Appendix 2

The Crystal and Molecular Structures of Di-μ-hydroxy-bis (di-2-pyridylamine)dinitratodicopper(II) and Aqua-μ-formato-triformato-bis(di-2-pyridylamine)dicopper(II) Monohydrate

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Abstract- The preparation, magnetic and spectroscopic properties, crystal and molecular structures of binuclear complexes of formulae $[Cu_2(dpyam)_2(OH)_2(ONO_2)_2]$ (I) $[Cu_2(dpyam)_2(O_2CH)_4(OH_2)].H_2O$ (II) are described. (I) consists of pairs of copper atoms linked by two hydroxo bridges. The co-ordination geometry at each copper atom is distorted square-pyramidal, the basal plane consisting of two hydroxo oxygen atoms and two nitrogen atoms from a dpyam ligand, while the axial co-ordination sites are occupied by nitrate oxygen atoms. The copper(II) ions in (II) are also in a distorted square-pyramidal environment. They are bridged by a formate group in an anti-syn configuration from a basal position to an axial position, while another axial position is occupied by the water oxygen atom. From magnetic susceptibility measurements at room temperature, both complexes are found to exhibit antiferromagnetic interactions and some magneto-structural trends are discussed.

The crystal structures of the known copper(II) dimers have been characterised [1,2]. Three copper environments are observed: rhombic coplanar, CuN_2O_2 [3]; square-based pyramidal, CuN_2O_2X [2,4,5,6,7] ; and elongated rhombic octahedral, $CuN_2O_2X_2$ [8,9]. Only two crystal structures of the dihydroxy-bridged copper(II) dimer involving the dpyam ligand have been reported: $[Cu_2(FBF_3)(OH)_2(dpyam)_2]$ (III) and $Cu_2(OH)_2(H_2O)(dpyam)_2]Cl_2.2H_2O$ (IV) [1,2]. Both complexes belong to the second group of the known copper(II) dimers and no crystal structure of the formato-bridged copper(II) dimer involving the dpyam ligand has been reported. While the corresponding dimeric (III) and (IV) complexes were obtained as the reoxygenation products [2], the $[Cu_2(ONO_2)_2(OH)_2(dpyam)_2]$ (I) and $[Cu_2(H_2O)(O_2CH)_4(dpyam)_2]$ $.H_2O$ (II) complexes were prepared directly from their components. As the electronic reflectance spectra of both complexes are comparable to those of (III) and (IV) including the evidence for the formation of the OH^- anion in (I), X-ray structure determination of (I) and (II) are performed.

EXPERIMENTAL

Synthesis of $[Cu_2(ONO_2)_2(OH)_2(dpyam)_2]$ (I)

Complex (I) was prepared by adding 30 ml of a boiling aqueous solution of $CuCO_3.Cu(OH)_2.H_2O$ (0.111 g, 0.5 mmol) and nitric acid (2 ml), to 30 ml of a hot ethanol solution of dpyam (0.171 g, 1.0 mmol), after which 0.138 g (2.0 mmol) $NaNO_3$ was added. On slow evaporation, (I) was deposited as steel-blue crystals. Yield 42%. Found: C, 38.3; H, 3.3; N, 17.9; Cu, 20.4%. Calculated for $C_{20}H_{20}Cu_2N_8O_8$: C, 38.3; H, 3.2; N, 17.9; Cu, 20.2%.

Synthesis of $[Cu_2(H_2O)(O_2CH)_4(dpyam)_2].H_2O$ (II)

Complex (II) was prepared by adding 30 ml of a hot ethanol solution of dpyam (0.171 g, 1.0 mmol), to 20 ml of the boiling aqueous solution of $CuCO_3.Cu(OH)_2.H_2O$ (0.111 g, 0.5 mmol) and formic acid (2 ml). On boiling, 0.272 g (4.0 mmol) HCOONa was added. After five days green crystals of (II) were deposited. Yield 76%. Found: C, 41.98; H, 3.85; N, 12.17; Cu, 18.39%. Calculated for $C_{24}H_{26}Cu_2N_6O_{10}$: C, 42.05; H, 3.82; N, 12.26; Cu, 18.54%.

