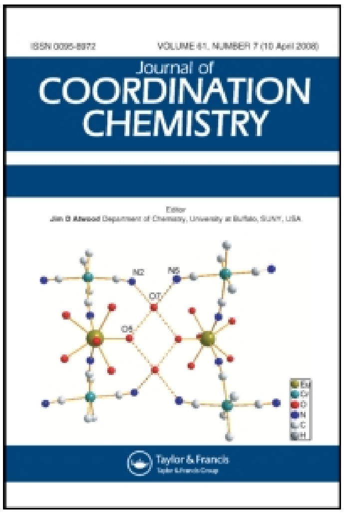

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Synthesis, crystal structures, and superoxide dismutase activity of two isostructural copper(II)-zinc(II) complexes derived from *N,N'*-bis(4-methoxysalicylidene)cyclohexane-1,2-diamine

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Synthesis, crystal structures, and superoxide dismutase activity of two isostructural copper(II)–zinc(II) complexes derived from *N*,*N′*-bis(4-methoxysalicylidene) cyclohexane-1,2-diamine

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Two new isostructural copper(II)–zinc(II) complexes, [$CuZnLBr_2$] (**1**) and [$CuZnLCl_2$] (**2**) ($H_2L = N,N'$-bis(4-methoxysalicylidene)cyclohexane-1,2-diamine), have been synthesized and characterized by elemental analyses, infrared spectroscopy, and single-crystal X-ray diffraction. Both complexes crystallize in the *P-1* space group. The Cu in each complex is four-coordinate square planar with two imines and two phenolates of L. The Zn in each complex is four-coordinate tetrahedral with two phenolates of L and two halides (Br for **1** and Cl for **2**). The superoxide dismutase (SOD) activity of the complexes indicates that both complexes are rudimentary models for SOD.

Keywords: Schiff base; Copper; Zinc; Crystal structure; Superoxide dismutase

1. Introduction

Dinuclear complexes particularly heterobimetallic systems are of special interest because of their relevance to physics, chemistry, and biology [1]. Superoxide dismutase (SOD) is an important enzyme in biological systems, which catalyzes the dismutation of the superoxide radical to hydrogen peroxide and molecular oxygen [2, 3]. Crystallographic studies show that the Cu–Zn SOD contains an imidazolato-bridged copper(II) and zinc(II) in the active site [4]. Coordination is distorted square pyramidal for copper(II) and tetrahedral for zinc(II). Considering that heterodinuclear Cu–Zn complexes are very rare to date [5–7], in this article, two isostructural dinuclear Cu–Zn complexes, [$CuZnLBr_2$] (**1**) and [$CuZnLCl_2$] (**2**) ($H_2L = N,N'$-bis(4-methoxysalicylidene) cyclohexane-1,2-diamine), have been synthesized and structurally characterized.

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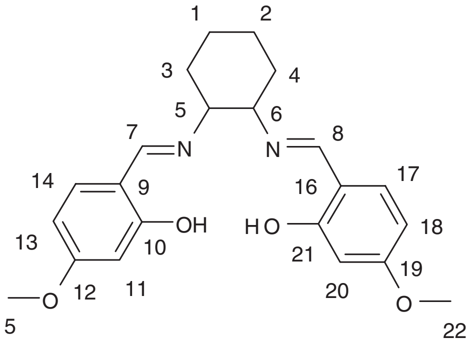
The SOD activity of the complexes was tested. To our knowledge, the complexes derived from the Schiff-base H_2L have not been reported.



H_2L

2. Experimental

2.1. *Materials and methods*

All chemicals (reagent grade) were commercially available and used without purification. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C elemental analyzer. Infrared (IR) spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets from 4000 to 400 cm^{-1}. ^1H NMR spectra were recorded on a Mercury Vx300 spectrometer (300 MHz) at room temperature using $CDCl_3$ as solvent and tetramethylsilane as internal standard. Molar conductance was measured with a Shanghai DDS-11A conductometer. Electronic absorption spectra were recorded on acetonitrile solutions of the complexes on a Shimadzu UV-Vis 160 spectrophotometer.

