### Accepted Manuscript

Accepted Date:

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PII:	\$0020-1693(13)00297-1
DOI:	http://dx.doi.org/10.1016/j.ica.2013.05.024
Reference:	ICA 15479
To appear in:	Inorganica Chimica Acta
Received Date:	7 September 2012
Revised Date:	10 May 2013

14 May 2013



Please cite this article as: R.N. Patel, D.K. Patel, V.P. Sondhiya, K.K. Shukla, Y. Singh, A. Kumar, Synthesis, crystal structure and superoxide dismutase activity of two new bis(µ-acetato/µ-nitrato) bridged copper(II) complexes with *N*'-[phenyl(pyridin-2-yl)methylidene]benzohydrazone, *Inorganica Chimica Acta* (2013), doi: http://dx.doi.org/10.1016/j.ica.2013.05.024

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# Synthesis, crystal structure and superoxide dismutase activity of two new bis(μ-acetato/μ-nitrato) bridged copper(II) complexes with *N*'-[phenyl(pyridin-2-yl)methylidene]benzohydrazone

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Two homodinuclear copper(II) end-on bis( $\mu$ -acetato/ $\mu$ -nitrato) bridged complexes with two NNO donor ligands, *viz.*, [(L)Cu( $\mu$ -CH<sub>3</sub>COO)<sub>2</sub>Cu(L)] (1) and [(L)Cu( $\mu$ -NO<sub>3</sub>)<sub>2</sub>Cu(L)] (2) (where L = *N*<sup>-</sup>-[phenyl(pyridin-2-yl)methylidene]benzohydrazone) are reported. Both complexes are structurally characterized using single crystal X-ray diffraction studies and belong to monoclinic crystal system having space group *P* 2<sub>1</sub>/*n*. The distance between two copper centers is 3.344(8) and 3.406(7) Å respectively for 1 and 2. On the basis of density function theory (DFT) calculations, the electronic excitations involve transitions mainly from metal-ligand bonding MOs to the β-LUMO within the dominant Cu d<sub>xy</sub> character and to β-LUMO + 1. Epr spectra for polycrystalline samples exhibited the copper(II) hyperfine structures as well as zero-field splitting which are appropriate for triplet state of such a dimmers. Complexes effectively catalyze the dismutation of superoxide (O<sub>2</sub><sup>-</sup>) in alkaline nitro blue tetrazolium chloride assay and IC<sub>50</sub> values were determined.

Keywords: Crystal structure, hydrazone, density functional theory, epr, superoxide dismutase activity.

#### 1. Introduction:

Binuclear complexes have been receiving considerable interest due to their biological and industrial relevance [1]. Mixed ligand complexes formed between metal ions, Schiff bases and hetero aromatic nitrogen bases may be considered as models for substrate metal ion–enzyme interaction. Chelation causes changes in the biological properties of the ligands and also the metal. A number of Schiff-base complexes [2] have been tested for antibacterial activities, antibacterial [3], antifungal [4], anticancer [5], and herbicidal [6] activities. Superoxide ion is toxic to cells; a defense mechanism must have been initiated by nature.

Schiff base ligands, particularly molecules possessing nitrogen, oxygen and sulfur donor sites are important in the development of coordination chemistry as well as in the biomimetic chemistry of a number of metal ions, particularly the transition metals [7]. The ability of nitrogen and sulfur based donors to stabilize reduced and oxidized forms of copper(II) has sparked interest in their bioinorganic systems [8,9]. The properties of Schiff

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base metal complexes stimulated much interest for their contributions to single molecule-based magnetism, material sciences, catalysis of many reactions like carbonylation, oxidation, reduction and epoxidation, their industrial applications and complexing ability towards some toxic metals. The high affinity of the chelation of the Schiff bases towards the transition metal ions is utilized in preparing their solid complexes [10]. Schiff base complexes containing nitrogen and oxygen atom as donor atoms play an important role in biological systems and represent models for metallo-proteins and metallo-enzymes that catalyze the reduction of nitrogen and oxygen [11].

In continuation of our previous work [12], herein we report the synthesis of two  $\mu$ acetato/ $\mu$ -nitrato bridged copper(II) complexes using Schiff base ligand (HL). X-ray crystallography, epr, electronic spectroscopy, and magnetic susuptibility measurements have been carried out to characterize these two copper(II) complexes. Their redox properties using cyclic voltammetry along with SOD activity have also been measured and discussed.

