DOI: 10.17344/acsi.2024.8640 *Acta Chim. Slov.* **2024,** *71,* 236–243

Scientific paper

Synthesis, Crystal Structures and Urease Inhibition of Copper(II) and Zinc(II) Complexes Derived from *N,N'*-Bis(4-bromosalicylidene)-1,3-propanediamine

Hai-Ying Chen,[1,2] Rundong Lu,[3] Jinkai Lei,[3] Jiacheng Liu,[3] Chi Liu,[3] Liuxiu Chen[3] and Wu Chen[3,*]

[1] *Engineering Research Center of Clean Production in Textile Printing and Dyeing, Ministry of Education, Wuhan 430073, P. R. China*

[2] *School of Fashion, Wuhan Textile University, Wuhan 430200, P. R. China*

[3] *National Engineering Laboratory for Advanced Yarn and Fabric Formation and Clean Production, Wuhan Textile University, Wuhan 430200, P. R. China*

* *Corresponding author: E-mail: 86082321@qq.com*

Received: 01-23-2024

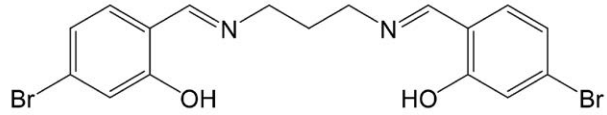
Abstract

A new tetranuclear copper(II) complex $[Cu_4L_2(N_3)_2(CH_3OH)_2](NO_3)_2{\cdot}4CH_3OH$ (**1**) and a new trinuclear zinc(II) complex $[Zn_3L_2(CH_3COO)_2]$ (**2**) have been prepared from the bis-Schiff base *N,N'*-bis(4-bromosalicylidene)-1,3-propanediamine (H_2L) with copper nitrate and zinc acetate, respectively, in the presence of sodium azide. The complexes were characterized by elemental analysis, IR and UV-Vis spectroscopy. Molecular structures of both complexes were confirmed by single crystal X-ray determination. The Cu(II) atoms in complex **1** are bridged by phenolate oxygen atoms and end-on azide ligands. The Zn(II) atoms in complex **2** are bridged by phenolate oxygen atoms and acetate ligands. The Cu(II) atoms in complex **1** are in square planar and square pyramidal coordination. The Zn(II) atoms in complex **2** are in square pyramidal and octahedral coordination. The Schiff base ligand coordinates to the metal atoms through two phenolate O and two imino N atoms. The biological assay reveals that the copper(II) complex has effective urease inhibition.

Keywords: Schiff base; copper(II) complex; zinc(II) complex; crystal structure; urease inhibition

1. Introduction

Urease, a Ni-containing enzyme, can catalyze the hydrolysis of urea to form ammonia rapidly.[1] The product is harmful for environment, agriculture and animals. In the last few years, a number of compounds have been reported to have urease inhibitory activities.[2] Schiff bases bearing azomethine groups (C=N) have widely biological applications like antibacterial,[3] antioxidant,[4] antitumor,[5] anti-inflammatory[6] and cytotoxic,[7] *etc*. In addition, Schiff bases readily coordinate to transition metal ions to form complexes with versatile structures.[8] Recent research indicated that Schiff bases and their metal complexes have shown urease inhibitory activities.[9] Copper and zinc are biological active trace elements in biological systems. In continuation of our work,[10] and aiming at obtaining new urease inhibitors, a copper(II) complex $[Cu_4L_2(N_3)_2(CH_3OH)_2](NO_3)_2{\cdot}4CH_3OH$ (**1**) and a zinc(II) complex $[Zn_3L_2(CH_3COO)_2]$ (**2**), where L is deprotonated form of *N,N'*-bis(4-bromosalicylidene)-1,3-propanediamine (H_2L) are present.



Scheme 1. H_2L

2. Experimental

2. 1. Materials and Methods

4-Bromosalicylaldehyde, propane-1,3-diamine, copper nitrate, zinc acetate and sodium azide were purchased from Aldrich. Solvent and other chemicals were obtained from Xiya Chemical Co. Ltd. CHN elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Infrared

spectra were recorded on a Jasco FT/IR–4000 spectrophotometer. Electronic absorption spectra were recorded with a Lambda 35 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra for H_2L were recorded on a Bruker 500 MHz spectrometer. Single crystal X-ray diffraction was carried out with a Bruker Apex II diffractometer. The molar conductivities were measured at 25 °C with a Synstronics conductivity bridge.

2. 2. Synthesis of *N,N'*-Bis(4-bromosalicylidene)-1,3-propanediamine (H_2L)

4-Bromosalicylaldehyde (4.0 g, 0.020 mol) was dissolved in 50 mL MeOH, to which was added dropwise 40 mL methanolic solution of propane-1,3-diamine (0.74 g, 0.010 mol). The mixture was stirred for 30 min under reflux. The solvent was removed by distillation under reduced pressure. The yellow solid residue was recrystallized from MeOH to give yellowish crystalline product. Yield 3.8 g (86%). Anal. Calcd for $C_{17}H_{16}Br_2N_2O_2$: C, 46.39; H, 3.66; N, 6.36%. Found: C, 46.51; H, 3.73; N, 6.27%. FT–IR data (KBr, cm^{-1}): ν(C=N) 1645, ν(Ar–O) 1296. UV–Vis data [10^{-3} mol L^{-1} in MeOH, λ/nm (ε/L mol^{-1} cm^{-1})]: 225 (17,530), 260 (12,380), 320 (4,535), 406 (2,720). ^{1}H NMR (500 MHz, d_6-DMSO, ppm): δ 11.38 (s, 2H, OH), 8.58 (s, 2H, CH=N), 7.53 (d, 2H, ArH), 7.35 (s, 2H, ArH), 7.15 (d, 2H, ArH), 3.72 (t, 4H, CH_2), 2.07 (m, 2H, CH_2). ^{13}C NMR (126 MHz, d_6–DMSO, ppm) δ 163.23, 156.12, 132.31, 125.02, 123.53, 120.38, 116.71, 59.71, 32.33.

