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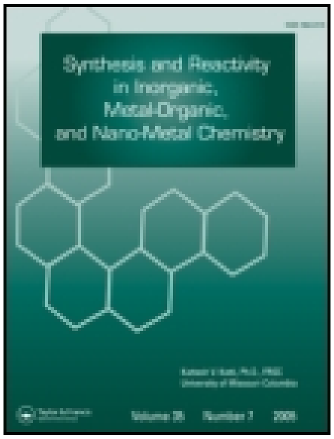

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
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Synthesis, Characterization, and Crystal Structures of Copper(II) and Zinc(II) Complexes Derived From the Tridentate Schiff Bases 2-[1-(pyridin-2-ylmethylimino) ethyl]phenol and (1-pyridin-2-ylethylidene)pyridin-2-ylmethylamine

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Synthesis, Characterization, and Crystal Structures of Copper(II) and Zinc(II) Complexes Derived From the Tridentate Schiff Bases 2-[1-(pyridin-2-ylmethylimino) ethyl]phenol and (1-pyridin-2-ylethylidene)pyridin-2-ylmethylamine

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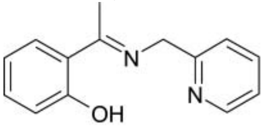
A centrosymmetric phenolate oxygen bridged dinuclear copper(II) complex $[Cu_2(L^1)_2(N_3)_2]$ (1) and a mononuclear zinc(II) complex $[Zn(L^2)(NCS)_2]$ (2), where HL^1 = 2-[1-(pyridin-2-ylmethylimino)ethyl]phenol and L^2 = (1-pyridin-2-ylethylidene)pyridin-2-ylmethylamine, were synthesized and structurally characterized by physicochemical methods and single-crystal X-ray diffraction. The Cu atom in (1) is five-coordinated in a slightly distorted square pyramidal geometry, and the Zn atom in (2) is five-coordinated in a severely distorted square pyramidal geometry.

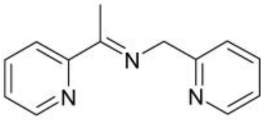
Keywords copper, crystal structure, Schiff base, synthesis, zinc

INTRODUCTION

Schiff bases and their complexes have been received considerable attention for their easy syntheses, versatile structures, and interesting properties including biological activities, magnetism, and catalysis.[1–6] Recently, we have reported the synthesis, structures, and urease inhibitory activities of some Schiff base complexes.[7–9] As an extension of the work on the preparation and structures of Schiff base complexes, in the present article, a centrosymmetric phenolate oxygen bridged dinuclear copper(II) complex $[Cu_2(L^1)_2(N_3)_2]$ (**1**) and a mononuclear zinc(II) complex $[Zn(L^2)(NCS)_2]$ (**2**), where HL^1 = 2-[1-(pyridin-2-ylmethylimino)ethyl]phenol and L^2 = (1-pyridin-2-ylethylidene)pyridin-2-ylmethylamine, were synthesized and structurally characterized.



HL^1



L^2

EXPERIMENTAL

Materials and Methods

2-Acetylphenol, 2-acetylpyridine, and 2-aminomethylpyridine of AR grade were purchased from Lancaster. Copper acetate, zinc acetate, sodium azide, ammonium thiocyanate, and solvents were purchased from Beijing Chemical Reagent Company and were used as received. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C elemental analyzer (Shanghai, China). Elemental analyses for Cu and Zn were determined by titration. The IR spectra were recorded on a Nicolet AVATAR 360 spectrometer (USA) as KBr pellets in the 4000–400 cm^{-1} region.

Synthesis of HL^1

To a methanol solution (20 mL) of 2-acetylphenol (1.0 mmol, 136 mg) was added a methanol solution (20 mL) of 2-aminomethylpyridine (1.0 mmol, 108 mg), with continuous stirring. The mixture was stirred for 30 min at room temperature to give a yellow solution. Then the methanol was evaporated to give yellow gummy product of HL^1. Anal. Calcd. $C_{14}H_{14}N_2O$: C, 74.3; H, 6.2; N, 12.4%. Found: C, 74.1; H, 6.3; N, 12.6%.