Both products were characterised using elemental analyses, IR and UV-vis spectroscopy and magnetic properties. Carbon, nitrogen and hydrogen analyses (microanalyses) were carried out in the Chemistry Department, Khon Kaen University on a Perkin-Elmer 2400 Series II CHNS/O analyser, while the copper analysis was obtained on a Shimadzu AA-6501F atomic absorption spectrophotometer. Infrared spectra were recorded on a Biorad FTS-7/PC) FTIR spectrophotometer as KBr pressed pellets in the 4000-450 cm^{-1} spectral range. The diffuse reflectance spectra were measured on polycrystalline samples using a Perkin-Elmer Lambda2S spectrophotometer in the 200-1100 nm spectral range. The magnetic moments at room temperature were obtained on powdered samples on a Faraday type microbalance. Experimental susceptibilities were corrected from diamagnetic contribution by using Pascal's constants and for the temperature independent paramagnetism, estimated to be $60+10^{-6}$ cm^3 mol^{-1} per Cu(II) ion. Supplementary data have been deposited with the CCDC, deposition numbers 102316 and 102317.

Crystallography

Data collection. A summary of the key crystallographic information is given in Table 1. For the $[Cu_2(ONO_2)_2(OH)_2(C_{10}H_9N_3)_2]$ complexes data were collected on a SMART CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å) with a detector distance of 4cm and swing angle of -35°. A hemisphere of the reciprocal space was covered by combination of three sets of exposures; each set had a different ϕ angle (0,88,180°) and each exposure of 30s covered 0.3° in ω. The collected data were reduced by using the program SAINT [10] and empirical absorption correction was carried out by using the SADABS [11] program. Reflections with 2θ ≤55° were used for further processing. The data collection for the $[Cu_2(OH_2)(O_2CH)_4$ $(C_{10}H_9N_3)_2].H_2O$ complex was done using a Siemens P4 diffractometer.

Structure solution and refinement. The structures of both the complexes were solved by direct methods and refined by least-squares on F_{obs}^2 by using the SHELXTL [12] software package. All non–H atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. For the

$[Cu_2(ONO_2)_2(OH)_2(C_{10}H_9N_3)_2]$, final conventional R(F)=0.0339 and $wR(F^2)$=0.0894 for $I > 2\sigma(I)$ with weighting scheme, $w=1/[\sigma^2(F_o^2)+(0.0501P)^2+0.856P]$, where $P=(F_o^2)+2Fc^2)/3$. For $[Cu_2(OH_2)(O_2CH)_4(C_{10}H_9N_3)_2].H_2O$, the corresponding R(F)=0.0319 and $wR(F^2)$=0.0872 for $I > 2\sigma(I)$ with weighting scheme, $w=1/[\sigma^2(F_o^2)+(0.0476P)^2+0.221P]$, where $P=(F_o^2)+2Fc^2)/3$. The molecular graphics were done using SHELXTL [12]. Supplementary data have been deposited with the CCDC, deposition numbers 102316 and 102317.

RESULTS AND DISCUSSION

Crystal structure. The structure of (I) (Fig. 1) is made up of a binuclear $[Cu_2(ONO_2)_2(OH)_2(dpyam)_2]$ unit. This unit is approximately planar with symmetrically bridging OH^- anions and terminal chelate dpyam ligands . The CuN_2O_2 chromophores are non-planar, with a restricted tetrahedral twist, evident from the dihedral angles of 20.73(8)° between the Cu(1B)O(4A)O(4B) and Cu(1B)N(1B)N(2B) planes and 16.70(8)° between the Cu(1A)O(4A)O(4B) and Cu(1A)N(1A)N(2A) planes. The fifth axial co-ordination site of each copper(II) ion is occupied by an O atom from each nitrate group at the distances of 2.408(2) and 2.500(2) Å for the Cu(1B)-O(1B) and Cu(1A)-O(1A) bonds, respectively, to complete the distorted square pyramidal CuN_2O_2O' chromophores. However, these axial positions involve the weak semi-coordination [13]. The stronger Cu(1B)-O(1B) bond in an axial position reflects in the larger displacement of the Cu(1B) atom [0.1421(3) Å] from the mean N_2O_2 plane, towards the nitrate group compared to that of the Cu(1A) atom [0.0791(3)Å]. The other four bonds to copper occur in two sets: the copper to hydroxyl-bridged oxygen, which average 1.940(2)Å, and the copper to dpyam nitrogen, which average 2.014(2)Å. The average Cu-O(H) distance of 1.94 Å within a dimer agrees well with that of 1.92 Å found in the corresponding bipyridyl copper(II) dimer [7]. The bridging Cu(1A)-O(4B)-Cu(1B) and Cu(1A)-O(4A)-Cu(1B) angles are 98.93(9) and 99.41(9) °, respectively, significantly greater than 90 °, and the O(4A)-Cu(1B)-O(4B) and O(4A)-Cu(1A)-O(4B) angles of 80.48(8) and 80.72(8)°, respectively are significantly less than 90 °. The bite angles of dpyam ligands [N(1B)-Cu(1B)-N(2B) 92.13(8)° and N(1A)-Cu(1A)-N(2A) 91.91(8)°] are only slightly greater than 90 °. The Cu-Cu distance is 2.9539(3) Å. There are no unusual bond lengths and angles in the dpyam ligand [14] (Table 2) and the individual pyridine rings are essentially planar. The