2. 3. Synthesis of $[Cu_4L_2(N_3)_2(CH_3OH)_2](NO_3)_2{\cdot}4CH_3OH$ (1)

The Schiff base H_2L (0.44 g, 1.0 mmol) was dissolved in MeOH (30 mL), to which was added a methanolic solution of copper nitrate trihydrate (0.48 g, 2.0 mmol). The mixture was stirred at room temperature for 10 min. Then, sodium azide (0.13 g, 2.0 mmol) was added to the mixture. The final mixture was further stirred at room temperature for 30 min and filtered. The filtrate was kept still in air for a week to give brown block-shaped single crystals. Yield: 0.43 g (56%). Anal. Calcd for $C_{40}H_{52}Br_4Cu_4N_{12}O_{16}$: C, 31.39; H, 3.42; N, 10.98. Found: C, 31.25; H, 3.50; N, 10.87%. FT–IR data (KBr, cm^{-1}): 2072 ν(N_3), 1628, 1617 ν(C=N), 1584, 1545, 1469, 1386, 1353, 1277, 1213, 1139, 1072, 915, 820, 797, 689, 610, 596, 557, 467. UV-Vis data [10^{-3} mol L^{-1} in methanol, λ/nm (ε/L mol^{-1} cm^{-1})]: 225 (18,270), 250 (13,550), 275 (8,335), 360 (3,127). Λ_M (10^{-3} M in MeOH): 235 Ω^{-1} cm^2 mol^{-1}.

2. 4. Synthesis of $[Zn_3L_2(CH_3COO)_2]$ (2)

The Schiff base H_2L (0.44 g, 1.0 mmol) was dissolved in MeOH (30 mL), to which was added a methanolic solution of zinc acetate dihydrate (0.44 g, 2.0 mmol). The mixture was stirred at room temperature for 30 min and filtered. The filtrate was kept still in air for a week to give colorless block-shaped single crystals. Yield: 0.30 g (51%).

Table 1. Crystal data for the complexes

	1	**2**
Formula	$C_{40}H_{52}Br_4Cu_4N_{12}O_{16}$	$C_{38}H_{34}Br_4N_4O_8Zn_3$
FW	1530.74	1190.44
Crystal shape/colour	block/brown	block/colorless
Crystal size /mm	0.21 × 0.18 × 0.18	0.33 × 0.32 × 0.32
Crystal system	Triclinic	Monoclinic
Space group	*P*Ī	*C*2/*m*
a (Å)	10.838(2)	15.6867(11)
b (Å)	10.836(2)	13.6689(10)
c (Å)	12.548(2)	10.9660(12)
α (°)	75.559(1)	90
β (°)	75.559(1)	107.335(1)
γ (°)	85.902(1)	90
V (Å^3)	1381.9(4)	2244.5(3)
Z	1	2
λ (MoK*α*) (Å)	0.71073	0.71073
T (K)	298(2)	298(2)
μ (Mo*Kα*) (cm^{-1})	4.482	5.202
R_{int}	0.0658	0.0278
Reflections/parameters	5521/351	6057/141
Unique reflections	4041	2193
Observed reflections [$I \geq 2\sigma(I)$]	1348	1787
Restraints	1	0
Goodness of fit on F^2	0.815	1.077
R_1, wR_2 [I ³ 2$s(I)$]	0.0887, 0.2053	0.0275, 0.0616
R_1, wR_2 (all data)	0.2055, 0.2463	0.0367, 0.0639

Anal. Calcd for $C_{38}H_{34}Br_4N_4O_8Zn_3$: C, 38.34; H, 2.88; N, 4.71. Found: C, 38.46; H, 2.81; N, 4.80%. FT-IR data (KBr, cm^{-1}): 1628 ν(C=N), 1580, 1529, 1473, 1453, 1425, 1402, 1386, 1293, 1201, 1137, 1070, 915, 848, 786, 599, 537, 456. UV–Vis data [10^{-3} mol L^{-1} in methanol, λ/nm (ε/L mol^{-1} cm^{-1})]: 240 (14,670), 270 (8,150), 345 (4,030). Λ_M (10^{-3} M in MeOH): 32 Ω^{-1} cm^2 mol^{-1}.

2. 5. X-Ray Crystallography

X-ray diffraction data for the copper(II) and zinc(II) complexes were collected at 298(2) K with graphite–monochromated Mo Kα radiation (0.71073 Å). The collected data were reduced with SAINT.[11] Multi-scan absorption correction was performed with SADABS.[12] Structures of the complexes were solved by direct method with SHELX-TL, and refined against F^2 by full-matrix least-squares method.[13] All non-hydrogen atoms the complexes were refined anisotropically. The H8 atom of complex **1** was located from a difference Fourier map and refined with O–H distance restrained to 0.85(1) Å. The remaining H atoms were placed in calculated positions and constrained to ride on their parent atoms. Crystallographic data for the complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Table 2. Selected bond lengths (Å) and angles (°) for the complexes