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Synthesis of L^2

To a methanol solution (20 mL) of 2-acetylpyridine (1.0 mmol, 121 mg) was added a methanol solution (20 mL) of 2-aminomethylpyridine (1.0 mmol, 108 mg) with continuous stirring. The mixture was stirred for 30 min at room temperature to give a yellow solution. Then the methanol was evaporated to give yellow oil of L^2. Anal. Calcd. $C_{13}H_{13}N_3$: C, 73.9; H, 6.2; N, 19.9%. Found: C, 73.6; H, 6.2; N, 20.1%.

Synthesis of $[Cu_2(L^1)_2(N_3)_2]$ (1)

The Schiff base HL^1 (0.1 mmol, 22.6 mg), sodium azide (0.2 mmol, 13.0 mg), and copper acetate (0.1 mmol, 20.0 mg) were mixed and stirred in methanol (15 mL) for 30 min at room temperature. The mixture was filtered and the blue block-shaped single crystals of (**1**), suitable for X-ray diffraction, were formed on slow evaporation of the filtrate in air. Yield: 38%. Anal. Calcd. $C_{28}H_{26}Cu_2N_{10}O_2$: C, 50.8; H, 4.0; N, 21.2; Cu, 19.2%. Found: C, 50.4; H, 4.1; N, 21.0; Cu, 19.7%.

Synthesis of $[Zn(L^2)(NCS)_2]$ (2)

The Schiff base L^2 (0.1 mmol, 21.1 mg), ammonium thiocyanate (0.2 mmol, 15.2 mg), and zinc acetate (0.1 mmol, 22.0 mg) were mixed and stirred in methanol (15 mL) for 30 min at room temperature. The mixture was filtered and the colorless block-shaped single crystals of (**2**), suitable for X-ray diffraction, were formed on slow evaporation of the filtrate in air. Yield: 45%. Anal. Calcd. $C_{15}H_{13}N_5S_2Zn$: C, 45.9; H, 3.3; N, 17.8; Zn, 16.6%. Found: C, 46.1; H, 3.3; N, 18.0; Zn, 16.9%.

X-Ray Crystallography

Diffraction intensities for the complexes were collected at 298(2) K using a Bruker SMART 1000 CCD area-detector (Germany) with Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). The collected data were reduced with the SAINT program (Bruker, Madison, WI, USA),[10] and multiscan absorption corrections were performed using the SADABS program (Sheidrick, G.M., Germany).[11] Both structures were solved by direct methods. The complexes were refined against F^2 by full-matrix

TABLE 1
Crystallographic data for the complexes

	(**1**)	(**2**)
Formula	$C_{28}H_{26}Cu_2N_{10}O_2$	$C_{15}H_{13}N_5S_2Zn$
FW	661.7	392.8
Crystal shape/color	block/blue	block/colorless
Crystal size (mm)	0.37 × 0.35 × 0.32	0.17 × 0.15 × 0.15
T (K)	298(2)	298(2)
λ (Mo$K\alpha$) (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
a (Å)	10.076(3)	14.247(3)
b (Å)	8.039(2)	8.658(2)
c (Å)	16.656(4)	15.357(3)
β (°)	96.210(3)	110.947(2)
V (Å^3)	1341.2(6)	1769.1(7)
Z	2	4
μ (Mo$K\alpha$) (cm^{-1})	1.634	1.629
$T_{\min}$	0.583	0.769
$T_{\max}$	0.623	0.792
D_c (g cm^{-3})	1.638	1.475
Measured reflections	10938	4990
Unique reflections and R_{int}	3044 and 0.0506	1923 and 0.0231
Observed reflections	2203	1547
data/restraints/parameters	3044/0/191	1923/0/110
Goodness of fit on F^2	1.021	1.043
R_1 [$I \geq 2\sigma(I)$]	0.0401	0.0397
wR_2 [$I \geq 2\sigma(I)$]	0.0804	0.0952
R_1 (all data)	0.0649	0.0517
wR_2 (all data)	0.0896	0.1018
Large diff. peak and hole (e Å^{-3})	0.338, –0.385	0.613, –0.470

least-squares methods using the SHELXTL package (Sheidrick, G.M., Madison, WI, USA).[12] All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The complex (**2**) is disordered about the twofold rotation axis. The crystallographic data for the complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2. Crystallographic data for the complexes have been deposited with the Cambridge Crystallographic Data Center (CCDC 838625 for (**1**) and 838626 for (**2**)).