dpyam ligands are not planar, but involve the angles of 10.13(9) and 12.53(8)°, respectively, between the individual pyridine rings. Both nitrate anions are planar and weakly co-ordinated to the copper atoms in the axial positions. The nitrate group, which is bonded, to a Cu(1A) atom exhibits reasonable N-O bond lengths [1.224(3) to 1.256(3) Å] and O-N-O bond angles [119.3(3) to 120.6(3)°] for the monodentate nitrate ligand [15]. The other nitrate group has one oxygen bonded to another hydrogen bridged to the hydroxyl oxygen from the other dimer with a close contact distance of 2.025(*) Å. This bonding and bridging may be responsible for the evident distortion of this nitrate group (the O-N-O angles vary from 115.6(2) to 123.8(3)°).

The structure of (II) (Fig.2) consists of a binuclear $[Cu_2(H_2O)(O_2CH)_4(dpyam)_2]$ unit and an uncoordinated H_2O molecule. The copper atoms are bridged unsymmetrically by a formate group in an anti-syn arrangement [16,17]. The Cu (1A) atom exhibits a tetrahedral CuN_2O_2 chromophore, through a monodentate formate group, a bridging formate group and a dpyam ligand. The co-ordinated water molecule then occupies a fifth co-ordinate position at a distance of 2.297(2) Å, to give the square pyramidal CuN_2O_2O' chromophore. The Cu(1B) atom environment is also tetrahedrally distorted square pyramidal: two oxygen atoms of each monodentate formate group and with the two nitrogen atoms of a dpyam ligand, form the basal plane; the apical position is occupied by an oxygen atom from the bridging formate group at 2.414(2) Å from the copper atom. From both CuN_2O_2 chromophores, the average basal Cu-O distance is 1.960(2) Å and the average basal Cu-N distance is 1.999(2) Å. Both apical Cu-O distances, 2.297(2) and 2.414(2) Å for Cu(1A)-O and Cu(1B)-O bonds, respectively, are considerably longer than the four in-plane distances, but are within significant bonding distance of the Cu atoms [18]. The latter apical bond is weaker than that of the former one, resulting the small displacement of the Cu(1B) atom [0.1478(3) Å] from the mean N_2O_2 plane towards the bridged-formate oxygen atom, compared to that of the Cu(1A) atom, 0.1908(3) Å from the mean plane towards the water oxygen atom. Both CuN_2O_2 chromophores are non-planar with the tetrahedral twists, 16.01(7) and 19.35(9)° for the Cu(1A)N_2O_2 and Cu(1B)N_2O_2 chromophores, respectively. The planar pyridine rings form dihedral angles of 27.66(9) and 33.13(7)° for the ligands defined by N(1A)/N(2A) and N(1B)/N(2B) atoms, respectively. The formate groups in (II) act as the monodentate anions and a bidentate bridging anion. The bond lengths and angles within each

type are in accord with those found in $[Cu(dpyam)_2(O_2CH)][BF_4]$ [19] and $[Cu(dien)(HCO_2)_2]$ [17]. The second oxygen atoms of the monodentate formate groups are 2.903(2) and 2.733(3) Å apart from the Cu(1A) and Cu(1B) atoms, respectively, while that of a remaining disorder monodentate formate group bonded to the Cu(1B) atom, is more than 3.00 Å. However, these distances [Cu(1A)-O(2A) and Cu(1B)-O(2B)] are too long for even weak semi-coordination [13]. The bridging formate ligand joined copper atoms in an anti-syn configuration [17]. The apical Cu(1B)-O(bridging O_2CH^-) distance, 2.414(2) Å ,is significantly longer than that of similar contacts found in $[Cu(dien)(HCO_2)_2]$, 2.169(5) Å [17]. The O-C-O angle of bridging formate ligand, 129.5(3) Å is considerably larger than those of the remaining monodentate formate groups, 125.6-128.4 Å. Additionally, both C-O distances are almost equal compared to those of the monodentate formate groups. These are consistent with the bidentate bridging co-ordination mode of the formato ligand.

