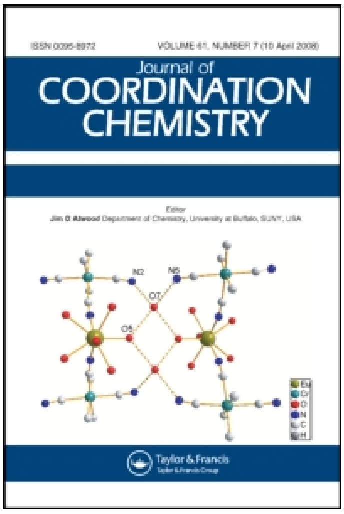

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Two complexes (Cu, Zn) with 1,10-phenanthroline and a tridentate amino-Schiff-base: crystal structures, spectra, thermogravimetric analyses and superoxide dismutase activity

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Two complexes (Cu, Zn) with 1,10-phenanthroline and a tridentate amino-Schiff-base: crystal structures, spectra, thermogravimetric analyses and superoxide dismutase activity

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Two transition metal (Zn, Cu) complexes with a Schiff base (salicylideneglycine) and 1,10-phenanthroline: $(C_9H_7NO_3)Zn(C_{12}H_8N_2)(H_2O)$ (**1**) and $(C_9H_7NO_3)Cu(C_{12}H_8N_2)$ (**2**) have been synthesized and characterized, including crystal structures, spectral characterization, thermogravimetric analyses and quantum chemistry calculations. X-ray crystallographic analysis shows the zinc to be six-coordinate mode, forming a slightly distorted octahedral geometry. The structure of **2** can be evaluated by the Addison distortion index ($\tau = 0.17$), which indicates that the coordination environment of Cu is distorted slightly from square pyramidal (SP). The superoxide dismutase mimetic activity of the complexes was investigated by NBT-illumination. Complex **2** ($IC_{50} = 6.15\,\mu M$) has better SOD–like activity than **1** ($IC_{50} = 0.79\,\mu M$), although the SOD-like activity for **2** is not higher than some reported, it shows the possibility of SOD-like activity for the complexes with this amino-Schiff-base ligand (salicylideneglycine).

Keywords: Transition metal complexes; Amino-Schiff-base; Crystal structure; Thermogravimetric analyses; SOD-like activity

1. Introduction

The superoxide anion free radical is related to aging, tumors and inflammation [1, 2]. In 1968, McCord and Fridovich found that superoxide dismutase (SOD), an important anti-oxidizing enzyme, might protect cells as a scavenger of superoxide anion free radical by transferring the $O_2^{\cdot -}$ into O_2 and H_2O_2 through a redox reaction. Although, application of the natural superoxide dismutase has been restricted by the disadvantages of lower stability, macromolecular weight, lower penetrability and immunogenic property, metal complexes which can undergo such redox cycling are

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likely to function as superoxide scavengers; copper has been proven to be the active metal center in the best studied SOD [3]. Many efforts have been devoted to research on the structures and function of SOD model complexes to get a profound understanding of the enzyme as well as coordination and biological medicinal chemistry [4]. Numerous Schiff bases and their metal complexes have been reported to have similar activity to the SOD enzyme [5–7]. Repulsions between non-bonded atoms in different ligand arms such as copper(II) complexes with salicylate [8], amino acids [9] and polypeptides [10] have been observed, but the relationship between structures and function has rarely been discussed. For this reason, various transition metal complexes preferring different coordination geometry are constructed, using suitable metals and weak interactions such as hydrogen bonding and π–π interactions [11, 12] in order to further investigate biological activity [13, 14]. In this article, we report the preparation, crystal structures and superoxide dismutase activity of two new transition metal complexes with an amino–Schiff–base (salicylideneglycine) and 1,10-phenanthroline: $(C_9H_7NO_3)Zn(C_{12}H_8N_2)(H_2O)$ (**1**) and $(C_9H_7NO_3)Cu(C_{12}H_8N_2)$ (**2**). The amino-Schiff-base (salicylideneglycine) is chosen not only because structures of such complexes are few, but also that such complexes can form an abundance of hydrogen bonds and different geometry structures, both essential to mimic SOD activity. Our aim is to synthesize new complexes, modifying the coordination environments of SOD mimics for better understanding of the SOD enzyme.