#### 2. Experimental

#### 2.1. Materials and Instrumentation

All reagents used in the syntheses were of analytical grade. The elemental analysis for carbon, hydrogen and nitrogen were performed on an Elementar Vario ELIII Carlo Erba 1108 Elemental analyzer. UV-vis spectra were recorded at room temperature on Shimadzu 1601 spectrophotometer. IR spectra were recorded in KBr medium on a Perkin-Elmer spectrophotometer. Cyclic voltammetry was carried out on a BAS-100 Epsilon electrochemical analyzer having an electrochemical cell with a three-electrode system. Ag/AgCl was used as the reference electrode, glossy carbon as the working electrolyte and DMSO as solvent. All measurements were carried out at 298 K under a nitrogen atmosphere. Magnetic susceptibility measurements were made on a Gouy balance using a mercury(II) tetrathiocynato cobaltate(II) as calibrating agent( $\chi_g$ =16.44 × 10<sup>-6</sup> c.g.s. units). Electron paramagnetic resonance (e.p.r.) spectra were recorded with a Varian E-line Century Series epr spectrometer equipped with a dual cavity and operating at X-band of 100 kHz modulation frequency. Tetracyanoethylene (TCNE) was used as field marker (g = 2.00277). The EPR Parameters for copper(II) complexes determined accurately from a computer simulation program[13-16].

#### 4.2. Synthesis of complexes

#### 4.2.1. Syntheses of Schiff base ligand (HL)

The Schiff base  $L^1$  was synthesized [17,18] by the condensation of benzoyalpyridine and benzoyl hydrazide in equimolar ratio 1:1. The reaction mixture in ethanol was stirred for 4 h, A colorless solution was obtained, which was filtered off and allowed for slow evaporation at room temperature. White block shape crystals were collected by filtration and washed with diethyl ether. *Anal.* Calc. C<sub>19</sub>H<sub>15</sub>N<sub>3</sub>O: C, 75.73; H, 5.02; N, 13.94 %. Found: C, 75.50; H 4.98; N, 14.02%. FAB-mass (m/z) Calc. 301.34; Found, 301.

#### 4.2.2. Synthesis of $[Cu_2(\mu-CH_3COO)_2L_2]$ (1)

A mixture of Cu(OAc)<sub>2</sub>  $^{2}$ H<sub>2</sub>O (1 mmol, 0.199g) and HL (1 mmol, 0.301g) in methanol was stirred for 5 h. Dark green solution was filtered and after slow evaporation green block shape crystals suitable for single crystal X-ray were obtained. Yield: 0.352 g, 70.57%. Elemental analysis (%): calc. for C<sub>42</sub>H<sub>34</sub>Cu<sub>2</sub>N<sub>6</sub>O<sub>6</sub> (M<sub>r</sub> = 845.84): C 59.64, H 4.05, N 9.94; found: C 59.36, H 4.52, N 9.89. IR (cm<sup>-1</sup>): 3424, 3020, 1541, 1422, 1375, 1217, 1082, 928, 770, 671, 625, 532, 488.

4.2.3. Synthesis of  $[Cu_2(\mu - NO_3)_2L_2]$  (2) Complex 2 was prepared in the similar way that described for 1, except that Cu(NO<sub>3</sub>)<sub>2</sub> <sup>3</sup>H<sub>2</sub>O (M.W. 241.60) was replaced Cu(OAc)<sub>2</sub> <sup>2</sup>H<sub>2</sub>O. Yield: 0.411 g, 79.76%. Elemental analysis (%): calc. for C<sub>38</sub>H<sub>28</sub>Cu<sub>2</sub>N<sub>8</sub>O<sub>8</sub> (M<sub>r</sub> = 845.84): C 53.58, H 3.31, N 13.16; found: C 53.32, H 3.80, N 13.05. IR (cm<sup>-1</sup>): 3448, 3278, 3021, 1555, 1491, 1428, 1372, 1217, 1083, 929, 769, 671, 625, 559, 498.

#### 4.3. Single crystal X-ray crystallography

Single crystal X-ray data were collected on CCD detector based Oxford Diffractometer using graphite monochromatized MoK $\alpha$  ( $\lambda = 0.71073$ Å). The diffraction data was solved using SIR-92[19] with GUI control and structure was refined by SHELXL-97 [20] refinement of  $F^2$  against all reflections. Non-hydrogen atoms were refined anisotropically and all hydrogen atoms

were geometrically fixed and allowed to refine using a riding model. Molecular graphics was generating using different software such as Diamond, ORTEP-3v2 for WINDOWS [21], PLATON and Mercury [22].

#### 4.4. Density functional theory calculations

Density Functional Theory (DFT) calculations on the complexes **1** and **2** with spin multiplicity were performed with the Gaussian 03 (G03) [23]. Optimized geometries were calculated with the widely adopted U-B3LYP [24] functional. For all the atoms 6-31G\*\* basis set was employed. The X-ray coordinates were used as starting positions in the optimization. Natural Bond Orbital (NBO) wave function analysis for the optimized structures was performed with NBO 3.1 [25]. Franck–Condon electronic excitation spectra were calculated on the optimized structures both in vacuum and in DMSO using the polarized continuum model (PCM) [26] within the Time Dependent-Density Functional Theory (TD-DFT) taking into account the lowest 30 excitations.

