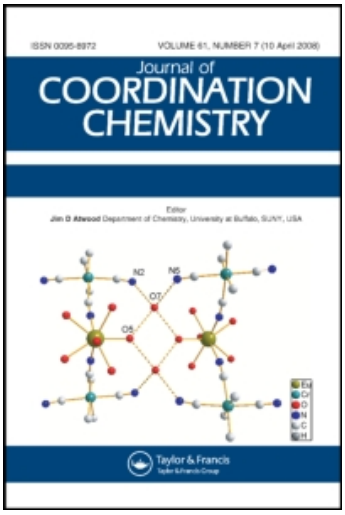

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Syntheses, characterizations and SOD-like activities of ternary copper(II) complexes with 1,10-phenanthroline and L-α-amino acids

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Online publication date: 22 September 2010

To cite this Article Liao, Sheng Rong , Le, Xue Yi and Feng, Xiao Long(2008) 'Syntheses, characterizations and SOD-like activities of ternary copper(II) complexes with 1,10-phenanthroline and L-**α**-amino acids', Journal of Coordination Chemistry, 61: 6, 847 — 856
To link to this Article: DOI: 10.1080/00958970701476943
URL: http://dx.doi.org/10.1080/00958970701476943

Journal of Coordination Chemistry
Vol. 61, No. 6, 20 March 2008, 847–856

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Syntheses, characterizations and SOD-like activities of ternary copper(II) complexes with 1,10-phenanthroline and L-α-amino acids

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(*Received 12 August 2006; revised 21 March 2007; in final form 4 April 2007*)

Three new complexes, [Cu(phen)(L-argH$^+$)Cl]Cl · 2.5H_2O (**1**), [Cu(phen)(L-leu)(H_2O)]Cl · 2.5H_2O (**2**) and [Cu(phen)(L-met)(H_2O)]Cl · 2H_2O (**3**), where phen = 1,10-phenanthroline, L-arg = L-argininate, L-leu = L-leucinate, and L-met = L-methioninate, were synthesized and characterized by elemental analysis, molar conductivity, IR and UV-Vis spectroscopies. Complex **1** was structurally characterized by single-crystal X-ray diffraction. The superoxide dismutase (SOD)-like activities of the three complexes were determined by the improved NBT method. The results show that the complexes have high superoxide dismutase-like activities and may act as good mimics for superoxide dismutases.

Keywords: Copper(II) complexes; Superoxide dismutase (SOD); SOD-like activity; L-α-amino acids

1. Introduction

Produced in proper amounts in organisms, superoxide radical anion ($\overline{O}_2^{\cdot}$) is a normal and useful metabolite serving important roles as a signaling molecule and even as a terminator of lipid peroxidation [1, 2]; however, when organisms were under stress such as toxicants, irradiation, hypoxia, freezing, drought and others, $\overline{O}_2^{\cdot}$ would overproduce and become poisonous. Surplus $\overline{O}_2^{\cdot}$ would initiate lipid peroxidation [3], cause nucleic acid and protein damage [4–6], and influence cellular signaling change [7], thus humans and animals might suffer from various diseases including inflammatory diseases [8], neurodegenerative diseases [9, 10], strokes [11], cancer [12, 13] and aging [14], and plants might grow slowly [15, 16] or even die. Although some native metal enzymes, superoxide dismutases (SODs), can very efficiently catalyze the dismutation of $\overline{O}_2^{\cdot}$ into H_2O_2 and O_2, the idea of their use as therapeutic agents has been problematic because

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701476943

of huge molecular weights, high costs, instability and the major problem of oxidant-antioxidant balance [2]. To make up for such limitations, considerable interest has been shown in designing synthetic SOD mimics [17–20] that have low molecular weights, biological stability, nontoxicity and cost effectiveness.