2.2. *Synthesis of H_2L*

To methanol solution (50 cm^3) of 4-methoxysalicylaldehyde (152.1 mg, 1.0 mmol) was added a methanol solution (30 cm^3) of cyclohexane-1,2-diamine (57.1 mg, 0.5 mmol) with stirring. The mixture was stirred for 10 min at room temperature to give a yellow precipitate. The product was filtered, washed three times with cold methanol, and dried in air. Yield: 96%. Anal. Calcd for $C_{22}H_{26}N_2O_4$ (%): C, 69.1; H, 6.8; N, 7.3. Found: C, 68.7; H, 6.9; N, 7.2. ^1H NMR ($CDCl_3$, 300 MHz) (ppm): $\delta = 12.03$ (b, OH); 8.23 (s, 2H, CH=N); 7.23 (d, 2H, Ar–H); 6.45 (d, 2H, Ar–H); 6.33 (s, 2H, Ar–H); 3.72 (s, 6H, OCH_3); 3.37 (m, 2H, chiral H); 1.83–1.40 (m, 8H, $(CH_2)_4$). ^{13}C NMR ($CDCl_3$, 300 MHz) (ppm): $\delta = 22.3$ (C1, C2), 29.7 (C3, C4), 55.3 (C15, C22), 62.3 (C5, C6), 98.7 (C11, C20), 104.5 (C13, C18), 118.2 (C9, C16), 127.7 (C14, C17), 160.3 (C10, C21), 164.1 (C7, C8), 167.2 (C12, C19).

2.3. *Synthesis of 1*

To methanol solution (10 cm^3) of H_2L (38.2 mg, 0.1 mmol) was added a methanol solution (10 cm^3) of $Cu(ClO_4)_2 \cdot 6H_2O$ (37.0 mg, 0.1 mmol) and $ZnBr_2$ (22.5 mg, 0.1 mmol) with stirring. The mixture was stirred for 30 min at room temperature to give a clear blue solution. After keeping the solution in air for a week, blue block-shaped crystals of **1**, suitable for X-ray crystal structural determination, formed at the bottom of the vessel on slow evaporation of the solvent. The crystals were isolated, washed three times with methanol, and dried in air. Yield: 72%. Anal. Calcd for $C_{22}H_{24}Br_2CuN_2O_4Zn$ (%): C, 39.5; H, 3.6; N, 4.2. Found: C, 40.1; H, 3.8; N, 4.0.

2.4. *Synthesis of 2*

Complex **2** was synthesized by similar method as described for **1**, with $ZnBr_2$ replaced by $ZnCl_2$ (13.7 mg, 0.1 mmol). Blue block-shaped crystals of **2**, suitable for X-ray crystal structural determination, were formed at the bottom of the vessel on slow evaporation of the solvent. The crystals were isolated, washed three times with methanol, and dried in air. Yield: 63%. Anal. Calcd for $C_{22}H_{24}Cl_2CuN_2O_4Zn$ (%): C, 45.5; H, 4.2; N, 4.8. Found: C, 45.0; H, 4.2; N, 4.7.

2.5. *X-ray structural determination*

Diffraction intensities for **1** and **2** were collected at 298(2) K using a Bruker SMART CCD area detector with Mo-Kα radiation ($\lambda = 0.71073$ Å). The collected data were reduced using SAINT [8] and empirical absorption corrections were performed using SADABS [9]. The structures were solved by direct methods and refined against F^2 by full-matrix least-squares using the SHELXTL package [10]. All non-hydrogen atoms were refined anisotropically. H atoms were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data for the two complexes are summarized in table 1. Selected bond lengths and angles are given in table 2.

2.6. *SOD measurement*

The SOD activity (the concentration of the complexes corresponding to 50% inhibition) of the complexes was measured by the Beauchamp–Fridovich assay [11]. Superoxide anions were produced from the riboflavin/methionine system. The indicator utilized in this case is nitroblue tetrazolium (NBT), which reacts with O_2^- to form blue formazane. Cells containing 3.3×10^{-6} M riboflavin, 0.01 M methionine, 4.6×10^{-5} M NBT, and 0.05 M phosphate buffer pH 7.4, and 10^{-7}–10^{-6} M complex or 2×10^{-9}–2×10^{-8} M native Cu–Zn SOD, were illuminated under fluorescent lamps. The absorbance at 560 nm increased linearly with time of illumination. The reduction of NBT was measured in terms of increased absorbance at 560 nm on a Shimadzu UV-240 spectrophotometer. All photo-induced reactions were performed at 25°C. Each test was performed in triplicate.