#### 4.4. Superoxide dismutase activity (SOD)

The in vitro SOD activity was measured using alkaline DMSO method, where alkanine DMSO was a source of superoxide radical (O2<sup>-</sup>) and nitro blue tetrazolium chloride (NBT) as  $O_2^{-1}$  scavenger [27].

#### 3. Results and discussion

#### 3.1 Synthesis of complexes

Both complexes were prepared by the interaction of copper(II) salt with hydrazone Schiff base ligand directly by conventional solution method and crystalline product suitable for single crystal X-ray diffraction studies obtained. The protocol used for the syntheses of these two bis( $\mu$ acetato/ $\mu$ -nitrato) copper(II) complexes is shown in Scheme I. The suitable crystals were selected for single crystal X-ray analysis.



Scheme I- Synthesis of complex 1 and 2

#### 3.2. X-ray crystallography structural characterization

Single crystal X-ray analysis indicates that copper(II) center is penta coordinated and OAc is making bridge between two copper ions in complex 1. Crystal structure refinement data related to both complexes are given in Table 1. ORTEP view of complex 1 is presented in Fig. 1. The lattice nature is monoclinic with space group  $P2_1/n$ . The compound exhibits a distorted square pyramidal geometry with the basal plane occupied by hydrazone ligand and acetate oxygen (O2) for both metal centre. The relevant bond lengths and angles are given in Table 2. The oxygen (O2a) from acetate group of the adjacent monomer plugs in to the axial position resulting in a dimer with a Cu-Cu separation 3.34 Å. The comparison of bond distances (Table 2) confirms the possibility of dinuclear structure. The Cu-N/O bond lengths and bond angles around the copper(II) ions are [Cu(1)-N(2) = 1.927 Å, Cu(1)-O(1) = 1.984 Å, Cu(1)-O(2) = 1.926 Å,Cu(1)-O(2a) = 2.312, Cu(1a)-O(2) = 3.312 and  $O(2)-Cu(1)-N(2) = 172.88^{\circ}$ ,  $O(2)-Cu(1)-O(1) = 172.88^{\circ}$ 102.90°, N(2)-Cu(1)-O(1) = 79.30°, O(2)-Cu(1)-N(1) = 97.99°, N(2)-Cu(1)-N(1) = 79.65, O(1)-Cu(1)-N(1) = 158.95] are similar to the recently reported bridged copper(II) complexes [28]. It is observed that copper atom is closer to hydrazone ligand moiety than the acetato group. Cu-N<sub>pyridyl</sub> bonds large than Cu-N<sub>imine</sub> bonds show the strength of azomethine nitrogen coordination. Most of the angles involving the central copper atoms are widely different from 90° and 180° indicating a significant distortion from the square pyramidal geometry.

The five coordinated copper(II) centre with distorted geometry is indicated by the structural index parameter  $\tau$ , which measures the degree of trigonality of penta coordinated geometry between the ideal square pyramidal ( $\tau = 0$ ) and a trigonalbipyramidal ( $\tau = 1$ ) extremes [29,30]. For the complex **1**,  $\tau$  value is 0.23. Coordination sphere of **1** is presented in Fig. 2. The bridging angle of O (2)-Cu(1)-O(2a) and Cu(1)-O(2)-Cu(1a) are 76.20° and 103.8°, respectively.

An ORTEP view of complex 2 is presented in Fig. 3. The complex crystallizes in monoclinic crystal system with the space group  $P_2 l/n$ . The structure of 2 is very similar to complex 1 and two copper centers are bridged with nitrato group. Both copper centers adopt a distorted square pyramidal structure. The  $\tau$  value for complex 2 0.26, confirms the distorted square pyramidal structure of the penta coordinated complex. The distorted basal planes are defined by N(1), N(2), O(1) and O(2). O(2a) of other nitrato group is present in the axial position. Coordination sphere is presented in Fig. 4. The bridging angle of O(2)-Cu(1)-O(2a) and Cu(1)-O(2)-Cu(1a) are 73.44° and 106.56° respectively. All the Cu-O/N bond distances [Cu(1)-N(2) = 1.927 Å, Cu(1)-N(1) = 1.991 Å, Cu(1)-O(1) = 1.946 Å, Cu(1)-O(2) = 1.960 Å, Cu(1)-O(2) Å, Cu(1)-O(2) = 1.960 Å, Cu(1)-O(2) Å, Cu(1)-O(2)O(2a) = 2.355 Å, Cu(1a)-O(2) = 2.355 Å] and the bond angles around the copper(II) ions [N(2)- $81.23^{\circ}$ , O(1)-Cu(1)-N(1) = 161.69^{\circ}, O(2)-Cu(1)-N(1) = 99.32^{\circ}] fall in to the normal range. The Cu-Cu separation in complex 2 is 3.40 Å. Both complexes 1 and 2 have essentially similar structures with identical metrical parameters (Table 2). A ball and stick view (Fig. S1 and S2) of the 2D-helical layer constructed by HL and the bridging ligands forms a structural assembly. It can be observed that the molecules are packed in a 2D helical layered arrangement of the rings.