2. Experimental

2.1. *Physical measurements*

Elemental analyses were performed on a P.E. 240C automatic analyzer. IR spectra were determined on a JASCO FT/IR–480 PLUS Fourier Transform spectrometer (200–4000 cm^{-1}, with pressed KBr pellets); UV–Vis spectra were determined on a JASCO V–570 UV–Vis spectrometer (200–1100 nm, CH_3OH solution); fluorescence spectra were determined by a JASCO FP–6500 spectrofluorimeter (solid sample).

2.2. *Crystallography*

The crystals of **1** and **2** were mounted on glass fibers for X-ray measurement. Reflection data were collected at room temperature on an APEX II CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å) and ψ scan mode. All measured independent reflections were used in the structural analyses, and semi-empirical absorption corrections were applied using the SADABS program. The crystal data, data collection, and refinement details are summarized in table 1.

The structures were solved by the direct method using SHELXS-86 and refined using SHELXTL-97. All non-hydrogen atoms were refined anisotropically and contributions of hydrogen atoms were included in calculated positions, constrained to ride on their carbon atoms with group U_{iso} values assigned. Atomic scattering factors and anomalous dispersion terms were as in SHELXTL-97. The drawings were made with Diamond and all calculations were performed on a Pentium 4 computer.

Table 1. Crystallographic data for **1** and **2**.

Formula	$C_{21}H_{17}N_3O_4Zn$	$C_{21}H_{15}N_3O_3Cu$
M ($g\,mol^{-1}$)	440.75	420.90
Crystal system	Monoclinic	Triclinic
Space group	$P2(1)/c$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	18.671(4)	8.122(7)
b	13.891(3)	13.290(11)
c	7.0660(16)	15.747(13)
α	90	82.340
β	100.280(3)	82.923
γ	90	89.902
V (Å^3)	1803.2(7)	1672(2)
Z	4	4
D_{Calcd}	1.623	1.673
Crystal size (mm^3)	$0.20 \times 0.18 \times 0.25$	$0.38 \times 0.103 \times 0.096$
$F(000)$	904	860
μ(Mo-Kα)(cm^{-1})	1.398	1.337
θ (°)	1.84–29.01	1.89–27.30
Reflections collected	11530	9747
Independent reflections ($I > 2\sigma(I)$)	3575	3714
Parameters	266	535
$\Delta(\rho)$ (e Å^{-3})	0.349 and −0.344	3.974 and −1.494
Goodness-of-fit	1.035	0.958
R^a	0.0305 (0.0415)	0.1070 (0.1715)
wR_2^a	0.0770 (0.0819)	0.2570 (0.3118)

[a] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $wR_2 = [(w(F_o^2 - F_c^2)^2]/[(w(F_o^2)^2]^{1/2}$; $[F_o > 4\sigma(F_o)]$.

[b] Based on all data.

2.3. *Preparations*

All chemicals used were of analytical grade and used without further purification. The amino-Schiff-base ligand was prepared by modified literature method [15] and all other reactants were used as purchased. All reactions were carried out at room temperature.

2.3.1. Preparation of KHL (potassium salt of salicylideneglycine) [15].

A solution of potassium hydroxide (10 mmol, 0.560 g) in 30 mL absolute ethanol was added to glycine (10 mmol, 0.750 g). The mixture was stirred until dissolution. Then the ethanolic solution (100 mL) of salicylaldehyde (10 mmol, 1.220 g) was added dropwise. The product was crystallized by diffusion of excess absolute diethyl ether into the solution. The product was filtered and dried in a vacuum desiccator. Yield: 1.590 g (73.0%). Anal. Calcd for $C_9H_8NO_3K$: C, 49.77; H, 3.69; N, 6.45%. Found: C, 48.98; H, 3.58; N, 5.89%. M.p.: 207°C. ^1H NMR(D_2O, δ): 4.26 (s, 2H, $-CH_2-COO^-$), 6.64–7.42 (m, 4H, –H–Ar), 8.26 (s, 1H, –C–H=N), 9.99 (s, H, –OH–Ar).

2.3.2. Preparation of complexes

2.3.2.1. *($C_9H_7NO_3$)Zn($C_{12}H_8N_2$)(H_2O) (**1**).* To a solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.110 g, 0.5 mmol) in methanol (10 mL) was added a solution of KHL (0.110 g, 0.5 mmol) and 1,10-phenanthroline ($C_{12}H_8N_2 \cdot H_2O$, 0.100 g, 0.5 mmol) in methanol (10 mL). The yellow solution was stirred for 2 h without precipitation. After 40 d, some yellow crystals were obtained, then dried under vacuum to afford 0.180 g of the product, with the yield being 80.40% (based on $Zn(CH_3COO)_2 \cdot 2H_2O$). Anal. Calcd for $C_{21}H_{17}N_3O_4Zn$ (**1**): C, 57.17; H, 3.86; N, 9.53. Found: C, 57.22; H, 3.79; N, 9.84%.