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

Complex	**1**	**2**
Emperical formula	$C_{22}H_{24}Br_2CuN_2O_4Zn$	$C_{22}H_{24}Cl_2CuN_2O_4Zn$
Formula weight	669.16	580.24
Temperature (K)	298(2)	298(2)
Crystal shape/color	Block/Blue	Block/Blue
Crystal system	Triclinic	Triclinic
Space group	*P-1*	*P-1*
Unit cell dimensions (Å, °)		
a	7.888(1)	7.881(1)
b	11.980(2)	11.676(1)
c	12.877(2)	12.794(1)
α	81.656(2)	81.262(2)
β	83.758(3)	84.263(2)
γ	78.728(3)	79.094(2)
Volume (Å^3), Z	1176.7(3), 2	1139.5(2), 2
Calculated density (g cm^{-3})	1.889	1.691
Absorption coefficient μ (Mo-Kα) (mm^{-1})	5.350	2.252
$F(000)$	662	590
Crystal size (mm^3)	$0.30 \times 0.30 \times 0.28$	$0.21 \times 0.20 \times 0.18$
Measured reflections	6713	6838
Independent reflections	4893 [R(int) = 0.0243]	4775 [R(int) = 0.0110]
Observed reflections [$I \geq 2\sigma(I)$]	3313	4052
Restraints	0	0
Parameters	291	291
Min. and max. transmission	0.297 and 0.316	0.649 and 0.687
Goodness-of-fit on F^2	1.037	1.053
Final R indices, [$I \geq 2\sigma(I)$][a]	$R_1 = 0.0435$, $wR_2 = 0.0941$	$R_1 = 0.0287$, $wR_2 = 0.0716$
R indices (all data)[a]	$R_1 = 0.0760$, $wR_2 = 0.1059$	$R_1 = 0.0359$, $wR_2 = 0.0753$
Largest difference peak and hole (e Å^{-3})	0.729 and −0.566	0.493 and −0.494

[a] $R_1 = F_o - F_c/F_o$, $wR_2 = [\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)^2]^{1/2}$, $w_1 = [\sigma^2(F_o^2) + (0.0452(F_o^2 + 2F_c^2)/3)^2]^{-1}$, $w_2 = [\sigma^2(F_c^2) + (0.0373(F_o^2 + 2F_c^2)/3)^2 + 0.4426(F_o^2 + 2F_c^2)/3]^{-1}$.

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

1			
Cu1–O1	1.914(3)	Cu1–O2	1.893(3)
Cu1–N1	1.896(3)	Cu1–N2	1.907(4)
Zn1–O1	2.030(3)	Zn1–O2	2.027(3)
Zn1–Br1	2.322(1)	Zn1–Br2	2.323(1)
Cu1–Zn1	2.998(1)		
O2–Cu1–N1	171.7(2)	O2–Cu1–N2	95.5(2)
N1–Cu1–N2	86.3(2)	O2–Cu1–O1	83.4(2)
N1–Cu1–O1	95.9(2)	N2–Cu1–O1	171.9(2)
O2–Zn1–O1	77.3(2)	O2–Zn1–Br1	112.2(1)
O1–Zn1–Br1	112.2(1)	O2–Zn1–Br2	112.7(1)
O1–Zn1–Br2	117.7(1)	Br1–Zn1–Br2	117.9(1)
2			
Cu1–O1	1.898(2)	Cu1–O2	1.912(2)
Cu1–N1	1.913(2)	Cu1–N2	1.901(2)
Zn1–O1	2.035(2)	Zn1–O2	2.040(2)
Zn1–Cl1	2.193(1)	Zn1–Cl2	2.193(1)
Cu1–Zn1	3.003(1)		
O1–Cu1–N2	170.5(1)	O1–Cu1–O2	83.7(1)
N2–Cu1–O2	96.0(1)	O1–Cu1–N1	95.5(1)
N2–Cu1–N1	86.4(1)	O2–Cu1–N1	170.4(1)
O1–Zn1–O2	77.2(1)	O1–Zn1–Cl2	113.4(1)
O2–Zn1–Cl2	111.0(1)	O1–Zn1–Cl1	111.9(1)
O2–Zn1–Cl1	118.2(1)	Cl2–Zn1–Cl1	118.3(1)

3. Results and discussion

Both complexes were synthesized by reaction of H_2L with copper(II) perchlorate and zinc(II) halide. The perchlorate anion does not coordinate, leading to formation of square planar Cu. The phenolate O atoms are good bridging groups [12, 13] and further coordinate to Zn forming dinuclear complexes. The halides complete the tetrahedral coordination of Zn. Both isostructural complexes are stable at room temperature, soluble in methanol, ethanol, and acetonitrile.

