# A doubly end-on azido-bridged trinuclear Cu(II) complex: synthesis, spectral and DFT functional studies Amitabha Datta<sup>a</sup>, Kuheli Das<sup>b</sup>, Wen-Yen Huang<sup>a</sup>, Jui-Hsien Huang<sup>a</sup>\*, Fu-Xing Liao<sup>a</sup> and Ching-Han Hu<sup>a</sup>

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A trinuclear, doubly azido-bridged Cu(II) complex,  $[Cu_{1.50}(L)(N_3)_3(CH_3OH)]_2$ ,  $(LH = [(CH_3)_2NCH_2CH_2N=CHC_6H_3(OH) (OMe)]$ ), has been synthesised and fully characterised by elemental analyses, IR, UV-Vis, EPR and DFT studies. Its single crystal X-ray structure reveals that adjacent Cu<sup>II</sup> ions are linked by double end-on azido-bridges; thus the full molecule is generated by the site symmetry of a crystallographic two-fold rotation axis.

Keywords: copper(II), Schiff base, azide bridge, X-ray structure

Schiff base complexes of transition metals have been widely employed in the development of heterogeneous catalysis,<sup>1</sup> molecular electronics, single-molecule-based magnetism, and photochemistry.<sup>2-5</sup> Their physical, optical, and electronic properties have been explored in different coordination environments with organic chelators, blockers, and suitable bridging units.<sup>6-8</sup> Such multidentate organic ligands<sup>9-11</sup> can accommodate one, two or more metal centres and thus may provide the basis of models for active sites of biological systems.<sup>12–14</sup> In recent years, an increasing effort has been focused on the preparation of mono- or di-nuclear mixed- ligand transition metal complexes containing neutral or chelating nitrogendonor ligands. Early and late transition metal complexes of this type and particularly those of copper have extensively been used as catalysts for a wide variety of reactions, including olefin polymerisation<sup>15-17</sup> and dioxygen activation.<sup>18-20</sup> Tridentate Schiff bases with N2O donor sets have been preferred because such ligands effectively act as chelates and can block the coordination sites of metal ions, leaving the metal ion coordinatively unsaturated. In order to saturate the coordination number of metal ions preferring square planar, square pyramidal and octahedral geometry, different bridging ligands (N<sub>3</sub>-, NCO<sup>-</sup>, NCS<sup>-</sup>, acetates, carboxylates) have been used, giving rise to dinuclear and multinuclear complexes.<sup>21-26</sup> As bridging ligands, depending upon the steric and electronic demand of coligands, the pseudohalide-bridged copper(II) complexes can change their coordination to either an end-on  $(\mu$ -1,1) or an end-to-end ( $\mu$ -1,3) mode.<sup>27,28</sup> Moreover, various interesting topologies have been prepared using different transition and non-transition metal ions as templates with Schiff bases as blocking units and pseudohalide-like azide as bridging ligand. Azide ion is known for its versatility as bridging ligand since it can bind two metal centres in end-on and/or end-to-end fashions.<sup>29,30</sup> Such azido-bridged copper(II) complexes are of great interest to biologists and bioinorganic chemists investigating the structure and role of active sites in copper proteins. Electron paramagnetic resonance (EPR) spectroscopy can notably indicate large coupling through intensity variation and can also extract small coupling with the use of multifrequency experimentation.31-34

We now describe the synthesis<sup>1</sup> and X-ray structural characterisation of a new doubly end-on azido-bridged trinuclear copper complex  $[Cu_{1,50}(L)(N_3)_3(CH_3OH)]_2$ ,  $[L = (2-[{[2-(dime$  $thylamino)ethyl]imino}methyl]-6-methoxyphenol)] (1) incor$ porated with a tridentate Schiff-base.<sup>35</sup> The complex has beencharacterised by elemental analysis, IR and UV-Vis spectra,EPR and DFT functional studies. The structure of the complexwas determined by X-ray diffraction using single crystals.