2.3.2.2. *($C_9H_7NO_3$)Cu($C_{12}H_8N_2$) (**2**).* The preparation of **2** is the same as for **1**. After 35 d, some green crystals were obtained, then dried under vacuum to afford 0.170 g of the product, yield 76.80% (based on $Cu(CH_3COO)_2 \cdot 2H_2O$). Anal. Calcd for $C_{21}H_{15}N_3O_3Cu$ (**2**): C, 59.87; H, 3.56; N, 9.98. Found: C, 59.72; H, 3.60; N, 9.84%. Both complexes were soluble in DMF, $CHCl_3$, CH_2Cl_2, DMSO, pyridine, CH_3CN and THF and insoluble in hexane and ether.

2.4. *Thermogravimetric assay of 1 and 2*

Thermogravimetric analyses (TGA) were carried out on a Perkin Elmer Diamond TG/DTA instrument. The samples are initially heated for 1 h at 50°C to remove air. During the simple ramping experiment, weight changes were recorded at $10°C\,min^{-1}$ temperatures between 50 and 1000°C in nitrogen. The masses of **1** and **2** are 2.141 mg and 2.391 mg, respectively.

2.5. *Methods of calculation*

MP2 calculations at 3-21*G**(6d, 7f) basis set level were carried out for the complexes with Gaussian 03W program. The calculation included 46 and 43 atoms, 313 and 442 basis functions, 315 and 920 primitive Gaussians for **1** and **2**, respectively. The parameters of the molecular structures come from the crystal structure data, and the molecular point groups and their symmetry (C_s) are also considered. The electronic structures and bonding characteristics of the complexes were analyzed with *ab initio* calculations and Natural Bonding Orbital analysis. The calculation gives the constitution and the energy of the molecular orbital and NBO atomic charge.

2.6. *SOD activity assay of 1 and 2*

The SOD activities of **1** and **2** were determined by the Beauchamp–Fridovich assay [16]. Cells containing 3.3×10^{-6} M riboflavin, 0.01 M methionine, 4.6×10^{-5} M NBT, 0.05 M phosphate buffer (pH = 7.8), and various concentrations ($5 \times 10^{-8} - 1.5 \times 10^{-6}$ M) of **1**, **2** or $2 \times 10^{-9} - 2 \times 10^{-8}$ M native Cu–Zn SOD, were illuminated by fluorescent lamps. The absorbance at 560 nm increased linearly with time of illumination. The reduction of NBT was measured in terms of increased absorbence at 560 nm on a Shimadzu UV-240 spectrophotometer. All photoinduced reactions were performed at 25°C in triplicate. The SOD activity of the complexes was evaluated by the 50% inhibitory concentration (IC_{50}) and was compared with the native Cu–Zn SOD enzyme.

3. Results and discussion

3.1. *Spectroscopic characterization*

3.1.1. IR spectra of 1 and 2. For **1** and **2**, the binding pattern of amino-Schiff-base to metal is evident from the IR spectra where the single strong C=N stretch is centered at 1638 cm^{-1} and 1636 cm^{-1}, lower frequency compared to $\upsilon_{C=N}$ at 1645 cm^{-1} in the free amino-Schiff-base [17]. Two strong and sharp bands of **1** and **2** at 1579, 1386 cm^{-1} and 1600, 1449 cm^{-1} are attributed to asymmetric and symmetric stretching vibrations of coordinated carboxylate [15, 17]. The bands at 1453, 856 and 729 cm^{-1} for **1**, 1449, 835 and 726 cm^{-1} for **2** are assigned to vibration of 1,10-phenanthroline. The spectra displayed bands at 1150 cm^{-1} and 750 cm^{-1} for **1**, 1516 and 756 cm^{-1} for **2**, which could be assigned to stretching vibrations of $\upsilon_{(C=C)aromatic}$ and $\upsilon_{(C–H)aromatic}$ from amino-Schiff-base. Coordination to metal is confirmed by bands at 521 cm^{-1}, 525 cm^{-1} for $\upsilon_{(M–N)}$, at 469 cm^{-1}, 469 cm^{-1} of $\upsilon_{(M–O)hydroxyl}$, and at 421 cm^{-1}, 424 cm^{-1} of $\upsilon_{(M–O)C=O}$ for **1** and **2**, respectively [15].