Based on amino acid-copper(II) complexes having SOD-like activity [19, 21] and phenanthroline-copper(II) complexes having antioxidant activity [22, 23], in this work, three new SOD mimics (complexes), phen-Cu(II)-L-α-amino acids [phen = 1, 10-phenanthroline, L-α-amino acids = L-argininate (L-arg), L-leucinate (L-leu), and L-methioninate (L-met)] have been synthesized and characterized by single-crystal X-ray diffraction, elemental analysis, IR and UV-Vis spectroscopies. The catalytic activities of the complexes toward the dismutation of O_2^- were determined by the improved NBT method. The results show that all the complexes have high SOD-like activities in water.

2. Experimental

All chemicals were analytical grade and used without further purification.

2.1. *Syntheses of the complexes*

The synthetic methods of the three SOD mimics were similar to each other. $CuCl_2 \cdot 2H_2O$ (0.5 mmol) and 1,10-phenanthroline (0.5 mmol) were dissolved in 10 mL of 95% ethanol with stirring, followed by adding 5 mL of aqueous solution of L-α-amino acid (0.5 mmol). The pH of the mixtures were then adjusted pH = 5–6 with NaOH aqueous solution (0.2 mol L^{-1}). The solutions were stirred and heated for about 30 min, then cooled and filtered. The resulting solutions were left to evaporate at room temperature for several days until blue crystals of the desired complexes were obtained. The yields for complexes **1, 2**, and **3** are 61, 73 and 67%, respectively.

Anal. Calcd for **1** ($C_{18}H_{27}Cl_2CuN_6O_{4.5}$) (%): C 40.49; H 5.10; N 15.74. Found: C 40.43; H 5.13; N 15.70.

Anal. Calcd for **2** ($C_{18}H_{27}ClCuN_3O_{5.5}$) (%): C 45.76; H 5.76; N 8.90. Found: C 45.04; H 5.72; N 8.68.

Anal. Calcd for **3** ($C_{17}H_{24}ClSCuN_3O_5$) (%): C 42.41; H 5.02; N 8.73. Found: C 42.85; H 4.96; N 8.75.

2.2. *Physical measurements*

Elemental analyses for C, H and N were carried out on a Perkin–Elmer 240 C microanalyzer. Molar conductivity measurements were performed with a DDS-11A conductivity gauge. The IR spectra in KBr disks were measured with a Nicolet 170SX spectrophotometer. The UV-Vis spectra in aqueous solutions were recorded on a Pharmacia 4000 UV-Vis spectrophotometer.

2.3. *X-ray structural determination of (1)*

A single crystal ($0.48 \times 0.45 \times 0.28\,mm^3$) of the complex was selected for X-ray diffraction measurement on a Bruker Smart 1K CCD system diffractometer with graphite monochromated Mo-Kα radiation at $\lambda = 0.71073$ Å. The SMART program was applied to search for diffraction peaks to determine cell parameters, and the collected data were reduced using the SAINT + program [24]. Absorption corrections were applied with the Siemens Area Detector ABSorption (SADABS) program [25].

The structure was solved by direct and Fourier methods and refinements were carried out by full-matrix least squares on F^2 with positional and anisotropic thermal parameters. The atomic coordinates and anisotropic thermal parameters for nonhydrogen atoms were refined to converge. All hydrogen atoms were placed in calculated positions. Atomic scattering factors were taken from International Tables for X-ray Crystallography [26]. All calculations were performed on a PC with the Siemens SHELXS-97 [27] and SHELXL-97 [28] program packages.

2.4. *SOD-like activities*

The SOD-like activities of the complexes were determined by the improved indirect method of nitro blue tetrazolium (NBT) photoreduction [29]. A blank solution was used containing nitro blue tetrazolium 9.32×10^{-5} M, riboflavin 6.80×10^{-6} M, and tetramethyl ethylenediamine 1.0×10^{-4} M in phosphate buffer (0.05 M, pH = 7.8), and competitive solutions were also used containing concentrations of the complexes (0.01–0.4 μM) or native CuZnSOD (0.005–0.08 μM) in the blank solution. 3 mL of the blank solution or the competitive solutions (in 1 cm thermostatted cuvettes, 25 ± 0.3°C) were illuminated under a fluorescence lamp and detected by monitoring the formation of the NBT reduction at 560 nm. Three parallel determinations for each solution were carried out.