1			
Cu1–N1	1.954(12)	Cu1–N2	1.891(13)
Cu1–O1	1.957(10)	Cu1–O2	1.960(9)
Cu2–N3	1.951(11)	Cu2–O1	1.988(9)
Cu2–O2	1.993(10)	Cu2–N3A	2.003(11)
Cu2–O8	2.273(12)		
N2–Cu1–N1	99.5(5)	N2–Cu1–O1	170.6(5)
N1–Cu1–O1	89.9(5)	N2–Cu1–O2	92.0(5)
N1–Cu1–O2	167.9(5)	O1–Cu1–O2	78.7(4)
N3–Cu2–O1	101.6(4)	N3–Cu2–O2	165.6(5)
O1–Cu2–O2	77.2(4)	N3–Cu2–N3A	79.0(5)
O1–Cu2–N3A	162.5(5)	O2–Cu2–N3A	97.8(4)
N3–Cu2–O8	93.4(5)	O1–Cu2–O8	101.2(4)
O2–Cu2–O8	100.9(4)	N3–Cu2–O8A	96.2(5)

Symmetry code for A: 1 – *x*, 1 – *y*, 1 – *z*

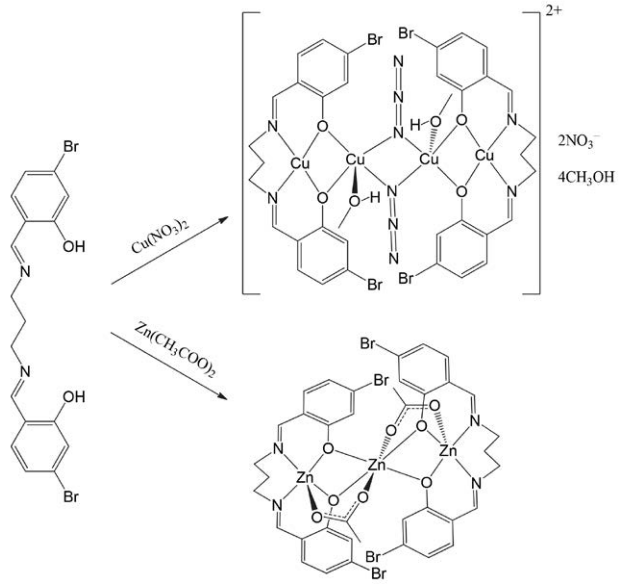
2			
Zn1–O1	2.0634(17)	Zn1–O2	1.998(3)
Zn1–N1	2.058(2)	Zn2–O3	2.069(2)
Zn2–O1	2.1275(17)		
O2–Zn1–N1A	101.74(8)	O2–Zn1–N1	101.74(8)
N1–Zn1–N1A	93.34(13)	O2–Zn1–O1A	99.14(8)
N1–Zn1–O1A	158.21(9)	O2–Zn1–O1	99.15(8)
N1–Zn1–O1	88.42(8)	O1–Zn1–O1A	82.18(10)
O3–Zn2–O3A	180	O3–Zn2–O1B	92.06(7)
O3–Zn2–O1	87.94(7)	O1–Zn2–O1A	79.20(9)
O1–Zn2–O1AA	100.80(9)		

Symmetry codes: A: *x*, 1 – *y*, *z*; B: 1 – *x*, 1 – *y*, 1 – *z*; AA: 1 – *x*, *y*, 1 – *z*.

3. Results and Discussion

3. 1. Synthesis

The Schiff base compound H_2L was prepared by reaction of 2:1 molar ratio of 4-bromosalicylaldehyde and propane-1,3-diamine in MeOH. The copper(II) and zinc(II) complexes were prepared by the self-assembly of H_2L with metal salts in MeOH (Scheme 2). Single crystals of both complexes were generated from their methanolic solution. Molar conductivities of complexes **1** and **2** in methanolic solution at concentration of 1.0×10^{-3} mol L^{-1} are 235 and 32 Ω^{-1} cm^2 mol^{-1}, respectively, indicating the 1:2 electrolytic and non-electrolytic nature.[14]



Scheme 2. The synthetic procedure for the complexes

3. 2. Structure Description of Complex 1

Molecular structure of the tetranuclear copper(II) complex is shown in Figure 1. The compound contains a copper(II) complex cation, two nitrate anions and four methanol molecules of crystallization. The Cu···Cu distances are 3.002(2) and 3.051(2) Å, respectively. The compound possesses crystallographic inversion center symmetry. The center is located at the midpoint of the two inner Cu(II) atoms. The Schiff base ligand coordinates to the Cu(II) atoms through the imino N and phenolate O atoms, generating three six-membered chelate rings. The outer Cu1 atom is coordinated by two imino N (N1, N2) and two phenolate O (O1, O2) atoms, forming square planar coordination. The distance between the Cu1 atom and the O4 atom of a methanol molecule is about 2.45 Å. If consider this proximity, the geometry can be considered as square pyramidal. The Cu1 atom deviates from the least-squares plane defined by the four donor atoms by 0.029(2) Å. The inner Cu2 atom is in square pyramidal coordina-