Structural comparisons. The square pyramidal CuN_2O_2O' chromophores of (I) and (II) correspond to the square pyramidal CuN_2O_2X chromophore observed from the copper environments of the known dimer structures, $[Cu_2(FBF_3)(OH)_2(dpyam)_2]$ (III), $Cu_2(OH)_2(H_2O)(dpyam)_2]Cl_2.2H_2O$ (IV) [1,2]. The structure of (I) is very comparable to that of (III), both involve the hydroxyl bridging in equatorial planes and the fifth axial positions occupied by the nitrate and tetrafluoroborate anions, respectively, while in (IV) the dihydroxy-bridged structure with the additional longer bonded bridging water molecule in a fifth position is observed. Consequently, (IV) involves the square pyramidal CuN_2O_2O' chromophore and the triply bridged dimer. The apical Cu-O distances in (I) [2.408(2) and 2.500(2) Å] and (II) [2.297(2) and 2.414(2) Å] are comparable to that of (IV) [2.414(3) Å], while in (III) a significantly longer distance of 2.745(7) Å is observed. These values are typical of the Cu-O distance of 2.2-2.7 Å in the fifth ligand position observed in other pyramidal copper(II) complexes [1]. However, the marked tetrahedral twists in (I), (II) and (III) [dihedral angles 20.73(8) and 16.70(8); 16.01(7) and 19.35(9); and 24.2 °, respectively] are less usual, while in (IV) the CuN_2O_2 chromophore is planar with a slight tetrahedral twist, dihedral angle of 3.91 °. The Cu-Cu separation of 2.954(3) Å in (I) is significantly longer than that of (IV) [2.799(1) Å], while in (III) a more comparable distance of 2.919(5) Å is observed. However, these distances are typical in the range previously observed, 2.80-3.00 Å [1,2,7,9,20].

In (II) the large bridging formato anion result in a long Cu-Cu distance of 5.552(*) Å and the copper(II) ions are linked by a formate group in an anti-syn bridging arrangement. The structurally characterised examples in which anti-syn O-C-O bridges are operated, are to date far less numerous than those with the syn-syn configuration [22]. However, it was observed in the infinite chain complexes $[CuL(H_2O)]_n$, $[Cu_2(OAc)_2A]_n$, $[Cu(NH_3)_2(OAc)Br]_n$ and $[Cu(dien)(HCO_2)][HCO_2]$ [17,22], while the syn-syn configuration with strong antiferromagnetic interaction was first observed in $Cu_2(CH_3COO)_4.2H_2O$, in which two copper(II) ions are bridged symmetrically by four acetate groups [22].

Spectroscopic Properties. The infrared spectrum of (I) shows a strong and broad band at 3475 cm^{-1} owing to the bridging hydrogen-bonded OH^- group [21]. The symmetric and antisymmetric NO stretchings appear as the strong bands at 1310 and 1380 cm^{-1}, respectively, consistent with the monodentate nitrate group [21]. The infrared spectrum of (II) shows two strong and broad bands centered at 1600 and 1530 cm^{-1} owing to the antisymmetric OCO^- stretchings of the monodentate and bidentate bridging co-ordination modes, respectively, of the formate groups within a dimer and a medium broad band at 1420 cm^{-1} owing to the symmetric OCO^- stretchings [24]. The coexistence of crystallisation and co-ordinated water molecules is consistent with the occurrence of a strong and broad absorption centered at 3400 cm^{-1} (symmetric and antisymmetric OH stretchings); medium intensity peaks at 1640 cm^{-1} (HOH bending), 670 and 510 cm^{-1} (rocking and wagging frequencies of co-ordinated water) are marked by the dpyam peaks [9, 23]. The electronic reflectance spectra of both (I) and (II) show a broad band at the same frequency of 15 670 cm^{-1} and are comparable to that of (III), 15 600 cm^{-1}, while (IV) has a higher energy broad band at 17 500 cm^{-1}. These observed single broad peaks are consistent with the square pyramidal stereochemistry and assigned to be the d_{xz}, d_{yz} ----- $d_x2_{-y}2$ transition [1].