RESULTS AND DISCUSSION

The tridentate Schiff bases HL^1 and L^2 were prepared in quantitative yields in methanol. The copper(II) and zinc(II) complexes were prepared according to the same synthetic procedures. Both complexes crystallize in well-shaped single crystals, which are stable in air at room temperature, and are soluble in methanol, ethanol, and acetonitrile. It is well known that the pseudohalide anions such as azide and thiocyanate readily bridge different metal atoms, forming polynuclear complexes,[13–16] however, in the present work, the azide and thiocyanate anions coordinate to the metal atoms through terminal coordination mode.

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

(**1**)			
Bond lengths			
Cu1-O1	1.9226(19)	Cu1-N1	1.974(2)
Cu1-N2	2.004(2)	Cu1-N3	1.963(3)
Cu1-O1$^{\mathrm{i}}$	2.377(2)		
Bond angles			
O1-Cu1-N3	95.67(10)	O1-Cu1-N1	90.40(9)
N3-Cu1-N1	167.52(11)	O1-Cu1-N2	171.56(9)
N3-Cu1-N2	92.56(10)	N1-Cu1-N2	81.89(10)
O1-Cu1-O1$^{\mathrm{i}}$	85.11(8)	N3-Cu1-O1$^{\mathrm{i}}$	99.62(9)
N1-Cu1-O1$^{\mathrm{i}}$	91.73(8)	N2-Cu1-O1$^{\mathrm{i}}$	91.65(8)
(**2**)			
Bond lengths			
Zn1-N1	2.155(2)	Zn1-N2	2.084(3)
Zn1-N3	1.975(3)	Zn1-N1$^{\mathrm{ii}}$	2.155(2)
Zn1-N3$^{\mathrm{ii}}$	1.975(3)		
Bond angles			
N3-Zn1-N3$^{\mathrm{ii}}$	105.27(16)	N3-Zn1-N2$^{\mathrm{ii}}$	127.36(8)
N3-Zn1-N2	127.36(8)	N3-Zn1-N1$^{\mathrm{ii}}$	96.64(10)
N2-Zn1-N1$^{\mathrm{ii}}$	76.08(7)	N3-Zn1-N1$^{\mathrm{ii}}$	96.64(10)
N3-Zn1-N1	100.16(10)	N2-Zn1-N1	76.08(7)
N1-Zn1-N1$^{\mathrm{ii}}$	152.15(14)		

Symmetry operations for equivalent atoms: i) –*x*, 1 – *y*, –*z*; ii) 1 – *x*, *y*, 1/2 – *z*.

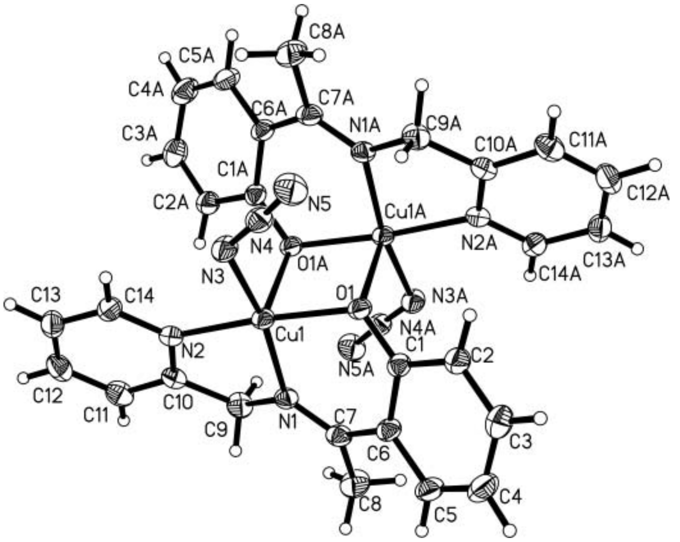

FIG. 1. Molecular structure of (**1**) at 30% probability ellipsoids.