tion, with two phenolate O (O1, O2) of the Schiff base ligand and two N atoms (N3, N3A) from two azide ligands defining the basal plane, and with the methanol O atom (O8) at the apical site. The Cu2 atom deviates from the least-squares plane defined by the four basal donor atoms by 0.273(2) Å. The τ value for Cu2 coordination is 0.05, which suggests a typical square pyramidal geometry.[15] There are three four-membered chelate rings (Cu1–O1–Cu2–O2, Cu2–N3–Cu2A–N3A, Cu1A–O1A–Cu2A–O2A) in the complex molecule, which leads to the deviation of the square planar and square pyramidal geometries. The square pyramidal geometry is distorted, which is demonstrated from the *cis* and *trans* bond angles of 77.2(4)–101.6(4)° and 162.5(5)–165.6(5)°, respectively at the basal plane, and from the angles among the apical and basal donor atoms of 93.4(5)–101.2(4)°. The outer and inner Cu(II) atoms are bridged by two phenolate O atoms, and the two inner Cu(II) atoms are bridged by two end-on azide ligands. The bond lengths around the Cu(II) atoms are within normal values with the Schiff base copper(II) complexes.[16] The dihedral angle between the two benzene rings is 35.5(5)°. The two four-membered chelate rings Cu1–O1–Cu2–O2 and Cu2–N3–Cu2A–N3A form a dihedral angle of 32.3(4)°.

In the crystal structure of the compound, the complex cations are linked by nitrate anions and methanol molecules through O–H···O and O–H···N hydrogen bonds (Table 3), to form one dimensional chain along the *b* axis (Figure 2).

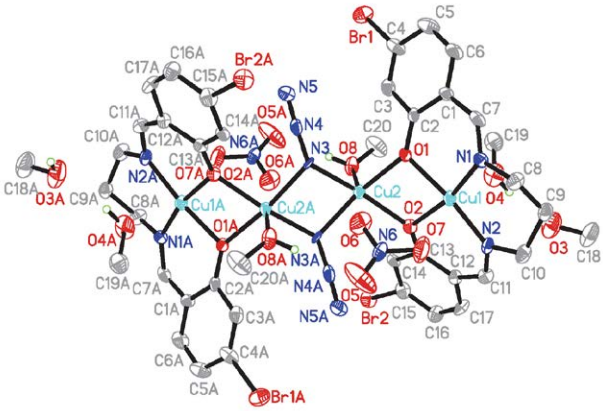


Figure 1. Molecular structure of complex **1**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at 30% probability level. Atoms labeled with the suffix A are related to the symmetry operation 1 – *x*, 1 – *y*, 1 – *z*. Hydrogen atoms except for OH groups are omitted for clarity.

In the crystal structure of the compound, the complex cations are linked by nitrate anions and methanol molecules through O–H···O and O–H···N hydrogen bonds (Table 3), to form one dimensional chain along the *b* axis (Figure 2).

3. 3. Structure Description of Complex 2

Molecular structure of the trinuclear zinc(II) complex is shown in Figure 3. The Zn···Zn distance is 3.0626(5) Å. The compound possesses crystallographic inversion center symmetry. The center is located at Zn2 atom. The Schiff base ligand coordinates to the Zn(II) atoms through the imino N and phenolate O atoms, generating three six-membered chelate rings. The outer Zn1 atom is in square pyramidal coordination, with two phenolate O (O1, O2) and two imino N (N1, N2) atoms of the Schiff base ligand defining the basal plane, and with acetate O (O2) atom at the apical site. The Zn1 atom deviates from the least-squares plane defined by the four basal donor atoms by 0.205(2) Å. The square pyramidal geometry is dis-

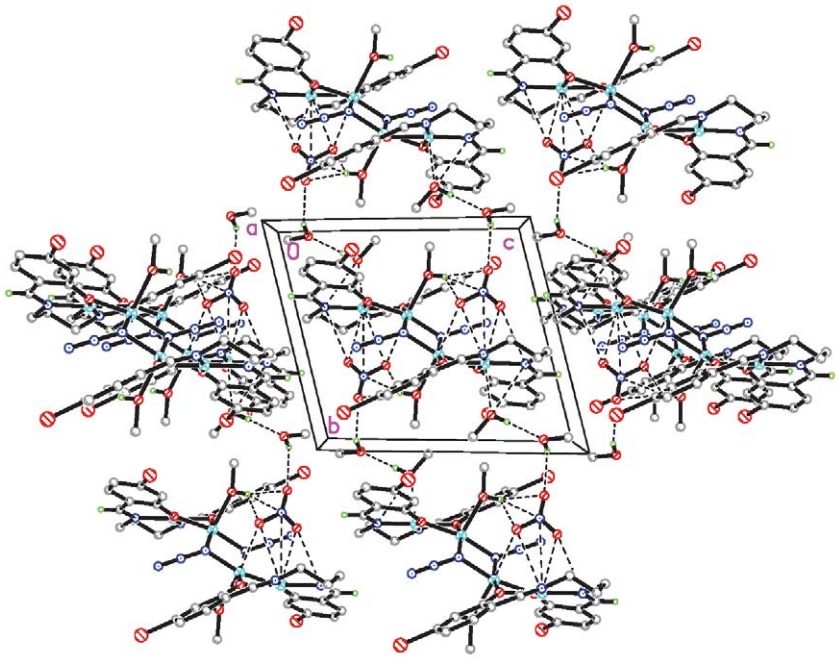


Figure 2. Molecular packing structure of complex **1**, viewed down the *a* axis. Hydrogen bonds are drawn as dotted lines.

torted, which is demonstrated from the *cis* and *trans* bond angles of 82.18(10)–93.34(13)° and 158.21(9), respectively at the basal plane, and from the angles among the apical and basal donor atoms of 99.14(8)–101.74(8)°. The central Zn2 atom is in octahedral coordination, with four phenolate O (O1, O1A, O1B, O1AA) atoms from two Schiff base ligands defining the equatorial plane, and with two acetate O (O3, O3A) atoms at the axial sites. There are two four-membered chelate rings (Zn1–O1–Zn2–O1A, Zn1A–O1AA–Zn2–O1B) in the complex molecule, which leads to the deviation of the square pyramidal and octahedral geometries. The octahedral geometry is distorted, which is demonstrated from the *cis* bond angles of 79.20(9)–100.80(9)° at the equatorial plane, and from the angles among the axial and equatorial donor atoms of 87.94(7)–92.06(7)°. The outer and inner Zn(II) atoms are bridged by two phenolate O atoms and one acetate ligand. The bond lengths around the Zn(II) atoms are within normal values with the Schiff base zinc(II) complexes.[17] The dihedral angle between the two benzene rings is 80.9(4)°. The two four-membered chelate rings Cu1–O1–Cu2–O2 and Cu2–N3–Cu2A–N3A form a dihedral angle of 32.3(4)°.