#### 3.3. Density functional theory

Natural Bond Orbital (NBO) wave function analysis [25] has been performed in order to gain insight into the molecular orbitals. The main compositions of the LUMO and HOMO orbitals for **1** are shown in Fig 5. The electronic excitations involve transitions mainly from metal–ligand bonding MOs to the  $\beta$ -spin LUMO with dominant Cu d<sub>xy</sub> character, and to  $\beta$ -LUMO+1. Since each absorption line in a TD-DFT spectrum (Fig. 5) can arise from a several single orbital excitations, a description of the transition character is generally not straightforward. However, approximate assignments can be made, although they provide a simplified representation of the transitions. TD-DFT excitations were calculated both in the gas

phase and in the solvent using the PCM (DMSO). By comparing the calculated spectra it is evident that calculated transitions do not exhibit significant solvatochromic effects. In this view, only the PCM model results are presented in the Table 3. The experimental UV-Vis spectrum presents a very weak and broad absorption centered at ~700 nm and 400 nm alongwith the shoulder at ~820 nm. The calculated electronic excitations give rise to the same pattern of bands, at energies in good agreement with the experimental ones.

#### 2.3. Magnetic studies

The magnetic data of the complexes were collected at 278 K on a Gouy Balance. The effective magnetic moment ( $\mu_{eff}$ ) of [Cu<sub>2</sub>( $\mu$ -CH<sub>3</sub>COO)<sub>2</sub>L<sub>2</sub>] (**1**) and [Cu<sub>2</sub>( $\mu$ -NO<sub>3</sub>)<sub>2</sub>L<sub>2</sub>] (**2**) were measured to be 1.67 and 1.68 B.M. The effective magnetic moment ( $\mu_{eff}$ ) for both complexes at room temperature is below the theoretical value expected for a copper(II) centre with S = ½ and indicative of net antiferromagnetic couple between the copper(II) ions through bridging units in the polycrystalline state [31]. The antiferromagnetic behavior of the binuclear complexes is attributed to spin-spin interaction via the super-exchange pathway provided by the bridging groups rather than a direct metal-metal interaction [32]. The copper-copper distance in complex **1** and **2** are observed to be 3.34 and 3.40 Å respectively from X-ray diffraction studies. This separation generally rules out any significant amount of direct copper-copper interactions.

#### 2.4. Epr spectral study

The X-band epr spectra of complexes **1** and **2** in polycrystalline state at room temperature and in frozen DMSO solution at 77 K was recorded. These spectra are shown in Fig. 6 and 7. The epr spectra of the complexes provide information about the coordination environment around copper(II) in these complexes The epr spectra in polycrystalline state at room temperature showed two broad signals (~2835 and ~3500 G). The half-field signals ( Ms = ±2) are observed inboth complexes and polycrystalline spectra at room temprature at round 1600 G with  $g_{nf} = ~4.16$ . These characters reveals clearly the presence of magnetic interaction between two copper(II) ions through µ-nitrato/µ-acetato bridge.

The geometric parameters (G) also estimate from g-values of polycrystalline spectra. The parameter is the measure of the exchange interaction between the copper centers in polycrystalline state and this could be calculated using the equation  $G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.00$ 

2.0023) for axial spectra and  $G = (g_1 - 2.0023)/(g_2 - 2.0023)$  for rhombic spectra [33]. The value of g less than 4 for present complexes reveal the considerable exchanges interaction and if G > 4, the exchange interaction is negligible [34]. The frozen solution epr spectra of complexes **1** and **2** are axially symmetric  $(g_{\parallel} > g_{\perp} > 2.0023)$  having a quartet hyperfine structures on the parallel components. Frozen solution spectra of these complexes with  $g_{\parallel} > g_{\perp} > 2.0023$  are consistent with a  $d_{x^2.y^2}$  ground state in a square planner or square pyramidal geomentry [35,36]. The epr spectra of complexes **1** and **2** showed seven and five nitrogen superhyperfine lines in the  $g_{\perp}$  region. On expanded scale superhyperfine nitrogen lines ( $A_N = 15.7 \times 10^{-4} \text{ cm}^{-1}$ ) are more clear. Still the pattern in the  $g_{\parallel}$  region and specially the feature at ~3615 G are typical of a bridge species. The "g value" is 1.83 for complex **1** and **2** which is not a value that can be attributed to a monomeric copper species. Thus these are the experimental evidence for the Cu-Cu moiety in the complex and epr observations are consistent with single crystal X-ray data.