3. Results and discussion

The elemental analyses for the complexes are in good agreement with the formulas. All the complexes are soluble in methanol and ethanol, but not in ether and other less polar organic solvents. Molar conductivities in ethanol for complexes **1**, **2**, and **3** are, respectively, 35.2, 26.8, and 24.4 $S\,cm^{-2}\,mol^{-1}$, indicating that the complexes may be 1 : 1 electrolytes [30].

3.1. *Crystal structure of [Cu(phen)(L-argH$^+$)Cl]Cl · 2.5H$_2$O*

Crystal data and refinement parameters of [Cu(phen)(L-argH$^+$)Cl]Cl · 2.5H$_2$O are given in table 1. Selected bond lengths and angles are listed in table 2. The perspective view of [Cu(phen)(L-argH$^+$)Cl]$^+$ cations and the packing view of **1** are shown in figures 1 and 2, respectively.

The crystal of **1** consists of [Cu(phen)(L-argH$^+$)Cl]$^+$ cations, Cl^- anions and H_2O molecules. In the unit cell of the complex, there are four independent cations, with each

Table 1. Crystal data and structure refinement details for [Cu(phen)(L-argH$^+$)Cl]Cl · 2.5H$_2$O.

Formula	$C_{36}H_{54}Cl_4Cu_2N_{12}O_9$
Formula weight	1067.79
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.3879(13)
b (Å)	12.4296(15)
c (Å)	18.955(2)
α (°)	94.608(2)
β (°)	104.819(2)
γ (°)	101.020(2)
V (Å^3)	2300.8(5)
Z	2
D_{Calcd} (g cm^{-3})	1.541
$F(000)$	1104
R_{int}	0.0247
θ range for data collection (°)	1.12–27.16
Limiting indices	$-13 \le h \le 12$, $-15 \le k \le 15$, $-24 \le l \le 24$
Reflections collected/unique	19827/17716
Data/restraints/parameters	17716/33/1189
Goodness-of-fit on F^2	1.045
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0446$, $wR_2 = 0.1091$
R indices (all data)	$R_1 = 0.0702$, $wR_2 = 0.1224$
Largest diff. peak and hole (e Å^{-3})	0.842 and −0.474

Table 2. Selected bond lengths (Å) and angles (°) of [Cu(phen)(L-argH$^+$)Cl]Cl · 2.5H$_2$O.