Magnetic Properties. The complexes (I) and (II) are characterised by having low room-temperature magnetic moments [(I), u_{eff} = 1.62 BM; (II), u_{eff} = 1.37 BM], indicating significant antiferromagnetic coupling between the copper(II) centres. For bis(u-hydroxo)copper(II) complexes, a rather significant linear relationship has been

found between magnetic exchange coupling and the Cu-O-Cu angle [9,24]. The exchange interaction for (I) should be antiferromagnetic for Cu-O-Cu angle more than 97.5 °, consistent with the experimental results. Using this established relationship for (III), the Cu-O-Cu bridging angle of 99.3(2) ° [2] is more than 97.5 °, also suggesting an antiferromagnetic interaction between the two copper(II) centres. In contrast, the room temperature magnetic moment per copper(II) ion reported for the closely related complex (III) of 1.90 BM [2], is significantly higher than those of (I) and (II) and falls in the range expected for essentially magnetically diluted d^9 species. The result is surprising, as $[Cu_2(II)(chelate)_2(OH)_2X_2]$ complexes are generally antiferromagnetic and the tetrahedral twists of the CuN_2O_2 chromophores in (I), (II) and (III) are comparable. That of (IV) is also previously reported to be significantly lower at 1.75 BM [2], indicative of the antiferromagnetic behaviour.

As noted previously for the few well-characterised copper(II) complexes with bridging anti-syn COO groups, much smaller (antiferro- or ferromagnetic) interactions were found, compared to the strong antiferromagnetic interactions empirically observed for the syn-syn configuration adopted by the triatomic O-C-O bridges [22,25]. The exchange for the anti-syn COO groups is usually ferromagnetic. Hence, a point of interest in complex (II) is that it has been shown to be an antiferromagnet which is also observed in the anti-syn bridged complexes $[Cu_2(OAc)_2A]_n$ and $[Cu(NH_3)_2(OAc)Br]_n$.

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Table 1. Crystal data and structure refinement for $[Cu_2(ONO_2)_2(OH)_2(C_{10}H_9N_3)_2]$ and $[Cu_2(OH_2)(O_2CH)_4(C_{10}H_9N_3)_2].H_2O$.

	$[Cu_2(ONO_2)_2(OH)_2(C_{10}H_9N_3)_2]$	$[Cu_2(OH_2)(O_2CH)_4(C_{10}H_9N_3)_2].H_2O$
Formula	$C_{20}H_{20}Cu_2N_8O_8$	$C_{24}H_{26}Cu_2N_6O_{10}$
Formula weight	627.52	685.59
Colour	Blue	Green
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
A/Å	8.9463(1)	7.3752(4)
B/Å	9.8234(2)	11.2058(7)
C/Å	14.4495(1)	17.3299(12)
α/°	75.734(1)	79.847(5)
β/°	83.175(1)	87.899(5)
γ/°	70.472(1)	72.542(4)
V/Å^3	1158.99(3)	1344.7(2)
Z	2	2
D_c/g.cm^{-3}	1.798	1.693
μ/mm^{-1}	1.902	1.650
F(000)	636	700
Crystal size/mm	0.48×0.36×0.21	0.52×0.50×0.44
θ ranges/°	2.80–27.50	1.19–27.50
H / k / l	-11,11/-12, 12/0,18	-1,9/-14,14/-22,22
Reflections collected	7540	7569
Independent reflections	5131	6141
Absorption correction	Empirical	Semi-empirical
$T_{max.}$ and $T_{min.}$	0.752, 0.487	0.481, 0.531
No. restraints	0	0
No. parameters	423	501
GOF	1.047	1.073
Final R indices[I>2σ(I)]	R1 = 0.0339, wR2 = 0.0894	R1 = 0.0319, wR2 = 0.0872
R indices(all data)	R1 = 0.0404, wR2 = 0.0949	R1 = 0.0401, wR2 = 0.0909
Largest peak and hole/e·Å^{-3}	0.543, -0.463	0.706,-0.411

Table 2. Selected bond lengths(Å) and angles(°) for $[Cu_2(ONO_2)_2(OH)_2(C_{10}H_9N_3)_2]$ and $[Cu_2(OH_2)(O_2CH)_4(C_{10}H_9N_3)_2].H_2O$.