3.1.2. UV–Visible absorption spectroscopy. The electronic absorption spectra of **1** and **2** are recorded in CH_3OH solution. Bands at 222, 266 nm for **1**, 236, 262 nm, sharper and stronger for **2**, are assigned as π–π* transitions of the aromatic-like chromophore from 1,10-phenanthroline or phenylene. Bands at 366 nm for **1** and 368 nm for **2** are attributed to transitions of the O-hydroxy of the amino-Schiff-base [18] to Zn and Cu.

3.1.3. Fluorescence spectra. The fluorescence emission spectra of **1** show emission at 512 nm (exciting wavelength = 350 nm). The emission spectra of **1** may originate from π–π * (LLCT) and amino-Schiff-base ligand to metal charge transition (LMCT), based on emission spectra of free ligand (amino-Schiff-base). Comparing zinc(II) complex fluorescence emission spectra ($\lambda = 446$ nm for $(C_9H_{10}N_6B)_2Zn$, $\lambda = 445$ nm for $(C_9H_7NO_3)Zn(C_3H_4N_2)_2$) [19], **1** exhibits a red luminescence at 512 nm upon 450 nm excitation due to the strongly conjugated interaction of 1,10-phenanthroline ring, showing that luminescence properties of the complexes are related to not only coordinated metal center but also to the coordination steric configuration of ligands.

3.2. *Structural description*

A Diamond representation of $(C_9H_7NO_3)Zn(C_{12}H_8N_2)(H_2O)$ with the atom-numbering scheme is given in figure 1(a) and selected interatomic distances and angles are listed in table 2. The zinc is six-coordinate with distorted octahedral geometry. The O1, O2 and N1 from amino-Schiff-base ligand and N3 from 1,10-phenanthroline occupy the equatorial plane, while O4 from water and N2 occupy the apical positions. The Zn lays −0.0371(7) Å above the N1–O1–N3–O2 coordination plane. The average deviated distance of the four coordinated atoms from the coordination plane is 0.0000(8) Å.

There are two types of hydrogen bonds in **1** as shown in figure 1(b): hydrogen bonds between a terminal oxygen of water and an uncoordinated carboxyl oxygen of the amino-Schiff-base from a neighboring molecule O3A–H–O4 (2.763(1) Å; A: *x*, $1.5 - y$,