Cu(1)–O(1)	1.918 (6)	Cu(2)–O(3)	1.953 (6)
Cu(1)–N(3)	1.994 (7)	Cu(2)–N(7)	1.997 (7)
Cu(1)–N(1)	2.020 (7)	Cu(2)–N(9)	2.000 (6)
Cu(1)–N(2)	2.021 (6)	Cu(2)–N(8)	2.041 (7)
Cu(1)–Cl(1)	2.510 (2)	Cu(2)–Cl(2)	2.618 (2)
Cu(3)–O(5)	1.964 (6)	Cu(4)–O(7)	1.949 (6)
Cu(3)–N(15)	1.976 (7)	Cu(4)–N(19)	2.004 (7)
Cu(3)–N(14)	2.004 (7)	Cu(4)–N(21)	2.030 (7)
Cu(3)–N(13)	2.032 (7)	Cu(4)–N(20)	2.057 (8)
Cu(3)–Cl(3)	2.622 (2)	Cu(4)–Cl(4)	2.500 (2)
O(1)–Cu(1)–N(3)	84.6 (3)	O(3)–Cu(2)–N(7)	92.5 (3)
O(1)–Cu(1)–N(1)	165.5 (2)	O(3)–Cu(2)–N(9)	84.2 (2)
N(3)–Cu(1)–N(1)	99.5 (3)	N(7)–Cu(2)–N(9)	171.2 (3)
O(1)–Cu(1)–N(2)	90.6 (2)	O(3)–Cu(2)–N(8)	162.7 (3)
N(3)–Cu(1)–N(2)	162.1 (3)	N(7)–Cu(2)–N(8)	81.6 (3)
N(1)–Cu(1)–N(2)	81.2 (3)	N(9)–Cu(2)–N(8)	99.3 (3)
O(1)–Cu(1)–Cl(1)	99.36 (19)	O(3)–Cu(2)–Cl(2)	101.16 (18)
N(3)–Cu(1)–Cl(1)	98.1 (2)	N(7)–Cu(2)–Cl(2)	97.1 (2)
N(1)–Cu(1)–Cl(1)	93.8 (2)	N(9)–Cu(2)–Cl(2)	91.5 (2)
N(2)–Cu(1)–Cl(1)	99.63 (19)	N(8)–Cu(2)–Cl(2)	95.70 (19)
O(5)–Cu(3)–N(15)	84.3 (3)	O(7)–Cu(4)–N(19)	91.2 (3)
O(5)–Cu(3)–N(14)	92.4 (3)	O(7)–Cu(4)–N(21)	83.6 (3)
N(15)–Cu(3)–N(14)	169.4 (3)	N(19)–Cu(4)–N(21)	165.3 (3)
O(5)–Cu(3)–N(13)	165.4 (3)	O(7)–Cu(4)–N(20)	165.4 (3)
N(15)–Cu(3)–N(13)	99.0 (3)	N(19)–Cu(4)–N(20)	81.6 (3)
N(14)–Cu(3)–N(13)	81.8 (3)	N(21)–Cu(4)–N(20)	100.1 (3)
O(5)–Cu(3)–Cl(3)	100.02 (19)	O(7)–Cu(4)–Cl(4)	100.19 (19)

(*Continued*)

Table 2. Continued.

N(15)–Cu(3)–Cl(3)	94.3 (2)	N(19)–Cu(4)–Cl(4)	98.8 (2)
N(14)–Cu(3)–Cl(3)	96.1 (2)	N(21)–Cu(4)–Cl(4)	95.7 (2)
N(13)–Cu(3)–Cl(3)	93.9 (2)	N(20)–Cu(4)–Cl(4)	93.5 (2)
N(5)···O(2) #3	2.926 (9)	N(9)···Cl(1) #2	3.339 (7)
N(6)···O(2) #3	2.886 (11)	N(5)···Cl(2) #4	3.291 (7)
N(12)···O(4) #1	2.872 (10)	N(3)···Cl(2) #4	3.427 (7)
N(17)···O(6) #3	2.907 (10)	N(21)···Cl(3) #2	3.327 (7)
N(23)···O(8) #1	3.005 (11)	N(23)···Cl(3) #2	3.274 (8)
N(24)···O(8) #1	2.859 (11)	N(15)···Cl(4) #4	3.389 (7)

Symmetry transformations used to generate equivalent atoms: #1 $x-1, y, z$; #2 $x, y+1, z$; #3 $x+1, y, z$; #4 $x, y-1, z$.