I. $[Cu_2(ONO_2)_2(OH)_2(C_{10}H_9N_3)_2]$

Cu(1A)-O(4A)	1.934(2)
Cu(1A)-O(4B)	1.941(2)
Cu(1A)-N(1A)	2.008(2)
Cu(1A)-N(2A)	2.015(2)
Cu(1A)-O(1A)	2.500(2)
Cu(1A)-Cu(1B)	2.9539(3)
O(4A)-Cu(1B)	1.939(2)
Cu(1B)-O(4B)	1.946(2)
Cu(1B)-N(1B)	2.015(2)
Cu(1B)-N(2B)	2.019(2)
Cu(1B)-O(1B)	2.408(2)
O(4A)-Cu(1A)-O(4B)	80.72(8)
O(4A)-Cu(1A)-N(1A)	94.77(8)
O(4B)-Cu(1A)-N(1A)	171.41(9)
O(4A)-Cu(1A)-N(2A)	164.12(9)
O(4B)-Cu(1A)-N(2A)	94.32(8)
N(1A)-Cu(1A)-N(2A)	91.91(8)
O(4A)-Cu(1A)-O(1A)	103.55(8)
O(4B)-Cu(1A)-O(1A)	87.58(9)
N(1A)-Cu(1A)-O(1A)	86.37(8)
N(2A)-Cu(1A)-O(1A)	91.22(8)
O(4A)-Cu(1A)-Cu(1B)	40.35(5)
O(4B)-Cu(1A)-Cu(1B)	40.60(6)
N(1A)-Cu(1A)-Cu(1B)	135.08(6)
N(2A)-Cu(1A)-Cu(1B)	131.74(6)
O(1A)-Cu(1A)-Cu(1B)	100.53(4)
O(4A)-Cu(1B)-O(4B)	80.48(8)
O(4A)-Cu(1B)-N(1B)	172.84(8)
O(4B)-Cu(1B)-N(1B)	93.00(8)
O(4A)-Cu(1B)-N(2B)	95.01(8)
O(4B)-Cu(1B)-N(2B)	159.00(10)
N(1B)-Cu(1B)-N(2B)	92.13(8)
O(4A)-Cu(1B)-O(1B)	96.65(8)
O(4B)-Cu(1B)-O(1B)	105.62(10)
N(1B)-Cu(1B)-O(1B)	82.20(8)
N(2B)-Cu(1B)-O(1B)	95.25(8)
O(4A)-Cu(1B)-Cu(1A)	40.24(5)
O(4B)-Cu(1B)-Cu(1A)	40.46(6)
N(1B)-Cu(1B)-Cu(1A)	132.95(6)
N(2B)-Cu(1B)-Cu(1A)	133.37(6)
O(1B)-Cu(1B)-Cu(1A)	101.29(5)

II. $[Cu_2(OH_2)(O_2CH)_4(C_{10}H_9N_3)_2].H_2O$.

Cu(1A)-O(1A)	1.956(2)
Cu(1A)-O(3A)	1.976(2)
Cu(1A)-N(1A)	1.987(2)
Cu(1A)-N(2A)	1.998(2)
Cu(1A)-O(1W)	2.296(2)
O(4A)-Cu(1B)	2.414(2)
Cu(1B)-O(3BB)	1.890(6)
Cu(1B)-O(3BA)	1.927(2)
Cu(1B)-O(1B)	1.981(2)
Cu(1B)-N(2B)	1.992(2)
Cu(1B)-N(1B)	2.017(2)