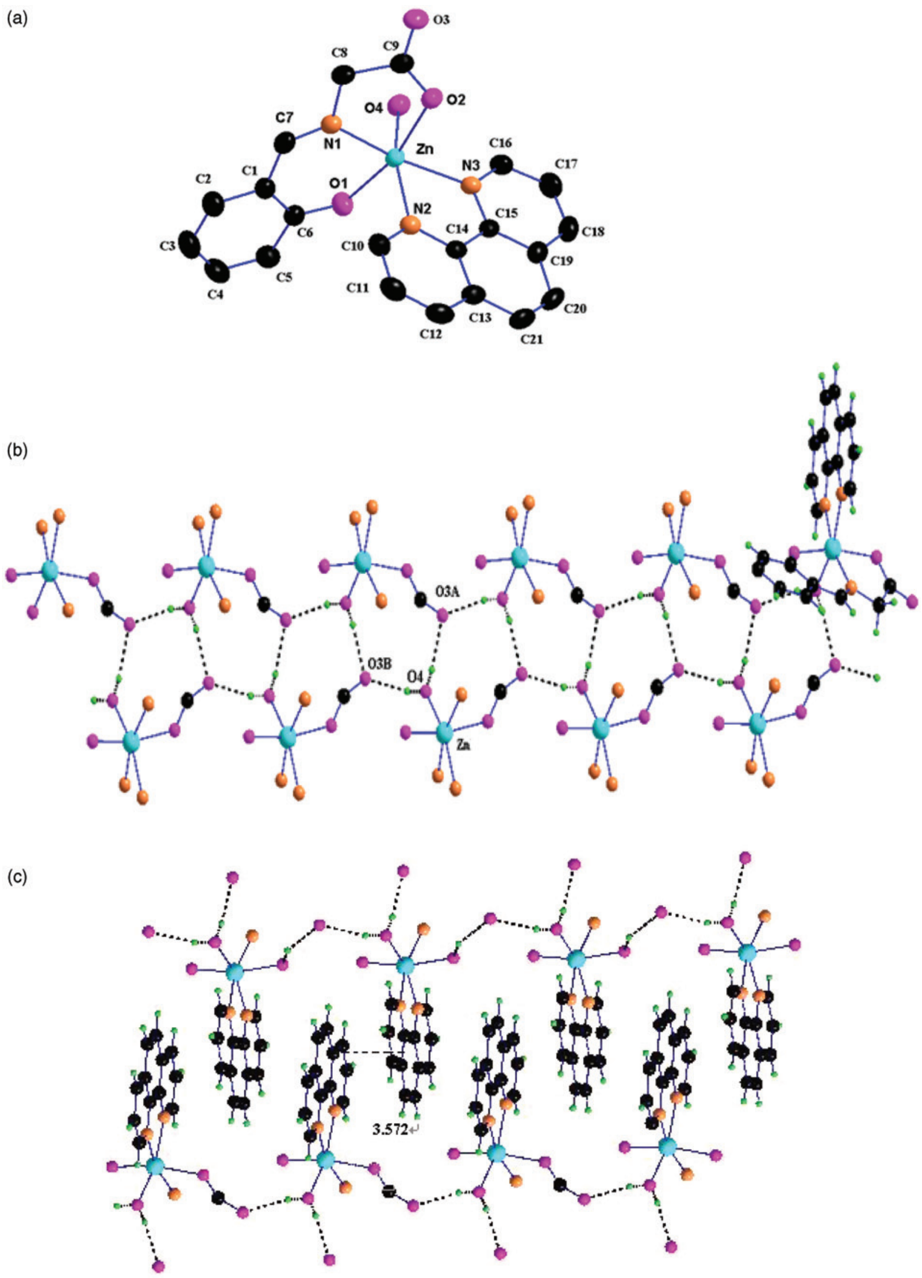

Figure 1. (a) The crystal structure of **1**. (b) The hydrogen bonds of **1** (only the Zn and coordinated atoms are shown for clarity). (c) π–π interactions between the phen molecules in **1** (only the Zn and coordinated atoms are shown for clarity).

$0.5+z$); O3B–H–O4 (2.768(1) Å; B: x, y, $1+z$), form a one-dimensional zigzag chain along the c axis. The π-overlap between 1,10-phenanthrolines from neighboring molecules leads to an extended assembly. The adjacent one–dimensional zigzag chains are packed through the intermolecular π–π interactions between the

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

Zn–O(1)	2.0446(14)	N(1)–Zn–O(2)	77.63(6)	O(4)–Zn–N(2)	161.76(6)
Zn–N(1)	2.0831(15)	N(3)–Zn–O(2)	89.59(5)	C(6)–O(1)–Zn	128.01(12)
Zn–N(3)	2.1401(15)	O(1)–Zn–O(4)	89.99(6)	C(9)–O(2)–Zn	115.75(12)
Zn–O(2)	2.1516(14)	N(1)–Zn–O(4)	98.85(6)	C(7)–N(1)–Zn	126.94(13)
Zn–O(4)	2.1661(14)	N(3)–Zn–O(4)	87.11(6)	C(8)–N(1)–Zn	114.40(11)
Zn–N(2)	2.2268(16)	O(2)–Zn–O(4)	89.53(5)	C(10)–N(2)–Zn	128.86(13)
O(1)–Zn–N(1)	87.48(6)	O(1)–Zn–N(2)	88.15(6)	C(14)–N(2)–Zn	113.32(12)
O(1)–Zn–N(3)	105.51(5)	N(1)–Zn–N(2)	99.19(6)	C(16)–N(3)–Zn	126.28(13)
N(1)–Zn–N(3)	165.79(6)	N(3)–Zn–N(2)	75.94(6)	C(15)–N(3)–Zn	116.06(12)
O(1)–Zn–O(2)	164.85(5)	O(2)–Zn–N(2)	96.92(5)		

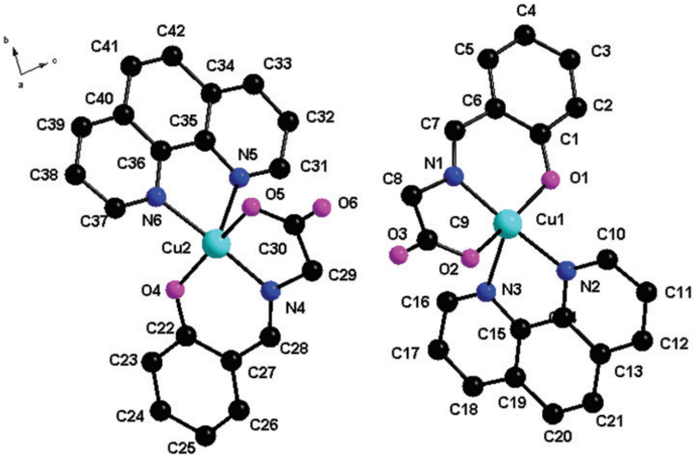

Figure 2. The crystal structure of **2**.