3.1. *Spectroscopic study*

IR spectra of H_2L and the two complexes provide information about metal–ligand bonding. Assignments are based on typical group frequencies. Weak and broad absorptions at $3433\,\mathrm{cm^{-1}}$ substantiate the presence of phenol in H_2L, which disappear in the complexes. The strong absorption at $1637\,\mathrm{cm^{-1}}$ in the spectrum of H_2L assigned to the azomethine ν(C=N) [14] shifts to lower wave number in the complexes, $1617\,\mathrm{cm^{-1}}$ for **1**, and $1616\,\mathrm{cm^{-1}}$ for **2**, attributed to coordination of nitrogen to Cu. The strong absorption of Ar–O in H_2L at $1232\,\mathrm{cm^{-1}}$ [15] is located at lower frequencies for the complexes, namely $1203\,\mathrm{cm^{-1}}$ for **1** and $1202\,\mathrm{cm^{-1}}$ for **2**. Weak absorptions indicative of Zn–Br in **1** and Zn–Cl in **2** are at 246 and $293\,\mathrm{cm^{-1}}$, respectively.

Both complexes show two typical absorption bands at about 640 and 490 nm in the visible electronic spectra. The first corresponds to typical d–d band in a square planar coordination around copper(II), which is in agreement with the crystal structures of the complexes. The second could be attributed to a ligand-to-metal charge transfer transition (LMCT).

3.2. *Structure description of 1 and 2*

The single-crystal X-ray diffraction shows that **1** and **2** are isostructural dinuclear copper(II)–zinc(II) complexes (figures 1 and 2). The dihedral angles between the corresponding benzene rings are 25.3(3)° in **1** and 27.0(3)° in **2**. Both cyclohexyl rings in the complexes adopt chair conformations. The $\mathrm{Cu} \cdots \mathrm{Zn}$ distances are 2.998(1) and 3.003(1) Å in **1** and **2**, respectively.

The Cu in each complex is coordinated by two imine nitrogens and two phenolate oxygens of L, forming a slightly distorted square plane. The two trans angles are 171.7(2)° and 171.9(2)° in **1**, and 170.4(1)° and 170.5(1)° in **2**. The Cu lies in the least-squares plane. The coordinate bond lengths related to Cu are comparable to each other and also comparable to corresponding values observed in similar complexes [16–18].

The Zn in each complex is coordinated by two phenolate oxygens of L and two halides (Br for **1** and Cl for **2**), forming a slightly distorted tetrahedral coordination. The Br1–Zn1–Br2 plane in **1** and the Cl1–Zn1–Cl2 plane in **2** are nearly perpendicular to the CuL units, which can decrease the steric effects between them. The Zn–N bond lengths in both complexes are comparable to each other, but the Zn–Br bonds in **1** are much longer than the Zn–Cl bonds in **2**. All the coordinate bond lengths are comparable to corresponding values observed in similar complexes [16–18].

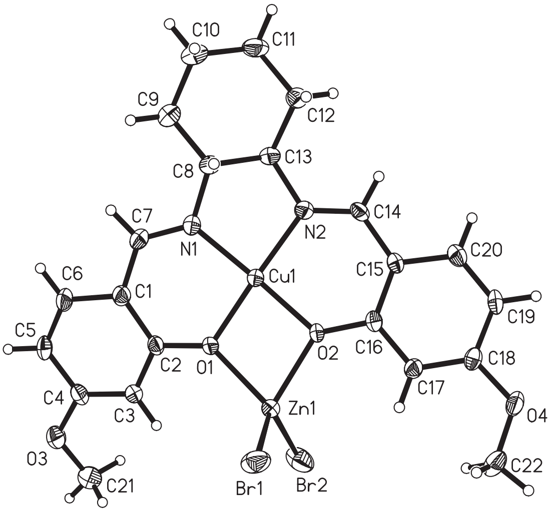


Figure 1. The structure of **1**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at 30% probability and H atoms are shown as small spheres of arbitrary radii.

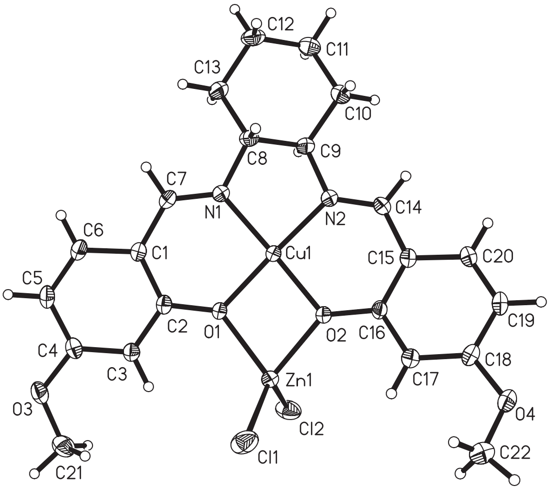


Figure 2. The structure of **2**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at 30% probability and H atoms are shown as small spheres of arbitrary radii.