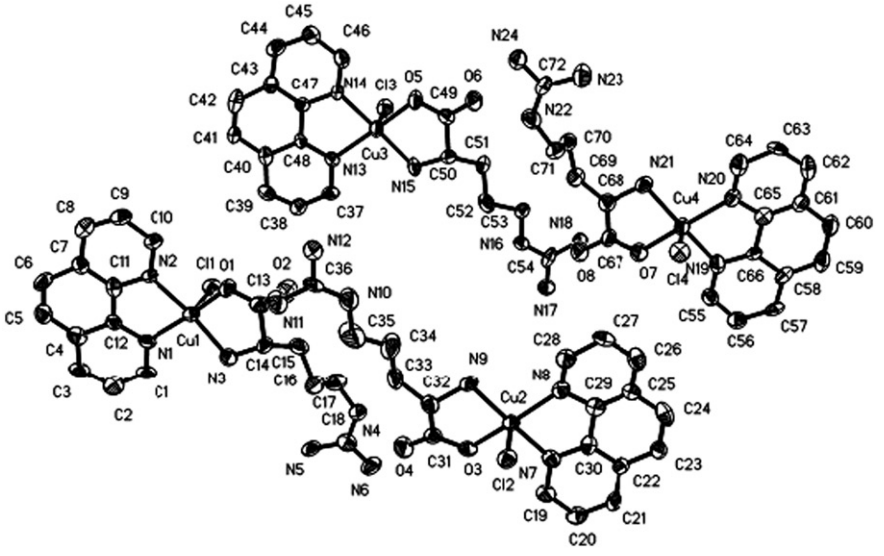

Figure 1. ORTEP plot showing the structure of $[Cu(phen)(L\text{-}argH^+)Cl]^+$ cations and the atom-numbering scheme for **1**.

copper(II) bonded to two nitrogen atoms of 1,10-phenanthroline(N,N), the L-α-amino nitrogen atom and one carboxylate oxygen of L-argininate(N,O) in the equatorial plane, and bonded to a chloride on the axis, forming a slightly distorted square-pyramidal geometry. The Cu(1) deviates from the least-squares plane defined by N(1), N(2), O(1), and N(3); Cu(2) deviates from that defined by N(7), N(8), O(3), and N(9); Cu(3) deviates from that defined by N(13), N(14), O(5), and N(15), and Cu(4) deviates from that defined by N(19), N(20), O(7), and N(21) by 0.0109, 0.0058, 0.0151 and 0.0176 Å, respectively, showing that the central copper(II) is almost coplanar with the four ligating atoms. The average distances between intermolecular phen-rings of molecules containing Cu(1) and Cu(4) and Cu(2) and Cu(3) are 3.580 and 3.762 Å, respectively, and the planar angles between Cu(1) and Cu(4) and Cu(2) and Cu(3) are 1.7 and 2.7°, respectively, indicating that intermolecular phen-ring stacking interactions exist in the crystal of the complex [31]. In addition, there are many intermolecular hydrogen bonds [N–H···O hydrogen bonds with the N···O separations of

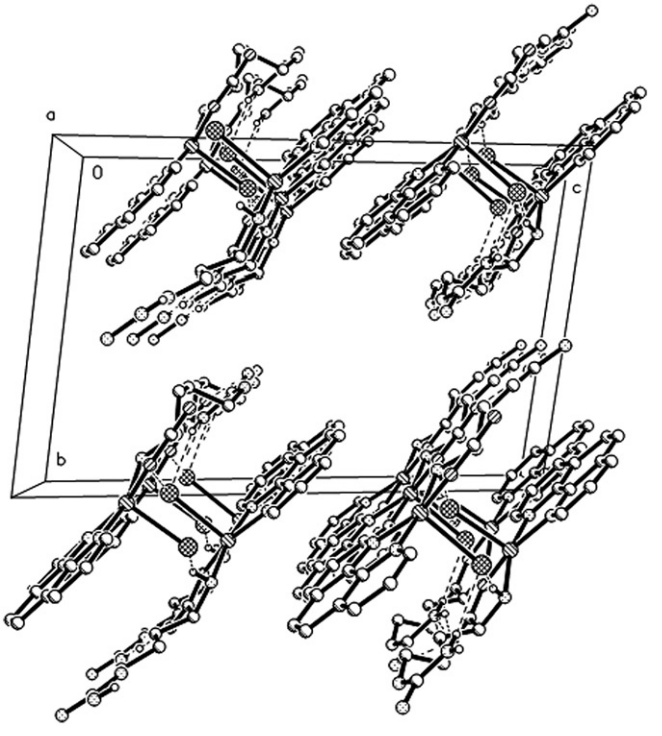

Figure 2. Molecular packing view for **1**.

Table 3. Main infrared spectral data of the complexes (cm^{-1}).