1,10-phenanthroline molecules with a distance of 3.572(1) Å, which results in a zipper-like supramolecular network. The zipper-like structure of **1** with hydrogen bonds and π–π stacking interaction is shown in figure 1(c).

In an asymmetric unit of **2**, there are two molecules. A Diamond representation of $(C_9H_7NO_3)Cu(C_{12}H_8N_2)$ **2** with the atom–numbering scheme is given in figure 2, which is similar to a reported structure [20]. Selected interatomic bond lengths and angles are listed in table 3. The copper is five-coordinate, coordinated to N1, O1 and O2, from amino-Schiff-base and N2 and N3 from 1,10-phenanthroline. The structure of **2** can be evaluated by the Addison distortion index τ [21]: $\tau = |\beta - \alpha|/60^\circ$, α and β being the two largest angles around the central atom. In a five-coordinate system, values for τ are 1.0 for trigonal bipyramidal and 0.0 for square pyramidal. The values of τ are 0.27, 0.24 for Cu(1) and Cu(2), indicating that the coordination environment is distorted slightly from square pyramidal. The average deviation of the four atoms [N1, O1, O2, N3 for Cu(1), N4, O4, O5, N6 for Cu(2)] from the square plane are 0.0001(5) Å and 0.0001(3) Å, respectively; N2 and N5 (2.0568 (9) Å and 2.3748 (9) Å) occupy the axial positions.

As shown in table 4, comparing the distances and angles around the central atoms to the Schiff base, Zn–N, Zn–$O_{hydroxy}$ and Zn–$O_{carboxy}$ distances for **1** are longer than those

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Cu(1)–O(1)	1.895(6)	O(1)–Cu(1)–N(3)	109.8(3)	N(4)–Cu(2)–N(6)	169.5(3)
Cu(1)–N(1)	1.922(7)	N(1)–Cu(1)–N(3)	110.8(3)	O(5)–Cu(2)–N(6)	91.2(3)
Cu(1)–O(2)	1.980(7)	O(2)–Cu(1)–N(3)	86.2(3)	O(4)–Cu(2)–N(5)	109.7(3)
Cu(1)–N(2)	2.006(7)	N(2)–Cu(1)–N(3)	77.3(3)	N(4)–Cu(2)–N(5)	110.9(3)
Cu(1)–N(3)	2.309(7)	C(1)–O(1)–Cu(1)	126.6(6)	O(5)–Cu(2)–N(5)	86.1(3)
Cu(2)–O(4)	1.905(6)	C(9)–O(2)–Cu(1)	116.3(6)	N(6)–Cu(2)–N(5)	77.6(3)
Cu(2)–N(4)	1.925(7)	C(7)–N(1)–Cu(1)	126.6(6)	C(22)–O(4)–Cu(2)	127.4(6)
Cu(2)–O(5)	1.972(6)	C(8)–N(1)–Cu(1)	111.5(5)	C(30)–O(5)–Cu(2)	115.3(6)
Cu(2)–N(6)	2.030(7)	C(10)–N(2)–Cu(1)	124.9(6)	C(28)–N(4)–C(29)	121.0(7)
Cu(2)–N(5)	2.309(7)	C(14)–N(2)–Cu(1)	118.0(5)	C(28)–N(4)–Cu(2)	125.9(6)
O(1)–Cu(1)–N(1)	93.7(3)	C(16)–N(3)–Cu(1)	133.4(6)	C(29)–N(4)–Cu(2)	112.6(5)
O(1)–Cu(1)–O(2)	163.5(3)	C(15)–N(3)–Cu(1)	107.3(5)	C(31)–N(5)–Cu(2)	132.9(6)
N(1)–Cu(1)–O(2)	83.8(3)	O(4)–Cu(2)–N(4)	94.0(3)	C(35)–N(5)–Cu(2)	107.7(5)
O(1)–Cu(1)–N(2)	88.6(3)	O(4)–Cu(2)–O(5)	163.7(3)	C(37)–N(6)–Cu(2)	123.7(6)
N(1)–Cu(1)–N(2)	170.0(3)	N(4)–Cu(2)–O(5)	83.5(3)	C(36)–N(6)–Cu(2)	116.5(5)
O(2)–Cu(1)–N(2)	91.2(3)	O(4)–Cu(2)–N(6)	88.5(3)		