A representation of the molecular structure of complex 1 is depicted in Fig. 1 and selected bond lengths and angles are shown in Table 2. Complex 1 features a doubly end-on azidobridged Cu(II) trinuclear unit as shown in Fig. 1. The solid crystallises in the monoclinic unit cell of the C2/c space group with the tricopper unit situated in a special position of 0, y,  $\frac{1}{4}$  such that only half of the tricopper complex exists in an asymmetric unit. The full molecule is generated by the site symmetry of a crystallographic two-fold rotation axis. The coordination environment of the central copper atom can be described as a distorted octahedron. It is coordinated by two cis- methanol molecules and four bridging azide ligands. The two unique quasi-linear bond angles at this copper atom are 168.51(10) and  $170.79(15)^\circ$ . The copper atom at the flank also has distorted octahedral coordination geometry. It is ligated by one terminal and two cis-bridging azide ligands and the tridentate ONN ligand via the phenolato-oxygen atom, the amine and the imine nitrogen atoms. The extent of distortion at this copper atom is less than that at the central copper atom as evidenced by the three larger quasi-linear bond angles, which are 173.63(12), 176.91(11), and 175.18(12)°. The bonding distances and angles between the tridentate ONN ligand to this copper atom are entirely normal with respect to similar compounds in the literature.<sup>34,35</sup> The Cu–N distance from the terminal azide is short [1.942(3) Å] compared with those from the bridging azide [1.966(3)-2.213(3) Å]. These Cu-N distances are within the normal range of similar compounds.36-38



**Fig. 1** Representation of the molecular structure of compound **1**. Ellipsoids are drawn from 40% probability level. Hydrogen atoms have been omitted for clarity.

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The non-bonding Cu-Cu distance of 3.224(1) Å is long compared with those in similar copper azide complexes.<sup>36-3</sup> For example, the Cu…Cu distance in the relevant  $[Cu(\mu_{1,1} N_{3}_{2}(N_{3})_{4}^{1-2}$  anion is 3.126(2) Å.<sup>38</sup> The Cu–N(azide)–Cu angle of 99.4(1)° is markedly wider than that of 89.1° in the dicopper complex bearing a structurally very similar tridentate ONN ligand and bridging azido ligands reported earlier,<sup>36</sup> but is slightly smaller than that of 103.2(2)° in another related dicopper azide complex also reported by us previously.<sup>37</sup> One of the bridging azide ligands is noticeably bent with a short N-N-N bond angle of 168.2(6)°, compared with those of 174.7(4) and 179.1(4)° at the other two azide ligands. A strong intramolecular hydrogen bond of the type O-H-O exists between the proton on a coordinated methanol molecule and the phenolato-oxygen atom of the tridentate ligand with the H…O contact distance of 1.80(4) Å and O–H…O contact angle of 160(4)°. A short non-classical intermolecular hydrogen bond of the type C-H...N also exists between a methylene hydrogen atom on the tridentate ligand and a nitrogen atom on the bridging azide ligand, linking tricopper complexes into infinite one-dimensional chains. The H…N contact distance and angle are 2.33 Å and 152° respectively. A weaker, nonclassical intermolecular hydrogen bonding of similar C-H···N type further links these chains into a densely-packed infinite three-dimensional network. The contact distances and angles of these interactions fall into ranges of 2.46-2.53 Å and 106-154°, respectively. The crystallographic packing diagram is shown in Fig. 2 along the *b*-axis.

In the IR spectra of **1**, a peak at 1626 cm<sup>-1</sup> can be assigned as the stretching frequency of the azomethine group of the Schiff base. A well-resolved strong band at 2044 cm<sup>-1</sup> and a bifurcated peak at 2066 cm<sup>-1</sup> were also observed and assigned to  $v_{N=N}$  of the azide group coordinated to two different metal centres and to terminal ligands respectively.<sup>39</sup> The ligand coordination to the copper centre is substantiated by two bands appearing for **1**, at 412 and 423 cm<sup>-1</sup> attributable to  $v_{Cu-N}$ and  $v_{Cu-O}$ , respectively. The bands in the range, 3544 and 1631 cm<sup>-1</sup> are attributable to O–H stretching and bending of water ligands.<sup>39</sup>

The electronic spectrum of **1** exhibits two strong absorption bands at 232 and 281 nm, which are due to ligand

charge-transfer transitions. The UV absorption bands observed at 362 nm can be assigned to ligand-to-metal charge-transfer transitions. The spectrum also shows a low-intensity absorption band at 558 nm, originating from d–d transitions.<sup>40-41</sup>

The experimental powder EPR spectrum (X-band, recorded at room temperature) is composed of allowed ( $\Delta M_s = \pm 1$ ) transitions centred at g = 2.021 and of a weak intensity, nominally forbidden, half-field ( $\Delta M_s = \pm 2$ ) peak observable at g = 4.682.