#### 2.5. UV-Visible Spectrometry

UV-spectra of the complexes **1** and **2** have been recorded in DMSO and in solid state (reflectance spectra). In the visible region, each of these spectra involves two ligand field bands appearing at 680 nm and 1100 nm regions, corresponding to the transitions  $d_z^2 \rightarrow d_x^2 \cdot y^2$  and  $d_{xz}$ ,  $d_{yz} \rightarrow d_x^2 \cdot y^2$  respectively, as expected for distorted square pyramidal geometry [37,38]. The longer wavelength absorption for **1** and **2** in DMSO suggests the typical signals for bridged dicopper systems in solution and is in agreement with their single crystal x-ray structural analysis. The complexes also show strong band in the near UV region at 400nm (Fig. S3) and is tentatively assigned to  $\mu$ -acetato/ $\mu$ -nitrato<sup>--</sup>Cu(II) charge transfer. These types of spectra are characteristic of dinuclear copper(II) complexes in which there is a magnetic interaction between the two copper centers [39-41].

#### 2.6. Electrochemistry

The electrochemical properties of two complexes have been studied by cyclic voltammetry in DMSO solution with 0.1 M NaClO<sub>4</sub> as supporting electrolyte at glassy carbon working electrode. The cyclic voltammogram (CV) of the complexes are displayed in (Fig. 8). The CV of the complexes show two reduction waves at  $E^{1}_{1/2} = -0.135$  V and  $E^{2}_{1/2} = 0.205$  V for complex 1 and  $E^{1}_{1/2} = -0.120$  V and  $E^{2}_{1/2} = 0.250$  V for complex 2, corresponding to the Cu<sup>II</sup>Cu<sup>II</sup>

 $\longrightarrow$  Cu<sup>II</sup> Cu<sup>I</sup>  $\implies$  Cu<sup>I</sup> Cu<sup>I</sup> redox couples respectively [42]. These kinds of observations are indicative of significant metal coupling for both complexes [43,44]. The observed redox couples are irreversible with peak separation ~0.210 V. The stability of the mixed valent complexes is expressed by the conproportionation constant ( $K_{con}$ ) for the following equilibrium,

$$[\operatorname{Cu}^{\mathrm{II}}\operatorname{Cu}^{\mathrm{II}}] + [\operatorname{Cu}^{\mathrm{I}}\operatorname{Cu}^{\mathrm{I}}] \implies 2 [\operatorname{Cu}^{\mathrm{II}}\operatorname{Cu}^{\mathrm{I}}]$$

The  $K_{con}$  is usually estimated from the difference in the half-wave potential between metal center couples,  $\log K_{con} = 16.9 \ (\Delta E_{1/2}) \ [12]$ . The observed value of  $K_{con}$  for both complexes is given in Table 4. From Table 4, it is evident that the large  $K_{con}$  values indicate that the addition of a second electron is most difficult than of the first electron and the Cu<sup>II</sup> Cu<sup>I</sup> mixed valence species is stable with respect to conproportionation. This kind of observation is more common in several binuclear complexes [45-47].

#### 2.7. Superoxide dismutase activity (SOD)

The superoxide dismutase activity of complex 1 and 2 were investigated by NBT assay method and catalytic activity towards the dismutation of superoxide anion was measured. Superoxide dismutation is a redox process.  $IC_{50}$  value for SOD activity has been defined as the chromophore concentration required to yield 50% inhibition of the reduction of NBT. The  $IC_{50}$ value of the complexes 1 and 2 are  $35\pm5$  and  $26\pm5$   $\mu$ M, respectively. Present compounds showed SOD activity but are less active than the native SOD (IC<sub>50</sub> = 0.04  $\mu$ M). The good activities of these complexes may be attributed to the flexible nature of ligand used, which is able to accommodate the geometrical change from copper(II) to copper(I) [48] in catalytic process, just like the  $O_2^-$  in place of the water molecule bound to the copper site in the mechanism of dismutation of  $O_2^{-}$  by native SOD. The SOD activities exhibited by the two complexes survive in a bovine serum albumin. This kind of observation clearly shows that Schiff base is a stronger of copper(II) ions than bovine serum albumin. The inhibition concentration (IC<sub>50</sub>) of complex 2 is lower than complex 1. In other words, complex 2 is actually more active than complex 1. The SOD graph of 1 and 2 is presented in Fig. 9. The difference in the  $IC_{50}$  values for the two complexes should be ascribed to the evidence of discrepancy in the structures between them. The distorted geometry of complexes may favor the geometrical change, which is essential for the catalytic property of the complexes. Similar results have been reported by our group [49,14] and others [50,51] (Table 5). The higher  $IC_{50}$  can only be accredited to the vacant coordination site,

which facilitate the binding of superoxide anion, electron of aromatic ligands that stabilize Cu- $O_2^{\bullet}$  interaction and not only to the partial dissociation of complex in solution.