Table 4. Comparison of bond lengths and angles of similar complexes.*

Complexes	M–N (Å)	M–O$_{\text{phenyl}}$ (Å)	M–O$_{\text{carboxyl}}$ (Å)	N–M–O$_{\text{phenyl}}$ (°)	N–M–O$_{\text{carboxyl}}$ (°)	References
1	2.0831(15)	2.0446(14)	2.1516(14)	87.48(6)	77.63(6)	This work
2	1.914(6)	1.893(5)	1.980(7)	93.4(2)	83.8(3)	This work
3	1.9339(15)	1.9214(13)	1.9944(13)	92.63(6)	83.51(6)	19
4	2.034(14)	2.036(13)	2.201(11)	91.1(5)	78.0(5)	19

*__1__: $(C_9H_7NO_3)Zn(C_{12}H_8N_2)(H_2O)$; **2**: $(C_9H_7NO_3)Cu(C_{12}H_8N_2)$; **3**: $(C_9H_7NO_3)Cu(C_3H_4N_2)$;
4: $(C_9H_7NO_3)Zn(C_3H_4N_2)_2$.

of **2**, while N–Zn–O$_{\text{phenyl}}$ and N–Zn–O$_{\text{carboxyl}}$ angles are smaller. These differences are consistent with differences of the coordination numbers around the metals.

3.3. *Thermogravimetric analyses*

The thermogravimetric studies of **1** show three decomposition steps. The first occurred at 125–201°C with 4.62% weight loss, due to loss of H_2O (calculated value 4.09%). The second step occurred at 201–304°C with 10.92% weight loss, due to loss of CO_2 from the amino–Schiff–base (calculated value 10.00%). The third decomposition step which occurs in the temperature range of 304–857°C was due to loss of half 1,10-phenanthroline with a percentage weight loss of 19.65% (calculated value 20.46%). The DTA curve of **1** indicates the three stages are endothermic.

In the TG–DTG–DTA curve of thermal decomposition for **2**, the first stage, 161–216°C, has 11.09% mass loss corresponding to loss of CO_2 from the amino-Schiff-base (calculated value 10.45%) as an endothermic process. The second stage from 216–372°C with calculated mass loss of 42.30% is due to loss of 1,10-phenanthroline (calculated value 42.76%). The DTA curve shows that this is also an endothermic process.

Thermal decomposition analysis show that although coordination of the amino-Schiff-base to metal are the same (tridentate), decomposition processes of **1** and **2** are different.

Non-isothermal kinetics are provided in the Supplementary Material.

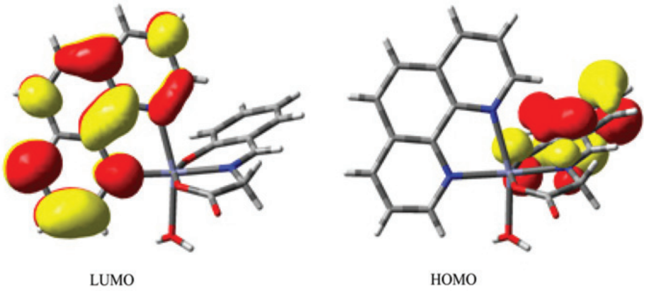

Figure 3. The main LUMO and HOMOs for **1**.

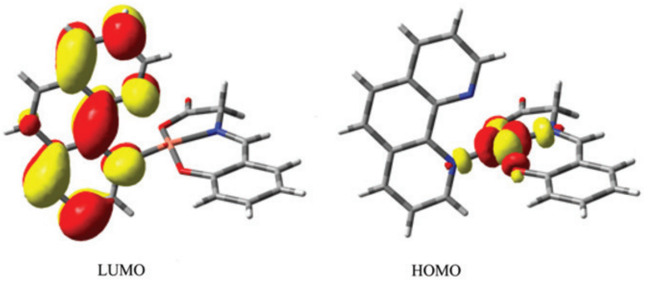

Figure 4. The main LUMO and HOMOs for **2**.

Table 5. Frontier molecular orbital eigenvalues (a.u.) for **1** and **2**.