In the crystal structure of the compound, the complex molecules are stack along the *a* axis (Figure 4).

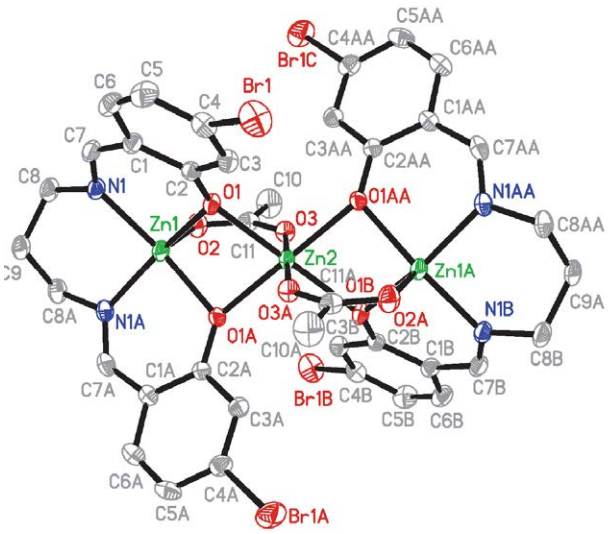


Figure 3. Molecular structure of the complex **2**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labeled with the suffix A and unlabeled atoms are related to the symmetry operation –*x*, –*y*, 1 – *z*. The methanol molecule is omitted for clarity.

Table 3. Hydrogen bond distances (Å) and bond angles (°) for complex **1**

D*–H···*A	***d*(*D*–H)**	***d*(H···*A*)**	***d*(*D*···*A*)**	**Angle (*D*–H···*A*)**
O3–H3A···O5$^{\#1}$	0.82	2.15	2.84(2)	141(3)
O4–H4···O3	0.82	1.89	2.70(3)	170(3)
O8–H8···N6$^{\#2}$	0.85(1)	2.61(8)	3.41(2)	158(5)
O8–H8···O5$^{\#2}$	0.85(1)	2.42(7)	3.25(3)	165(5)
O8–H8···O6$^{\#2}$	0.85(1)	2.15(7)	2.79(2)	132(5)

Symmetry codes: #1: *x*, –1 + *y*, *z*; #2: 1 – *x*, 1 – *y*, 1 – *z*.

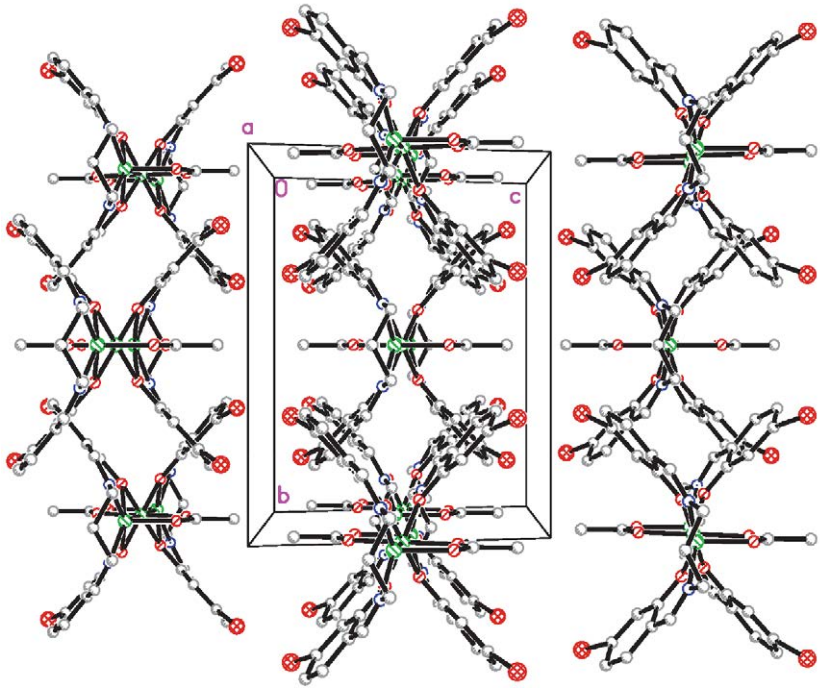


Figure 4. Molecular packing structure of the complex **2**, viewed down the *a* axis. Hydrogen bonds are drawn as dotted lines.