#### 4. Conclusions

We have synthesized two new copper(II) complexes viz.,  $[(L)Cu(\mu-CH_3COO)_2Cu(L)]$  (1) and  $[(L)Cu(\mu-NO_3)_2Cu(L)]$  (2) and characterized by various physicochemical techniques. The epr spectra for polycrystalline samples exhibited the copper(II) hyperfine structures as well as zero-field splitting which are appropriate for triplet state of such a dimers. Complex 2 showed the highest SOD activity. This activity however was still much lesser than the native enzyme. It was also observed that nitrato bridged complex is more bioactive than acetato bridged complex.

#### Abbreviations

HL/L	N'-[phenyl(pyridin-2-yl)methylidene]benzohydrazone
DMSO	Dimethyl sulphoxide
Epr	Electron paramagnetic resonance
DFT	Density functional theory
NBT	Nitro blue tetrazolium chloride
MO	Molecular orbital
SOD	Superoxide dismutase

#### Acknowledgements

Our grateful thanks to School of Chemistry, University of Hyderabad, Hyderabad for Single Crystal X-ray data collection, RSIC (SAIF) IIT, Bombay for epr measurements and SAIF, Central Drug Research Institute, Lucknow is thankfully acknowledged for providing elemental and IR spectral analysis. Financial assistance from CSIR New Delhi [Scheme no. 01(2451)/11/EMR-II] and MPCST, Bhopal [Project no. 5986/CST/R&D/2012] are also thankfully acknowledged.

#### Appendix. Supplementary material

CCDC 827920 and 827921 contain the supplementary crystallographic data for  $[(L)Cu(\mu-CH_3COO)_2Cu(L)]$  (1) and  $[(L)Cu(\mu-NO_3)_2Cu(L)]$  (2). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data\_request/cif</u> or from the Director, CCDC, 12 Union Road, Cambridge, CB2, IEZ, UK (fax: +44 1223 336 033; e-mail: <u>deposit@ccdc.cam.ac.uk</u>).

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#### **Figure Captions:**

- Fig.1 ORTEP view of  $[(L)Cu(\mu-CH_3COO)_2Cu(L)]$  (1).
- Fig. 2 Co-ordination sphere of  $[(L)Cu(\mu-CH_3COO)_2Cu(L)]$  (1).
- Fig. 3 ORTEP view of  $[(L)Cu(\mu-NO_3)_2Cu(L)]$  (2).

- Fig. 4 Co-ordination sphere of  $[(L)Cu(\mu-NO_3)_2Cu(L)]$  (2).
- Fig. 5 Selected orbital excitations for complex 1 (orbital contour value 0.005).
- Fig. 6 EPR spectra of [(L)Cu(μ-CH<sub>3</sub>COO)<sub>2</sub>Cu(L)] (1) in polycrystalline state (RT) and in DMSO solution at LNT.
- Fig. 7 EPR [(L)Cu(NO<sub>3</sub>)<sub>2</sub>Cu(L)] (2) in polycrystalline state (RT) and in DMSO solution at LNT.
- Fig. 8 Cyclic voltammograme of complex 1 and 2; scan rate 300 mV/s
- Fig. 9 Graphical representation of SOD activity of complexes 1 and 2.













Fig. 9

#### Supplementary Figure Caption:

Fig.S1 Supramolecular structure of  $[(L)Cu(\mu-CH_3COO)_2Cu(L)]$  (1).

Fig. S2 Supramolecular structure of  $[(L)Cu(\mu-NO_3)_2Cu(L)]$  (2).