Orbital	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO
1	−0.32647	−0.32301	−0.31551	−0.26100	0.05033
2	−0.32833	−0.29629	−0.25669	−0.08665	0.01970

3.4. *Quantum chemistry calculations of the complexes*

Molecular orbital theory shows that the larger the difference between the frontier orbits, the more stable the molecular structure is. The main compositions of the LUMO and HOMO orbitals for **1** and **2** are shown in figures 3 and 4. The energy values of ΔE ($\Delta E = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$) are 0.31133 and 0.10635, respectively, for **1** and **2** (table 5), showing the stability is **1** > **2**.

The atomic net charges for the complexes calculated in the NBO analysis are listed in table 6. The charge of Zn for **1** is 1.68664 and the net change of the terminal oxygen (O4) is −0.82636. The net charge of the other coordinated O and N atoms (O1, O2, O3; N1, N2, N3) are −0.91335, −0.90448 and −0.7487; −0.71818, −0.56921 and −0.59346, respectively. The charge of Cu for **2** is 1.72023. The net charges of the coordinated N atoms (N1, N2, N3) range from −0.76003 to −0.57597, the net charges of the coordinated/uncoordinated O atoms (O1, O2, O3) range from −0.93745 to −0.79852.

Table 6. The atomic net charges for **1** and **2**.

Atom	**1**	Atom	**2**
Zn	1.68664	Cu1	1.72023
O1	−0.91335	O1	−0.93745
O2	−0.90448	O2	−0.99189
O3	−0.7487	O3	−0.79852
O4	−0.82636	N1	−0.76003
N1	−0.71818	N2	−0.55424
N2	−0.56921	N3	−0.57597
N3	−0.59346		

Table 7. Selected NBO bond orders for **1**.

Bond	Zn–O2	Zn–N1	Zn–O1	Zn–N2	Zn–N3	Zn–O4
Wiberg bond index	0.1257	0.1081	0.1384	0.0665	0.0845	0.0726
NBO bond order	0.1547	0.1334	0.1695	0.0919	0.1052	0.0905

Table 8. Selected NBO bond orders for **2**.

Bond	Cu1–N1	Cu1–N2	Cu1–N3	Cu1–O1	Cu1–O2
Wiberg bond index	0.1288	0.0419	0.0943	0.1122	0.1059
NBO bond order	0.1566	0.0702	0.1224	0.1537	0.1494

Comparing both complexes, the net charges of the central metal is less than +2, showing that the metal coordinates the ligands and transfers charge to the ligands. The net charges of the coordinated N atoms for **2** are more negative than those of **1**. The net charges of metal for **1** and **2** are different, attributed to interaction between Cu and ligands for **2** are stronger than that of **1**, corresponding to the crystallographic data of the complexes.

Comparing the NBO bond order of **1** and **2** (tables 7 and 8) between metal and N, that of amino-Schiff base is stronger than that of 1,10-phenanthroline.

3.5. *Superoxide assays*

Superoxide dismutase (SOD) has ability to inhibit reduction of nitroblue tetrazolium chloride monohydrate (NBT). The metal complexes compete with NBT for oxidation of the generated superoxide ions in the SOD–like activity experiment. The lower the concentration that corresponds to 50% inhibition of NBT reduction, the more efficient the complex is; this concentration is termed IC_{50} for comparative purposes. The SOD-like activities of **1** and **2** were determined by NBT-illumination method. The SOD-like activity of complexes indicated 50% inhibition at 6.15 µM for **1** and 0.79 µM for **2**. That **2** has better SOD-like activity than **1** corresponds to reported mononuclear copper complexes, which have high SOD-like activity [22–25]. The weaker SOD-like activity of

1 may be attributed to greater steric hindrance of the coordinated water, hindering the action of O_2^- approaching the Zn(II).

4. Conclusion

Two crystal structures of amino-Schiff-base complexes are reported in this article. Competition with NBT toward superoxide show a certain extent for **1** and better for **2**. Although the SOD-like activity for **2** is not higher than that of some reported complexes, it shows the possibility of SOD-like activity for complexes with amino-Schiff-base ligands.

Supplementary material

Tables of atomic coordinates, an isotropic thermal parameter, and complete bond distances and angles have been deposited with the Cambridge Crystallographic Data Center. Copies of this information may be obtained free of charge by quoting the publication citation and deposition numbers CCDC: 650754 for **1**, 650755 for **2**, from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44–1223–336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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