3. 4. IR and UV Spectra

The C=N absorption of the free Schiff base H_2L is observed at 1645 cm^{-1}. However, in the spectra of the complexes, the bands are shifted to lower wavenumbers, *viz.* 1628 and 1617 cm^{-1} for **1**, and 1628 cm^{-1} for **2**.[18] There are two absorptions for C=N bonds, which agree well with that determined by single crystal X-ray determination. In the crystal structure of complex **1**, the bond lengths of the two C=N bonds are 1.26(2) and 1.33(2) Å, which are different from each other. The spectrum of complex **1** shows an intense band at 1386 cm^{-1} characteristic of ionic nitrate.[19] The intense band at 2072 cm^{-1} of complex **1** can be assigned to the azide ligands.[20] In the spectrum of complex **2**, the asymmetric and symmetric stretching vibrations of the acetate groups appear at 1580 and 1425 cm^{-1}, respectively. The difference between ν_{asym}(COO) and ν_{sym}(COO) ($\Delta\nu$ = 155 cm^{-1}), which is smaller than 164 cm^{-1} observed in ionic acetate, reflects the bidentate bridging coordination mode.[21] The UV–Vis spectra of the free Schiff base and the complexes display bands in the region 250-320 nm, which are assigned to the n–π^* transitions.[22] The charge transfer LMCT bands of the complexes are located in the region 345–360 nm.[22]

3. 5. Pharmacology Study

The assay for the urease inhibition was carried out with the literature method.[23] The free Schiff base H_2L has weak activity, with low percentage inhibition of 17.1 ± 1.6 at concentration 100 μmol L^{-1}. Interestingly, the copper(II) complex has strong activity than H_2L, with percentage inhibition of 98.7 ± 2.3 at the same concentration, and with IC_{50} value of 0.21 ± 0.7 μmol L^{-1}. The zinc(II) complex has medium activity with percentage inhibition of 33.6 ± 3.1. The copper(II) complex has obviously higher activity than acetohydroxamic acid (IC_{50} = 28.1 μmol L^{-1}), which was used as a reference. As comparison, the copper(II) complex has better activity than copper perchlorate (IC_{50} = 8.8 μmol L^{-1}). Thus, the copper(II) complex may be used as a new urease inhibitor.

4. Conclusion

In summary, a tetranuclear copper(II) complex and a trinuclear zinc(II) complex with the Schiff base ligand *N,N*'-bis(4-bromosalicylidene)-1,3-propanediamine have been prepared and characterized. The Cu(II) atoms in the copper(II) complex are in square planar and square pyramidal coordination. The Zn(II) atoms in the zinc(II) complex are in square pyramidal and octahedral coordination. The Schiff base coordinates to the metal ions through imino nitrogen and phenolate oxygen. The copper(II) complex has effective urease inhibitory activity, with IC_{50} value of 0.21 ± 0.7 μmol L^{-1}.

Supplementary Data

CCDC 2327652 (**1**) and 2327653 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

5. References

1. (a) K. Shahzadi, S. M. Bukhari, A. Zaidi, T. A. Wani, M. S. Jan, S. Zargar, U. Rashid, U. Farooq, A. Khushal, S. Khan, *Pharmaceuticals* **2023**, *16*, 1552; **DOI:**10.3390/ph16111552
(b) L. Z. Li, C. S. Zhao, X. H. Wang, Y. Tan, X. K. Wang, X. Z. Liu, B.B. Guo, *Environ. Res.* **2023**, *237*, 116781. **DOI:**10.1016/j.envres.2023.116781
2. (a) J. Valentová, L. Lintnerová, B. Sláviková, P. Baran, *Inorg. Chim. Acta* **2023**, *558*, 121707; **DOI:**10.1016/j.ica.2023.121707
(b) S. Ahmad, M. A. Qadir, M. Ahmed, M. Imran, M. Ahmad, N. Yousaf, T. A. Wani, S. Zargar, I. Ali, M. Muddassar, *ACS Omega* **2023**, *8*, 46165–46181; **DOI:**10.1021/acsomega.3c07275
(c) B. Awan, M. A. Khan, I. Ahmad, A. Masood, A. Raza, S. Khaliq, F. Ullah, J. Ahmed, M. R. Khan, *Future Med. Chem.* **2023**, **DOI:**10.4155/fmc-2023-0225
(d) W.-L. Duan, M.-Y. Yan, F. Yan, J. Luan, *CrystEngComm* **2023**, DOI: 10.1039/d3ce01109g; **DOI:**10.1039/D3CE01109G
(e) W. Yang, Z. Y. Peng, G. C. Wang, *J. Enzyme Inhib. Med. Chem.* **2023**, *38*, 361–375; **DOI:**10.1080/14756366.2022.2150182
(f) A. Saeed, A. Ahmed, M. B. Haider, H. Ismail, K. Hayat, G. Shabir, H. R. El-Seedi, *RSC Advances* **2024**, *14*, 1018–1033; **DOI:**10.1039/D3RA06812A
(g) H. Pervez, N. Khan, J. Iqbal, S. Zaib, M. Yaqub, M. M. Naseer, *Acta Chim. Slov.* **2018**, *65*, 108–118. **DOI:**10.17344/acsi.2017.3649
3. (a) M. Patel, T. Kikani, K. Patel, S. Thakore, *J. Mol. Struct.* **2024**, *129*, 136691; **DOI:**10.1016/j.molstruc.2023.136691
(b) S. H. Sumrra, W. Zafar, S. A. Malik, K. Mahmood, S. S. Shafqat, S. Arif, *Acta Chim. Slov.* **2022**, *69*, 200–216;
(c) F. M. Elantabli, R. G. Mohamed, S. M. El-Medani, M. Haukka, R. M. Ramadan, M. A. Afifi, *J. Mol. Struct.* **2024**, *1299*, 137230. **DOI:**10.1016/j.molstruc.2023.137230
4. Y. M. Abdel-Baky, A. M. Omer, E. M. El-Fakharany, Y. A. Ammar, M. S. Abusaif, A. Ragab, *Sci. Rep.* **2023**, *13*, 22792. **DOI:**10.1038/s41598-023-50130-3
5. (a) K. S. Kumar, K. K. Aravindakshan, *Pharm. Chem. J.* **2022**, *55*, 1378–1389; **DOI:**10.1007/s11094-022-02585-3
(b) M. Diz, M. L. Durán-Carril, J. Castro, S. Alvo, L. Bada, D. Viña, J. A. García-Vázquez, *J. Inorg. Biochem.* **2022**, *236*, 111975; **DOI:**10.1016/j.jinorgbio.2022.111975
(c) E. M. Fathalla, M. A. M. Abu-Youssef, M. M. Sharaf, A.