Fig.S3 UV- vis spectra of complexes 1 and 2 in 100% DMSO





Fig. S1





	1	2
Empirical formula	$C_{42} H_{34} Cu_2 N_6 O_6$	$C_{38} H_{28} Cu_2 N_8 O_8$
Formula weight	845.848	851.78
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
space group	$P 2_1/n$	$P2_1/n$
Unit cell dimensions		
a(A)	9.5631(17)	9.3768(16)
b(A)	13.101(2)	13.473(2)
$c(\text{\AA})$	15.193(3)	14.752(3)
α(°)	90	90
β(°)	100.668(3)	99.468(3)
γ(°)	90	90
Volume $(Å^3)$	1870.6(6)	1838.3(5)
Z	2	2
Calculated density	$1.509 \text{ Mg/m}^3$	$1.542 \text{ Mg/m}^3$
Absorption coefficient	1.195 mm <sup>-1</sup>	$1.222 \text{ mm}^{-1}$
F(000)	868.0	872
Crystal size	$0.26 \times 0.22 \times 0.16 \text{ mm}$	$0.41 \times 0.36 \times 0.26 \text{ mm}$
$\theta$ range for data collection	2.07 to 25.00°	2.06 to 25.99°
Limiting indices	-11<= <i>h</i> <=11, -15<= <i>k</i> <=15, -	-11<= <i>h</i> <=11, -16<= <i>k</i> <=16, -
6	18<=l<=18	18<= <i>l</i> <=18
Reflections collected / unique	17678 / 3299 [R(int) = 0.0331]	18652 / 3590 [R(int) = 0.0283]
Completeness to $\theta = 25.00^{\circ}$	100.0 %	99.9 %
Absorption correction	Semi-empirical from	None
1	equivalents	
Max. and min. transmission	1.0000 and 0.8846	-
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data / restraints / parameters	3299 / 0 / 253	3590 / 2 / 253
Goodness-of-fit on $F^2$	1.038	1.045
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0346, $wR2 = 0.0914$	R1 = 0.0360, wR2 = 0.0975
R indices (all data)	R1 = 0.0401, $wR2 = 0.0953$	R1 = 0.0411, $wR2 = 0.1013$
Largest diff. peak and hole ( $e A^{-3}$ )	$0.406 \text{ and } -0.233 \text{ e.A}^{-3}$	0.571 and $-0.377$ e.A <sup>-3</sup>
C		

Table 1 Crystal data and structure refinement parameters for complexes 1 and 2.

<u> </u>			
Complex I			
N(1)-Cu(1)	2.0195(19)	O(2)-Cu(1)	1.9261(16)
N(2)-N(3)	1.366(3)	O(2)-Cu(1)#1	2.3120(18)
N(2)-Cu(1)	1.927(2)	Cu(1)-O(2)#1	2.3120(18)
O(1)-Cu(1)	1.9843(16)		
C(1)-N(1)-C(5)	119.1(2)	O(2)-Cu(1)-N(2)	172.88(8)
C(1)-N(1)-Cu(1)	127.46(17)	O(2)-Cu(1)-O(1)	102.90(7)
C(5)-N(1)-Cu(1)	113.43(15)	N(2)-Cu(1)-O(1)	79.30(7)
C(6)-N(2)-N(3)	122.2(2)	O(2)-Cu(1)-N(1)	97.99(7)
C(6)-N(2)-Cu(1)	120.03(16)	N(2)-Cu(1)-N(1)	79.65(8)
N(3)-N(2)-Cu(1)	117.57(14)	O(1)-Cu(1)-N(1)	158.95(7)
C(13)-N(3)-N(2)	107.76(19)	O(2)-Cu(1)-O(2)#1	76.20(7)
C(13)-O(1)-Cu(1)	109.91(14)	N(2)-Cu(1)-O(2)#1	110.49(7)
C(20)-O(2)-Cu(1)	119.81(16)	O(1)-Cu(1)-O(2)#1	95.29(7)
C(20)-O(2)-Cu(1)#1	135.08(16)	N(1)-Cu(1)-O(2)#1	92.09(7)
Cu(1)-O(2)-Cu(1)#1	103.80(7)		
Complex 2			
Cu(01)-N(2)	1.912(3)	Cu(01)-N(1)	1.991(3)
Cu(01)-O(1)	1.946(3)	Cu(01)-O(2)#1	2.355(3)
Cu(01)-O(2)	1.960(3)	O(2)-Cu(01)#1	2.355(3)
N(2)-Cu(01)-O(1)	80.46(11)	O(1)-Cu(01)-O(2)#1	92.04(11)
N(2)-Cu(01)-O(2)	177.41(12)	O(2)-Cu(01)-O(2)#1	73.45(12)
O(1)-Cu(01)-O(2)	98.99(12)	N(1)-Cu(01)-O(2)#1	93.67(12)
N(2)-Cu(01)-N(1)	81.23(12)	C(13)-O(1)-Cu(01)	109.8(2)
O(1)-Cu(01)-N(1)	161.69(12)	N(4)-O(2)-Cu(01)	119.8(3)
O(2)-Cu(01)-N(1)	99.32(12)	N(4)-O(2)-Cu(01)#1	128.3(3)
N(2)-Cu(01)-O(2)#1	109.07(12)	Cu(01)-O(2)-Cu(01)#1	106.55(12)

Table 2 Bond lengths  $[A^{\circ}]$  and angles  $[^{\circ}]$  for 1 and 2.