O(1A)-Cu(1A)-O(3A)	88.11(7)
O(1A)-Cu(1A)-N(1A)	90.28(7)
O(3A)-Cu(1A)-N(1A)	165.67(7)
O(1A)-Cu(1A)-N(2A)	172.48(8)
O(3A)-Cu(1A)-N(2A)	91.05(7)
N(1A)-Cu(1A)-N(2A)	88.69(7)
O(1A)-Cu(1A)-O(1W)	91.54(7)
O(3A)-Cu(1A)-O(1W)	95.09(7)
N(1A)-Cu(1A)-O(1W)	99.18(8)
N(2A)-Cu(1A)-O(1W)	95.98(8)
O(3BB)-Cu(1B)-O(3BA)	27.9(3)
O(3BB)-Cu(1B)-O(1B)	96.7(3)
O(3BA)-Cu(1B)-O(1B)	89.22(12)
O(3BB)-Cu(1B)-N(2B)	162.3(3)
O(3BA)-Cu(1B)-N(2B)	169.46(13)
O(1B)-Cu(1B)-N(2B)	89.94(8)
O(3BB)-Cu(1B)-N(1B)	79.1(2)
O(3BA)-Cu(1B)-N(1B)	93.77(14)
O(1B)-Cu(1B)-N(1B)	163.65(8)
N(2B)-Cu(1B)-N(1B)	89.98(7)
O(3BB)-Cu(1B)-O(4A)	107.4(4)
O(3BA)-Cu(1B)-O(4A)	82.17(11)
O(1B)-Cu(1B)-O(4A)	98.87(7)
N(2B)-Cu(1B)-O(4A)	87.58(7)
N(1B)-Cu(1B)-O(4A)	97.46(7)

FIGURE CAPTIONS

Fig. 1. ORTEP view of $[Cu_2(ONO_2)_2(OH)_2(C_{10}H_9N_3)_2]$

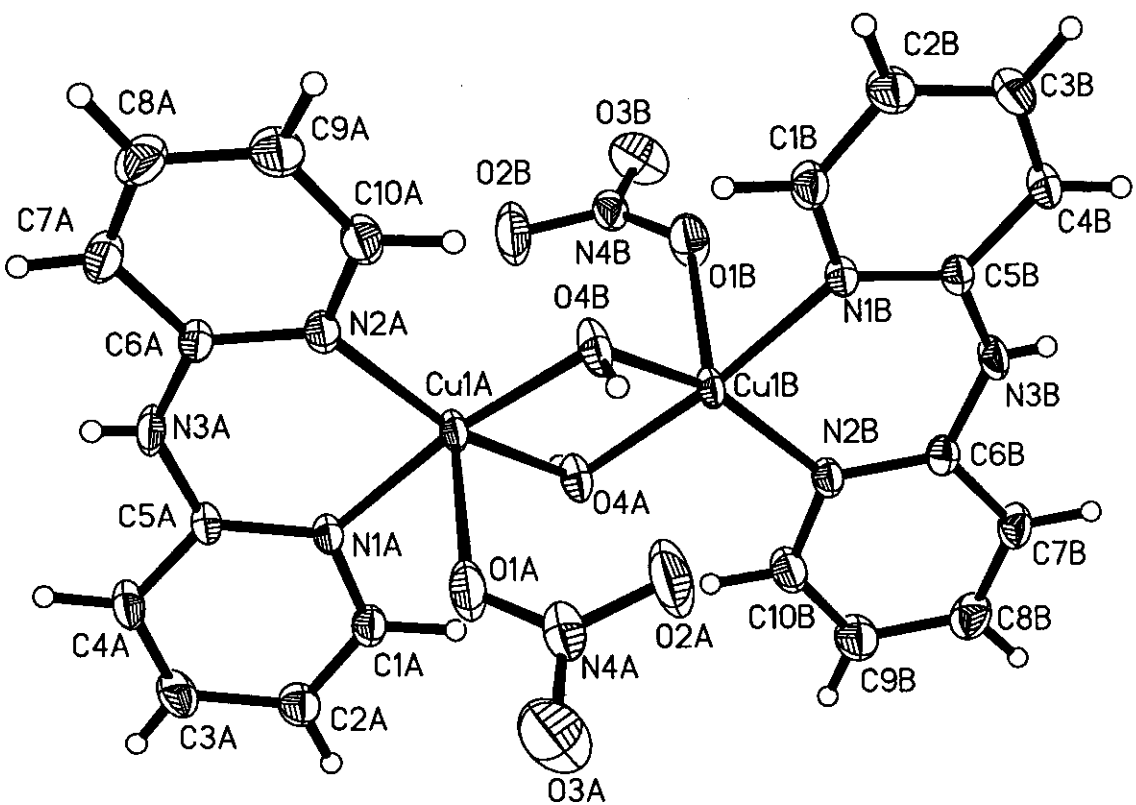

Fig. 2. ORTEP view of $[Cu_2(OH_2)(O_2CH)_4(C_{10}H_9N_3)_2].H_2O$.