Structure Description of Complex (1)

Figure 1 gives perspective view of complex (**1**). The complex is a centrosymmetric phenolate oxygen bridged dinuclear copper(II) compound, with the inversion center located at the midpoint of the two Cu atoms. The Cu···Cu distance is 3.182(2) Å. The Cu atom in the complex is five-coordinated in a distorted square-pyramidal coordination, with the three donor atoms of L^1 and one azide N atom defining the basal plane, and with one phenolate O atom occupying the apical position. The distortion of the coordination geometry can be calculated by the τ value, a reference to describe the degree of distortion for square-pyramid and trigonal-bipyramid [square pyramid, $\tau = 0$; trigonal bipyramid, $\tau = 1$; $\tau = (\beta - \alpha)/60°$, α and β are the two largest angles around the central atom].[17] The τ value for the complex is 0.068. Hence, the coordination of the Cu atom in the complex can be best described as a slightly distorted square-pyramid, rather than trigonal-bipyramid. The coordinate bond lengths and angles in the complex are comparable to those observed in other similar Schiff base copper(II) complexes.[18,19]

Structure Description of Complex (2)

Figure 2 gives perspective view of complex (**2**). The complex is a mononuclear zinc(II) compound. The Zn atom in the complex is five-coordinated in a distorted square pyramidal coordination, with the three N donor atoms of L^2, and with one thiocyanate N atoms defining the basal plane, and with another thiocyanate N atom occupying the apical position. The τ value for the complex is 0.413. Hence, the coordination of the Zn atom in the complex can be best described as a severely distorted square-pyramid, rather than trigonal-bipyramid. The coordinate bond lengths and angles in the complex are comparable to those observed in other similar Schiff base zinc(II) complexes.[20,21]

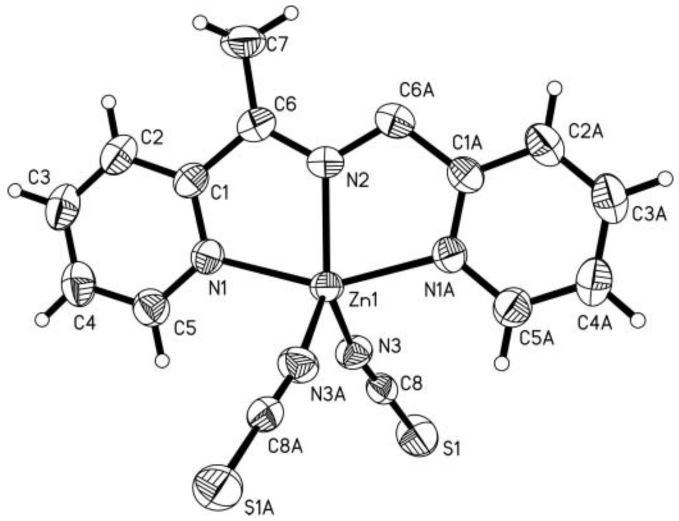

FIG. 2. Molecular structure of (**2**) at 30% probability ellipsoids.

Infrared Spectra

The strong absorption bands at 1637 $\mathrm{cm^{-1}}$ for HL^1 and 1649 $\mathrm{cm^{-1}}$ for L^2 are assigned to the azomethine groups, $\nu(C = N)$, which are shifted to lower or higher wave numbers in both complexes: 1625 $\mathrm{cm^{-1}}$ for (**1**) and 1662 $\mathrm{cm^{-1}}$ for (**2**). The shift of the absorption bands indicates the coordination of the azomethine N atoms to the metal atoms. The intense band indicative of the azide ligands in (**1**) is at 2049 $\mathrm{cm^{-1}}$, and that indicative of the thiocyanate ligands in (**2**) is at 2095 $\mathrm{cm^{-1}}$. The weak bands in the range 410–580 $\mathrm{cm^{-1}}$ are attributed to the M-O/N absorption.

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