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z

A

Excitation	Wavelength	Oscillator	Composition (%)	Nature of the transition and
Energy	(nm)	Strength		approximate assignment
(eV)		( <i>f</i> )		
1.511	820	0.011	$\beta \text{ HOMO-2} \rightarrow \beta \text{ LUMO+2}$ (21%) $\beta \text{ HOMO-2} \rightarrow \beta \text{ LUMO+3}$ (32%)	$Cu (d_z 2) \rightarrow Cu (d_x 2_{-y} 2)$ $Cu (d_z 2) \rightarrow Cu (d_x 2_{-y} 2)$
1.840	673	0.004	$β$ HOMO $\rightarrow$ $β$ LUMO (45%)	$\pi \rightarrow \pi^*$ and Cu (d <sub>z</sub> 2) $\rightarrow$ Cu (d <sub>x</sub> 2 <sub>-y</sub> 2)
2.942	421	0.493	$β$ HOMO $\rightarrow$ β LUMO (28%)	$\pi \rightarrow \pi^*$ and Cu (d <sub>7</sub> 2) $\rightarrow$ Cu (d <sub>x</sub> 2 <sub>-y</sub> 2)
2.971	417	0.045	β HOMO-1→ $β$ LUMO+1 (40%)	$\pi \rightarrow \pi^*$
3.075	403	0.363	$\beta$ HOMO-1 $\rightarrow$ $\beta$ LUMO+1 (24%) $\beta$ HOMO-1 $\rightarrow$ $\beta$ LUMO+3 (18%) $\beta$ HOMO $\rightarrow$ $\beta$ LUMO+2 (25%)	$\begin{array}{l} \pi \rightarrow \pi^{*} \\ \pi \rightarrow \pi^{*} \text{ and } \pi \rightarrow \text{Cu} (d_{x^{2} - y^{2}}) \text{ and } \pi^{*} \\ \pi \rightarrow \text{Cu} (d_{x^{2} - y^{2}}) \end{array}$
3.163	392	0.077	(25%) $\beta$ HOMO-2 $\rightarrow$ $\beta$ LUMO+3 (66%)	Cu $(d_z 2) \rightarrow$ Cu $(d_x 2 - y 2)$ and $\pi^*$

#### Table 3 TD-DFT calculated excitations and approximate assignments for 1

Table 4 Cyclic voltammetric data for 0.003 M solution of the Cu(II) complexes in DMSO containing 0.1 M NaClO<sub>4</sub> as supporting electrolyte.

С	omplex	E <sub>pc1</sub> (V)	E <sub>pa1</sub> (V)	E <sub>pc2</sub> (V)	E <sub>pa2</sub> (V)	$E^{1}_{1/2}$ (V)	$E^{2}_{1/2}$ (V)	K <sub>con</sub>
	1	0.10	0.32	-0.37	0.09	-0.135	0.205	$5.6 \times 10^{5}$
	2	0.15	0.38	-0.39	0.12	-0.120	0.250	$1.8 \times 10^{6}$

S. No.	Complexes	$IC_{50} (\mu mol  dm^{-3})$	Reference
1.	$[(L^1)Cu-(\mu-CH_3\overline{COO})_2Cu(L^1)]\cdot 4,4$ '-bipy	52	12
2.	$[(L^2)Cu-(\mu-NO_3)_2Cu(L^2)]$	58	12
3.	$[Cu(L)X_2]$	22	45
4.	[Cu(L)Br <sub>2</sub> ]	18	45
5.	$[Cu(L)_2(ImH)_2]$ ·CH <sub>3</sub> OH	27	46
6.	[Cu(L)(bipy)]	62	46
7.	[Cu(glygly)]·3H <sub>2</sub> O	132	47
8.	[Cu(glygly)(Phen)]·3H <sub>2</sub> O	32	47
9.	$[Cu(PSBP)_2(NO_3)(BF_4)]$	35	48
10.	$[(L)Cu(\mu-CH_3COO)_2Cu(L)]$	35	Present work
11.	$[(L)Cu(\mu-NO_3)_2Cu(L)]$	26	Present work

Table 5 Superoxide dismutase activity of some copper(II) complexes

#### Highlight

- 1. Homo bi-nuclear complex
- 2. Schiff base hydrazone ligand
- 3. Density functional theory
- Acceleration

#### **Graphical Abstract**

Two homodinuclear copper(II) end-on bis(µ-acetato/µ-nitrato) bridged complexes are synthesized. Both complexes structurally characterized using single crystal X-ray diffraction Acceleration studies and belong to monoclinic crystal system having space group P 21/n.

\*Graphical Abstract (pictogram) (for review)