El-Faham, A. Barakat, A. M. A. Badr, S. M. Soliman, A. M. Z. Slawin, J. D. Woollins, *Inorg. Chim. Acta* **2023**, *555*, 121586. **DOI:**10.1016/j.ica.2023.121586

6. (a) Seema, S. Sharma, P. Yadav, S. Kumari, M. Ranka, *Trans. Met. Chem.* **2023**, *48*, 389–400; **DOI:**10.1007/s11243-023-00551-w
(b) Q. U. Sandhu, M. Pervaiz, A. Majid, U. Younas, Z. Saeed, A. Ashraf, R. R. M. Khan, S. Ullah, F. Ali, S. Jelani, *J. Coord. Chem.* **2023**, *76*, 1094–1118. **DOI:**10.1080/00958972.2023.2226794
7. (a) R. N. Gomes, M. L. Silva, K. S. Gomes, J. H. G. Lago, G. Cerchiaro, *J. Inorg. Biochem.* **2024**, *250*, 112401; **DOI:**10.1016/j.jinorgbio.2023.112401
(b) M. Strzelecka, B. Wiatrak, P. Jawien, Z. Czyznikowska, P. Swiatek, *Bioorg. Chem.* **2023**, *139*, 106758. **DOI:**10.1016/j.bioorg.2023.106758
8. (a) L.-W. Xue, X. Fu, G.-Q. Zhao, Q.-B. Li, *Acta Chim. Slov.* **2021**, *68*, 17–24; **DOI:**10.17344/acsi.2020.5817
(b) Y. Yuan, X.-K. Lu, G.-Q. Zhou, X.-Y. Qiu, *Acta Chim. Slov.* **2021**, *68*, 1008–1015; **DOI:**10.17344/acsi.2021.7070
(c) J.-L. Hou, H.-Y. Wu, C.-B. Sun, Y. Bi, W. Chen, *Acta Chim. Slov.* **2020**, *67*, 860–865; **DOI:**10.17344/acsi.2020.5824
(d) P. Middya, Y. Chakravarty, S. Maity, S. Chattopadhyay, *J. Coord. Chem.* **2023**, *76*, 1777–1790; **DOI:**10.1080/00958972.2023.2280514
(e) Q.-U. Sandhu, M. Pervaiz, A. Majid, U. Younas, Z. Saeed, A. Ashraf, R. R. M. Khan, S. Ullah, F. Ali, S. Jelani, *J. Coord. Chem.* **2023**, *76*, 1094–1118; **DOI:**10.1080/00958972.2023.2226794
(f) J. P. Remiya, B. Shyni, T. S. Sikha, U. R. Parvathy, *J. Coord. Chem.* **2023**, *76*, 729–748. **DOI:**10.1080/00958972.2023.2199440
9. (a) S. Han, Y. Wang, *Acta Chim. Slov.* **2021**, *68*, 961–969; **DOI:**10.17344/acsi.2021.6965
(b) H. Zhao, X.-R. Liu, X. Wang, J. Hu, Y.-J. Cai, Q.-A. Peng, *Acta Chim. Slov.* **2021**, *68*, 804–810; **DOI:**10.17344/acsi.2021.6781
(c) B. H. He, Q. Y. Wang, X. Q. Zhang, D. H. Shi, Z. L. You, *Inorg. Chim. Acta* **2023**, *558*, 121738; **DOI:**10.1016/j.ica.2023.121738
(d) Q. Y. Wang, B. H. He, X. Q. Zhang, Y. Cao, A. Li, J. Q. Wang, D. H. Shi, Z. L. You, *J. Coord. Chem.* **2023**, **DOI:**10.1080/00958972.2023.2256935
(e) L. Zhang, Y.-Q. Gu, X.-H. Feng, T. Yang, X. Y. Li, J. Wang, Z. L. You, *Acta Chim. Slov.* **2022**, *69*, 674–680; **DOI:**10.17344/acsi.2022.7578
(f) J. Jiang, P. Liang, H. Y. Yu, Z. L. You, *Acta Chim. Slov.* **2022**, *69*, 629–637. **DOI:**10.17344/acsi.2022.7513
10. (a) W. Chen, Y. G. Li, Y. M. Cui, X. A. Zhang, H. L. Zhu, Q.-F. Zeng, *Eur. J. Med. Chem.* **2010**, *45*, 4473–4478; **DOI:**10.1016/j.ejmech.2010.07.007
(b) Y. M. Cui, Y. G. Li, Y. J. Cai, W. Chen, H. L. Zhu, *J. Coord. Chem.* **2011**, *64*, 610–616; **DOI:**10.1080/00958972.2011.552110
(c) Y. M. Cui, W. T. Liu, Y. Liu, W. Chen, Y. G. Li, *J. Coord. Chem.* **2011**, *64*, 3960–3968; **DOI:**10.1080/00958972.2011.634006
(d) Y.-M. Cui, X.-W. Dong, W. Chen, W.-J. Wang, Y.-G. Li, H.-L. Zhu, *J. Enzyme Inhib. Med. Chem.* **2012**, *27*, 528–532; **DOI:**10.3109/14756366.2011.599065
(e) Y. M. Cui, X. W. Dong, Y. G. Li, Z. W. Li, W. Chen, *Eur. J. Med. Chem.* **2012**, *58*, 323–331. **DOI:**10.1016/j.ejmech.2012.09.037
11. Bruker, SMART (Version 5.628) and SAINT (Version 6.02); Bruker AXS: Madison, Wisconsin, USA, **1998**.
12. G. M. Sheldrick, SADABS Program for Empirical Absorption Correction of Area Detector, University of Göttingen, Germany, **1996**.
13. G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122. **DOI:**10.1107/S0108767307043930
14. W. J. Geary, *Coord. Chem. Rev.* **1971**, *7*, 81–120. **DOI:**10.1016/S0010-8545(00)80009-0
15. A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356. **DOI:**10.1039/DT9840001349
16. (a) D. Sadhukhan, A. Ray, R. J. Butcher, C. J. G. Garcia, B. Dede, S. Mitra, *Inorg. Chim. Acta* **2011**, *376*, 245–254; **DOI:**10.1016/j.ica.2011.06.024
(b) S. Bandyopadhyay, J.-M. Lo, H.-H. Yao, F.-L. Liao, P. Chattopadhyay, *J. Coord. Chem.* **2006**, *59*, 2015–2021; **DOI:**10.1080/00958970600717975
(c) S. Hazra, S. Majumder, M. Fleck, N. Aliaga-Alcalde, S. Mohanta, *Polyhedron*, **2009**, *28*, 3707–3714. **DOI:**10.1016/j.poly.2009.08.007
17. (a) X.-X. Zhou, H.-C. Fang, Y.-Y. Ge, Z.-Y. Zhou, Z.-G. Gu, X. Gong, G. Zhao, Q.-G. Zhan, R.-H. Zeng, Y.-P. Cai, *Cryst. Growth Des.* **2010**, *10*, 4014–4022; **DOI:**10.1021/cg100612b
(b) J. Reglinski, S. Morris, D. E. Stevenson, *Polyhedron*, **2002**, *21*, 2175–2182; **DOI:**10.1016/S0277-5387(02)01172-5
(c) B. Dutta, P. Bag, U. Florke, K. Nag, *Inorg. Chem.* **2005**, *44*, 147–157. **DOI:**10.1021/ic049056a
18. K. R. Sangeetha Gowda, H. S. Bhojya Naik, B. Vinay Kumar, C. N. Sudhamani, H. V. Sudeep, T. R. Ravikumar Naik, G. Krishnamurthy, *Spectrochim. Acta A: Mol. Biomol. Spectrosc.* **2013**, *105*, 229–237. **DOI:**10.1016/j.saa.2012.12.011
19. M. F. Iskander, T. E. Khalil, R. Werner, W. Haase, I. Svoboda, H. Fuess, *Polyhedron* **2000**, *19*, 949–958. **DOI:**10.1016/S0277-5387(00)00340-5
20. M. Das, B. K. Shaw, B. N. Ghosh, K. Rissanen, S. K. Saha, S. Chattopadhyay, *J. Coord. Chem.* **2015**, *68*, 1361–1373. **DOI:**10.1080/00958972.2015.1014350
21. U. Kumar, J. Thomas, N. Thirupathi, *Inorg. Chem.* **2010**, *49*, 62–72. **DOI:**10.1021/ic901100z
22. A. Ray, D. Sadhukhan, G. M. Rosair, C. J. Gomez-Garcia, S. Mitra, *Polyhedron* **2009**, *28*, 3542–3550. **DOI:**10.1016/j.poly.2009.07.017
23. T. Tanaka, M. Kawase, S. Tani, *Life Sci.* **2003**, *73*, 2985–2990. **DOI:**10.1016/S0024-3205(03)00708-2