Complex	ν_{OH}	$\nu^{as}_{NH_2}$	$\nu^{s}_{NH_2}$	$\nu^{as}_{COO^-}$	$\nu^{s}_{COO^-}$	$\nu_{phen\text{-}ring}$
1	3400	3262	3119	1636	1382	1518
2	3440	3264	3125	1626	1394	1518
3	3404	3239	3116	1635	1383	1519

2.859(11)–3.005(11) Å (moderate strength) and N–H $\cdots$ Cl hydrogen bonds with the N $\cdots$ Cl distances of 3.274(8)–3.427(7) Å (weak strength)] in the crystal of the complex (table 2). Thus, one can conclude that the intermolecular aromatic-stacking and hydrogen-bond interactions make the crystal structure of the complex stable.

3.2. *IR spectra*

The IR spectra of the complexes between 4000–200 cm^{-1} are in table 3. Strong broad bands in the range 3440–3400 cm^{-1} are ν_{OH} of water, and the bands in the range 3264–3239 and 3125–3116 cm^{-1} can be attributed, respectively, to the $\nu^{as}_{NH_2}$ and $\nu^{s}_{NH_2}$ of the coordinated-NH_2 group. The absence of any band in the region 1750–1700 cm^{-1} in the IR spectra of the isolated complexes suggests coordination of the $-COO^-$ group of L-α-amino acids to the central copper(II) ions. The bands in the

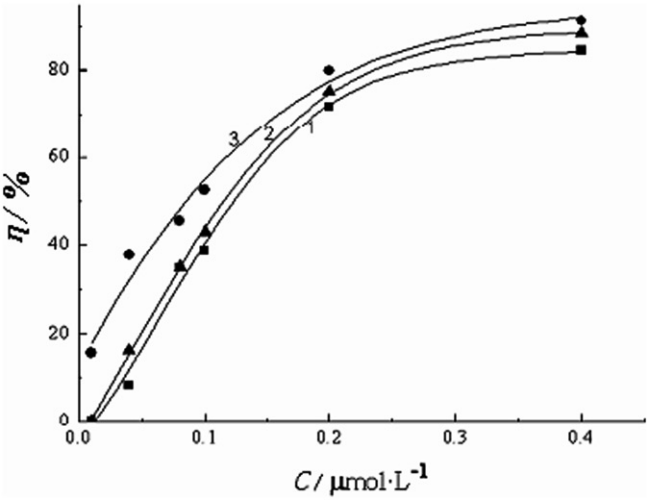

Figure 3. Relationships between the inhibition rate (η/%) and concentration ($c\,\mu mol^{-1}\,L^{-1}$) of **1**: [Cu(phen)(L-argH$^+$)Cl]Cl · 2.5H$_2$O; **2**: [Cu(phen)(L-leu)(H$_2$O)]Cl · 2.5H$_2$O; **3**: [Cu(phen)(L-met)(H$_2$O)]Cl · 2H$_2$O.

range 1636–1626 and 1394–1382 cm^{-1} can be attributed, respectively, to the $\nu^{as}_{COO^-}$ and $\nu^{s}_{COO^-}$ of the coordinated carboxylates, of which $\Delta\nu_{COO^-}$ values ($\nu^{as}_{COO^-} - \nu^{s}_{COO^-} > 200\,cm^{-1}$) are consistent with monodentate coordination of the carboxylate [32]. Thus, one can deduce that the L-α-amino acids are coordinated to the copper(II) ions as bidentate N,O-ligands, which agrees with the result obtained by single-crystal X-ray diffraction method for **1**. The band of all the complexes at 1518 cm^{-1} is most likely assigned to the $\nu_{phen-ring}$ of the phen ligand and confirms its coordination to the central copper(II) ions.

3.3. *UV-Vis spectra*

The strong absorption bands of **1, 2**, and **3** at 273, 271 and 273 nm, respectively, are ascribed to π–π* transitions of the phen ligands. Moreover, the complexes exhibit, respectively, a weak and broad visible absorption band at 613, 613 and 619 nm, of which spectral features can be explained by a d–d transition of Cu(II) in a distorted square-pyramidal geometry [33, 34].