Compound 1 has been investigated by theoretical calculations. For this purpose, the three-parameter hybrid of exact exchange and Becke's exchange energy functional has been used,42 plus Lee, Yang, and Parr's gradient-corrected correlation energy functional<sup>43</sup> (B3LYP). The 6-31G(d) basis set was applied in all computations. The Gaussian03 suite of programs was used in our study.<sup>45</sup> For the copper coordination compound 1, we found that the triplet state is significantly lower in energy than its singlet and quintet counterparts. In addition, we have located two isomers; among them the symmetric isomer lies at 22.3 kcal  $\mathrm{mol}^{\scriptscriptstyle -1}$  above the asymmetric isomer. In general, the theoretically-predicted geometrical parameters are in good agreement with those resolved by X-ray diffraction studies. The geometries predicted by DFT (first entry) and those resolved from the X-ray data (second entry) are presented and compared in Figs 3a and b.

## Experimental

Synthesis of the Schiff base ligand:  $[(CH_3)_2NCH_2CH_2N=CHC_6H_3(OH)(OMe)]$  (LH) was obtained by refluxing a methanolic solution (25 mL) of O-vanillin (1 mmol) and 2-dimethylaminoethylamine (1 mmol) for 30 minutes. The resulting orange–yellow solution containing the ligand was used without further purification.

1: To a methanolic solution (20 mL) of copper trichloroacetate (0.388 g, 1 mmol), LH (1 mmol) was added, which produced immediately an intensely green solution. The solution was then heated to boiling and then an aqueous solution (10 mL) of sodium azide (0.195 g, 3 mmol) was added dropwise slowly over 15 mins to the hot solution. After the completion of addition of sodium azide, the resulting solution was refluxed for another 10 min. On cooling and after slow evaporation of the brown solution, dark brown, rectangular shaped single crystals of the complex (1) separated out in 3 days. The crystals were filtered off, washed with water and dried in air



Fig. 2 Crystallographic packing diagram of 1.



on-Sym.)	
ym.)	

Rel. energy is  $\Delta H_{298}$ .

0 2 (S

Fig. 3 DFT predicted geometries (first entry) and those resolved from X-ray (second entry). (a) Non-symmetrical; (b) symmetrical.

(yield ca. 83%). A suitable, dark brown block crystal was selected for X-ray data collection. Anal. Calcd for  $C_{13}H_{22}Cu_{1.50}N_{11}O_3$ : C, 32.82; H, 4.66; N, 32.39. Found: C, 32.61; H, 4.73; N, 32.21%.

### Crystallographic data

Details concerning crystal data, data collection characteristics and structure refinement are summarised in Table 1. The crystal was mounted on capillaries and transferred to a goniostat and data were collected at 100 (2) K under a nitrogen gas stream on a Bruker SMART CCD diffractometer with graphite-monochromated Mo-K<sub>a</sub> radiation and the  $\omega$ :2 $\theta$  scan technique applied within a  $\theta$  range of 3.04–33.66°. No significant crystal decay was found. Data were corrected for absorption empirically by means of  $\boldsymbol{\psi}$  scans. A total of 16660 reflections were collected from which 5933 independent [R(int) = 0.0200] reflections were measured. The stability of the crystals was checked by measuring standard reflections at fixed intervals during the data collection. However, no significant loss of intensity was noted. Data were processed using the CRYSALIS-CCD and -RED45 programs. The structure was solved by direct methods using the SHELXTL PLUS<sup>46</sup> system and refined by a full-matrix least-squares methods based on  $F^2$  using SHELXL93<sup>47</sup> using all 19,594 data to final  $wR_2$  (on  $F^2$ , all data) = 0.1658 and  $R_1$  (on F, with  $[I > 2\sigma(I)]$ ) = 0.0585. The functions minimised were  $\sum w[|Fo|^2 - [|Fc|^2]^2$ , where  $w = [\sigma^2(I) + \sigma^2(I)]^2$  $(0.0849P)^2 + 0.3606P]^{-1}$  for 1 with  $P = (|Fo|^2 + 2|Fc|^2)/3$ . The hydrogen atom positions were calculated and they were constrained to idealised geometries and treated as riding where the H atom displacement parameter was calculated from the equivalent isotropic displacement parameter of the bound atom.