3.3. *SOD activity*

Schiff-base metal complexes have been widely investigated [19, 20]. Most Schiff bases and their complexes were investigated for biological activities, such as antibacterial [21, 22], cytotoxic [22], antifungal [23], and urease inhibition [24]. Further, a number of copper(II) complexes with Schiff bases have been investigated for their SOD activities [23, 25, 26]. However, Cu–Zn complexes with Schiff bases have seldom been reported for SOD activities.

The SOD activities of the two complexes in the present work are similar. The percentage of inhibition against complex concentration was plotted in figure 3.

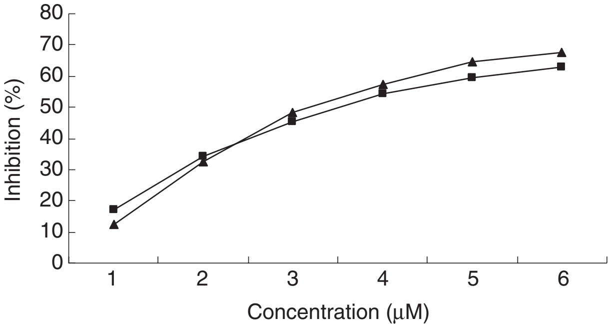


Figure 3. Percentage inhibition of NBT reduction plotted against the concentration of the complexes (■ for **1**, ▲ for **2**). Each point represents the mean ± SD of triplicate determination.

Table 3. SOD activities as IC_{50} for test materials.

Complex[a]	IC_{50} (μM)	Reference
1	3.506	This work
2	3.127	This work
$[Cu(C_9H_7NO_3)(C_{12}H_8N_2)]$	6.15	[26]
$[Cu(N\text{-meim})_6](sal)_2$	0.17	[28]
$[Cu(en)_2](sal)_2$	3.16	[29]
$[Cu(Pu\text{-}6\text{-}MePy)(H_2O)](ClO_4)_2$	2.25	[30]
$SALCuCl_2$	3.9	[31]
Cu–Zn SOD	0.005	This work

[a] $C_9H_7NO_3$ = salicylideneglycine; $C_{12}H_8N_2$ = 1,10-phenanthroline; *N*-meim = *N*-methylimidazole; sal = salicylate; en = ethylenediamine; $SALH_2$ = 4′,5′-bis(salicylideneimino)benzo-15-crown-5.

The values corresponding to IC_{50} were 3.506 μM for **1** and 3.127 μM for **2**. Native Cu–Zn SOD was used as a reference, with IC_{50} of 0.005 μM. Although the two complexes showed SOD activity, they are much weaker than native Cu–Zn SOD. The difference of the SOD activities among the complexes and the native SOD results from structural features. It is well-known that the active center of the native Cu–Zn SOD consists of copper(II) and zinc(II) ions bridged by a histidyl imidazolate anion. One water and three L-histidine molecules further coordinate copper(II) ion. Beside the imidazolato bridge the zinc(II) ion is bonded to an L-aspartic acid and two L-histidine molecules. The two complexes reported in this article are also Cu–Zn heterometallic complexes; however, the copper(II) and zinc(II) ions are bridged by two phenolate O atoms, and there are many other differences when compared with the native Cu–Zn SOD. Even though the native Cu–Zn SOD shows excellent activities, it is quite sensitive. Changes in temperature, solvating properties, etc. may easily lead to denaturation (frequently irreversibly). The two complexes reported in this article are very stable in solutions, the molar conductance values of the complexes measured in distilled water (containing small quantity of DMSO) at the concentration of $1.0 \times 10^{-3} mol\,L^{-1}$ are 15.7 and 17.2 $\mu S\,cm^{-1}$ for **1** and **2**, respectively, indicating the non-electrolytic nature of the complexes [27].

For comparison, the IC_{50} values of some copper(II) complexes and the native Cu–Zn SOD were also summarized in table 3. It can be seen that the IC_{50} values of the two complexes in this article are comparable or superior to those reported in the literature; however, they are significantly less active than the native enzyme. Nevertheless, the two complexes are potent SOD mimics considering their very low molecular weight compared with that of the native enzyme.

4. Conclusions

Two isostructural heterodinuclear copper(II)–zinc(II) complexes were synthesized and structurally characterized. Both complexes showed weak SOD activities, but are much more stable in solutions than native Cu–Zn SOD. Further work needs to be done to improve the mimic models of the native Cu–Zn SOD.

Supplementary material

Crystallographic data for the complexes have been deposited with the Cambridge Crystallographic Data Center (CCDC 720314 for **1** and 720315 for **2**).

Acknowledgements

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