Povzetek

Sintetizirali smo nov štirijedrni bakrov(II) kompleks $[Cu_4L_2(N_3)_2(CH_3OH)_2](NO_3)_2{\cdot}4CH_3OH$ (**1**) in nov trijedrni cinkov(II) kompleks $[Zn_3L_2(CH_3COO)_2]$ (**2**) iz bis-Schiffove baze *N*,*N*'-bis(4-bromosaliciliden)-1,3-propandiamin (H_2L) in bakrovega(II) nitrata oziroma cinkovega(II) acetata v prisotnosti natrijevega azida. Kompleksa smo okarakterizirali z elementno analizo, IR in UV-Vis spektroskopijo. Molekularno strukturo obeh kompleksov smo potrdili z rentgensko monokristalno analizo. V kompleksu **1** so atomi Cu(II) mostovno povezani preko fenolatnih kisikovih atomov in terminalnih azidnih ligandov. V kompleksu **2** so atomi Zn(II) mostovno povezani preko fenolatnih kisikovih atomov in acetatnih ligandov. Cu(II) atomi v kompleksu **1** imajo kvadratno planarno in kvadratno piramidalno koordinacijo. Atomi Zn(II) v kompleksu **2** imajo kvadratno piramidalno in oktaedrično koordinaciji. Ligand Schiffove baze je na kovinske atome koordiniran preko dveh fenolatnih O atomov in dveh imino N atomov. Biološki test je pokazal, da kompleks bakra(II) učinkovito zavira ureazo.