Crystallographic data for structural analysis have been deposited at the Cambridge Crystallographic Data Centre, bearing 790433. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK

## Table 1 Crystallographic data for 1

Empirical formula	$C_{13}H_{22}Cu_{1.50}N_{11}O_{3}$
Formula weight	475.73
Temperature	100(2) K
Wavelength	0.77490 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	$a = 29.894(3) \text{ Å} \alpha = 90^{\circ}$
	b = 8.2233(7)  Å
	$\beta = 110.3550(10)^{\circ}$
	$c = 16.2041(16) \text{ Å } v = 90^{\circ}$
Volume	3734.6(6) Å <sup>3</sup>
Ζ	8
Density (calculated)	1.692 Mg m⁻³
Absorption coefficient	2.233 mm <sup>-1</sup>
F(000)	1956
Crystal size	$0.23 \times 0.05 \times 0.01 \text{ mm}^3$
Theta range for data collection	3.04–33.66°
Reflections collected	19594
Independent reflections	5637 [ <i>R</i> (int) = 0.0402]
Data / restraints / parameters	5637/1/262
Goodness-of-fit on $F^2$	1.065
Final R indices $[/>2\sigma(l)]$	$R^1 = 0.0585$ , $wR^2 = 0.1581$
R indices (all data)	$R^{1} = 0.0711, \ wR^{2} = 0.1658$
Largest diff. peak and hole	1.460 and –1.600 e Å <sup>-3</sup>

22.3

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The authors gratefully acknowledge financial support from the National Science Council of Taiwan.

Table 2 Selected bond lengths (Å) and angles (°) for 1

1.897(3)	Cu(1)–O(2)	1.902(2)	Cu(1)–N(9)	1.942(3)
1.965(3)	Cu(1)–N(6)	2.009(3)	Cu(1)–N(1)	2.020(3)
2.086(3)	Cu(2)–O(3)	2.097(3)	Cu(2)–N(6)	2.213(3)
93.82(12)	N(2)–Cu(1)–N(9)	90.34(13)	O(2)–Cu(1)–N(9)	89.92(12)
173.63(12)	O(2)-Cu(1)-N(3)	89.09(10)	N(9)–Cu(1)–N(6)	175.18(12)
176.91(11)	N(3)#1–Cu(2)–O(3)	168.51(10)	N(6)–Cu(2)–N(6)#1	170.79(15)
168.2(6)	Cu(1)–N(6)–Cu(2)	99.44(12)	N(8)–N(7)–N(6)	179.1(4)
174.7(4)				
	1.897(3) 1.965(3) 2.086(3) 93.82(12) 173.63(12) 176.91(11) 168.2(6) 174.7(4)	$\begin{array}{c cccc} 1.897(3) & Cu(1)-O(2) \\ 1.965(3) & Cu(1)-N(6) \\ 2.086(3) & Cu(2)-O(3) \\ 93.82(12) & N(2)-Cu(1)-N(9) \\ 173.63(12) & O(2)-Cu(1)-N(3) \\ 176.91(11) & N(3)\#1-Cu(2)-O(3) \\ 168.2(6) & Cu(1)-N(6)-Cu(2) \\ 174.7(4) \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Received 24 November 2010; accepted 13 January 2011 Paper 1000444 doi: 10.3184/174751911X12972790588178 Published online: 23 March 2011

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