Based on the above results obtained, it can be inferred that the molecular formulas of **2** and **3** are, respectively, [Cu(phen)(L-leu)(H$_2$O)]Cl · 2.5H$_2$O (**2**) and [Cu(phen)(L-met)(H$_2$O)]Cl · 2H$_2$O (**3**), in which the central Cu(II) coordinates to phen, and the N,O of L-amino acids in the equatorial positions, a water oxygen atom at an axial position, forming a distorted square-pyramidal geometry, similar to corresponding complexes [35, 36].

3.4. *SOD-like activity of complexes*

The SOD-like activities of the complexes were investigated by the NBT assay. All exhibit catalytic activity toward the dismutation of superoxide anions. Figure 3 shows

Table 4. IC_{50} values of the complexes and native CuZnSOD for the catalytic dismutation of $\overline{O}_2^{\cdot}$.

Complex	IC_{50}[a] (μM)	References
Native CuZnSOD	0.0147	This work
1	0.123	This work
2	0.114	This work
3	0.086	This work
$[(tren)Cu(E\text{-}ImH)](ClO_4)_2$	175	[20]
$Cu(amino\ acid)_2$	0.300 ~ 6.00	[42]
$[CuL_2(4\text{-}mHim)_2]$	5.86	[43]

[a]IC_{50} is the concentration of 50% inhibition of NBT reduction.

the percentage inhibition (η/%) of the reduction of NBT plotted against the concentration of the complexes. Table 4 shows the IC_{50} values of the complexes which causes 50% inhibition of NBT reduction, the corresponding values of other copper(II) complexes with amino acid or imidazole ligands, and the native Cu, Zn-SOD-enzyme. The activity of native CuZnSOD determined in this work is similar to that reported by Bonomo *et al.* [37], indicating that the NBT method in the present study is credible.

The SOD-like activities of copper complexes depend on factors such as a fast exchange of molecules axially linked to the central metal ion, limited steric hindrance to the approach of the superoxide anion, and the distorted square-pyramidal geometry which is essential for catalysis as the geometry of copper(II) in SOD changes from distorted square pyramidal to distorted tetrahedral copper(I) during catalysis [37–39]. In addition, the charge or electron cloud delocalization (such as aromatic-ring effects in ligands) in complex molecules also has a huge influence on the SOD-like activities [10]. These requirements are satisfied in the tetragonally distorted complexes in this work. In the complexes, the weakly coordinated small molecules (H_2O, Cl^-) in the axial positions are being readily dissociated to provide the sites on copper(II) for $\overline{O}_2^{\cdot}$ bonding and the dissociation would also facilitate any necessary geometrical changes induced by $\overline{O}_2^{\cdot}$ bonding [40]. The phenanthroline has electron cloud delocalization important for high SOD-like activity [41]; all the complexes have good SOD-like activities compared with complexes previously reported [20, 42, 43]. Complex **1** has the lowest SOD activity, mainly because the Cl^- anion bonded on the axis made the effective positive charge of the central Cu less, hence disadvantageous to approach of $\overline{O}_2^{\cdot}$ compared with water bonded in the axes in complexes **2** and **3**. In addition, the SOD activity of **3** is higher than that of **2**, which may be related to the smaller steric hindrance of the side chain (CH_3–S–CH_2–CH_2–) of L-methioninate ligand for approach of $\overline{O}_2^{\cdot}$ to the central copper(II) compared with the side chain [$(CH_3)_2$–CH–CH_2–] of L-leucinate ligand in the latter.

Supplementary material

Detailed crystallographic data for complex **1** have been sent to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ,

UK (Fax: +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk) as supplementary material No. 278624 and can be obtained free of charge.

Acknowledgement

The authors thank the Natural Science Foundation of Guangdong Province, P.R. China, for research grant No. 04105986.

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