cu(1)–O(2)	2.5039(19)	Cu(1)–O(1)a	1.9167(17)
Cu(1)–N(13)	2.022(2)	Cu(1)–O(4)a	3.0469(19)
Cu(1)–N(23)	2.028(2)		
O(1)–Cu(1)–O(2)	100.59(7)	O(2)–Cu(1)–N(13)	87.61(7)
O(1)–Cu(1)–N(13)	95.06(8)	O(2)–Cu(1)–N(23)	101.89(7)
O(1)–Cu(1)–N(23)	157.06(8)	Cu(1)a–Cu(1)–O(2)	95.40(4)
Cu(1)a–Cu(1)–O(1)	40.86(5)	O(1)a–Cu(1)–O(2)	87.56(6)
O(1)–Cu(1)–O(1)a	82.04(7)	N(13)–Cu(1)–N(23)	90.36(8)
Hydrogen bonds:			
	D–H	H···A	D···A
			D–H···A
O1–H1···N31 [1/2–x, –1/2+y, 1/2–z]	0.58(3)	2.32(3)	2.876(3)
N17–H171···N11 [1–x, y, 1/2–z]	0.81(2)	2.15(2)	2.952(3)
N27–H271···N33 [–x, y, 1/2–z]	0.794(18)	2.150(18)	2.944(3)
N37–H371···N21 [–x, y, 1/2–z]	0.871(19)	2.180(18)	3.048(4)
N17–H172···O1 <sup>b</sup>	0.81(2)	2.209(13)	2.874(3)
N17–H172···O4 <sup>b</sup> [1/2–x, 1/2–y, 1–z]	0.81(2)	2.576(11)	3.132(3)

a = 1/2–x, 1/2–y, 1–z.

<sup>b</sup> Bifurcated hydrogen bond.

Table 3  
Dinuclear hydroxo-bridged copper(II) compounds with Cu–O–Cu angle near 98°

Compound <sup>a</sup>	Cu–Cu dist. (Å)	Cu–O–Cu angle (°)	Magnetic parameters			Ref.
			<i>J</i>	<i>g</i>	<i>zJ'</i>	
$\alpha$ -[Cu(dmaep)OH] <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	2.938(1)	98.35(9)	–2.35	2.08	–0.1	[13,14]
[Cu(ampym) <sub>2</sub> (OH)(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> ](ampym) <sub>2</sub> ( <b>1</b> )	2.9015(5)	97.96(8)	–7.2	2.09	2.7	this work
[Cu(ampym) <sub>2</sub> (OH)(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> ](ampym) <sub>2</sub> ( <b>1A</b> )	2.897(19)	97.5(2)	–1.8	2.12	1.4	this work

<sup>a</sup> dmaep = 2-(2-dimethylaminoethyl)pyridine, ampym = 2-aminopyrimidine.

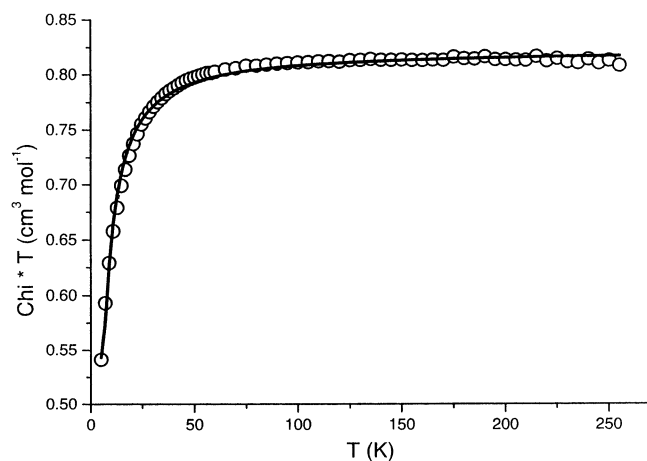


Fig. 2. A plot of temperature dependence of  $\chi_{\text{Cu}}T$  vs.  $T$ . The solid line represents the calculated curve for the parameters  $J = -7.2 \text{ cm}^{-1}$ ,  $g = 2.09$ ,  $zJ' = 2.7 \text{ cm}^{-1}$  and  $p = 5 \times 10^{-2}$  (see text).

The magnetic data were fitted to the equation given in the literature for dinuclear copper compounds [1]:

$$\chi_{\text{m}} = (2Ng^2\beta^2)[kT - (2zJ'/(3 + \exp(-J/kT)))]^{-1} [3 + \exp(-J/kT)]^{-1}(1 - p) + \chi_{\text{p}}p$$

$N$ ,  $g$ ,  $\beta$ ,  $k$  and  $T$  have their usual meanings. The parameter  $p$  denotes the molar fraction of paramagnetic impurity in the sample [1] and  $zJ'$  the interaction between neighbouring dinuclear identities. The fit was accomplished by minimisation of  $R = \sum(\chi_{\text{m}}T_{\text{calc}} - \chi_{\text{m}}T_{\text{obs}})^2/(\chi_{\text{m}}T_{\text{obs}})^2$  by least-squares procedure.

The best fit was obtained for  $J = -7.2 \text{ cm}^{-1}$ ,  $g = 2.09$ ,  $p = 5 \times 10^{-2}$  and  $zJ' = 2.7 \text{ cm}^{-1}$  with an  $R$  of  $3 \times 10^{-3}$ . Measurements of a freshly prepared second batch revealed the parameters:  $J = -1.8 \text{ cm}^{-1}$ ,  $g = 2.12$ ,  $p = 5 \times 10^{-2}$  and  $zJ' = 1.39 \text{ cm}^{-1}$ , with an  $R$  of  $3.1 \times 10^{-3}$ . From Table 3 it is seen that the Cu–O–Cu angles of compound **1** and compound **1A** are 97.96(8) and 97.5(2)°, respectively. According to the Hatfield Hodgson correlation formula [4] (see Section 1,  $J = -74.53\varphi + 7270 \text{ cm}^{-1}$ , in which  $\varphi$  is the Cu–O–Cu angle), the theoretical angles belonging to the observed  $J$  values of  $-7.2$  and  $-1.8 \text{ cm}^{-1}$ , would be 97.45 and 97.52°. For such small values these observed values are in very good agreement with empirical correlation. The

comparable compound  $\alpha$ -[Cu(dmaep)OH]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (in which dmaep = 2-(2-dimethylaminoethyl)pyridine) [13,14] with an Cu–O–Cu angle of 98.35(9)° and an experimental  $J$  value of  $-4.7 \text{ cm}^{-1}$  would correspond with a calculated angle of 97.48°.

#### 4. Conclusion

In this paper the synthesis and characterisation of the new dinuclear hydroxo-bridged Cu(II) compound [Cu(ampym)<sub>2</sub>(OH)(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>](ampym)<sub>2</sub> is presented. The X-ray structure of two different batches has been measured independently with different crystallographic equipment. The Cu–O–Cu angle was found to be 97.96(8)°, with 97.5(2)° for the second batch. Also, the magnetic susceptibilities of different crystalline batches have been measured and the exchange parameter  $J$  varies from  $-7.2$  to  $-1.8 \text{ cm}^{-1}$ . The data shown allow the conclusion, that  $J$  values should be interpreted with care, especially at very small exchange interactions.

#### 5. Supplementary material

Structural details and an ORTEP figure of compound **1A** are available as supplementary material from the author. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 163297 for structure **1** and 163421 for structure **1A**. 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>).

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