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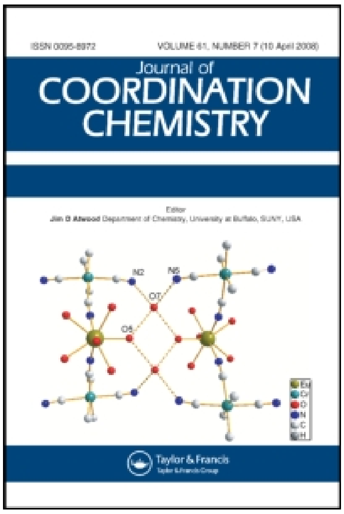

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Syntheses and structures of 2-bromo-4-chloro-6-(cyclopropyliminomethyl)phenol and its zinc(II) complex

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Syntheses and structures of 2-bromo-4-chloro-6-(cyclopropyliminomethyl)phenol and its zinc(II) complex

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A new Schiff-base ligand 2-bromo-4-chloro-6-(cyclopropyliminomethyl)phenol and its zinc(II) complex have been synthesized and characterized by elemental analyses, infrared spectroscopy, ^{1}H NMR, ^{13}C NMR, and single crystal X-ray determinations. The ligand and the complex crystallized in the space groups *Pnma* and $P2_1/c$, respectively. In the complex, the Zn atom is four-coordinate tetrahedral coordination with two imine N and two phenolate O atoms from two Schiff-base ligands. The bond lengths related to the donor atoms in the complex are different from those in the ligand. The coordination of the ligand to the zinc also was supported by IR spectra.

Keywords: Schiff base; Zinc(II) complex; Crystal structure; Coordination compound

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1. Introduction

Compounds containing Schiff bases have been of great interest for a long time [1–3], playing an important role in the development of coordination chemistry related to catalysis and enzymatic reactions [4, 5], magnetism and molecular architectures [6, 7]. Schiff-base complexes are of particular interest to inorganic chemists for their structural, spectral and chemical properties which often strongly depend on the detailed ligand structures. Zinc is a very important element in biological systems, as the active site of hydrolytic enzymes, such as carboxypeptidase and carbonic anhydrase where it is in a hard-donor coordination environment of nitrogen and oxygen [8].

In the present study, a new Schiff-base ligand 2-bromo-4-chloro-6-(cyclopropyliminomethyl)phenol (**1**) and its zinc(II) complex, *bis*[2-bromo-4-chloro-6-(cyclopropyliminomethyl)phenolato]zinc(II) (**2**), have been synthesized and characterized.

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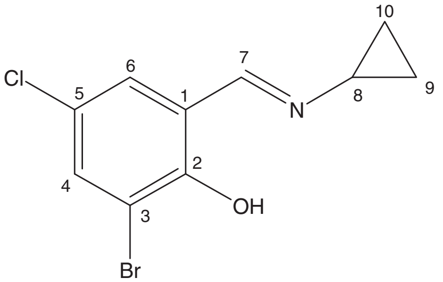
2. Experimental

2.1. *Materials and methods*

Solvents and reagents were purchased from Aldrich and used without further purification. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C elemental analyzer. The IR spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the 4000–400 cm^{-1} region. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer with tetramethylsilane as the internal reference.

2.2. *Synthesis of 2-bromo-4-chloro-6-(cyclopropyliminomethyl)phenol (1)*

To the MeOH solution (50 cm^3) of 3-bromo-5-chlorosalicylaldehyde (235.5 mg, 1.0 mmol) was added a MeOH solution (30 cm^3) of cyclopropylamine (57.0 mg, 1.0 mmol) with stirring. The mixture was stirred for 10 min at room temperature to give a clear yellow solution. After keeping the solution in air for a week, yellow block-shaped crystals of **1**, suitable for X-ray crystal structural determination, formed at the bottom of the vessel on slow evaporation of about 80% of the solvent. The crystals were isolated by filtration, washed three times with cold MeOH and dried in a vacuum desiccator using anhydrous $CaCl_2$. Yield, 203.0 mg (74.1%); m.p. 145.0–146.0°C. Anal. Calcd for $C_{10}H_9BrClNO$ (%): C, 43.8; H, 3.3; N, 5.1. Found: C, 43.5; H, 3.4; N, 5.0. ^{1}H NMR data ($CDCl_3$, ppm): $\delta = 8.22$ (s, 1H), 7.37 (s, 1H), 7.28 (s, 1H), 4.51 (s, 1H), 1.88 (m, 1H), 0.57 (m, 4H). ^{13}C NMR data ($CDCl_3$, ppm): 162.1 (C-7), 158.9 (C-2), 136.5 (C-4), 130.3 (C-6), 129.1 (C-5), 127.8 (C-1), 111.2 (C-3), 30.1 (C-8), 5.9 (C-9,10).



2.3. *Synthesis of bis[2-bromo-4-chloro-6-(cyclopropyliminomethyl) phenolato]zinc(II) (2)*

To the MeOH solution (20 cm^3) of **1** (137.3 mg, 0.5 mmol) was added a MeOH solution (20 cm^3) of $ZnCl_2$ (40.8 mg, 0.3 mmol) with stirring. The mixture was stirred for 30 min at room temperature to give a clear colorless solution. After keeping the solution in air for 3 days, colorless block-shaped crystals of **2**, 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 cold MeOH and dried in a vacuum desiccator containing anhydrous $CaCl_2$. Yield, 77.2 mg, 50.6% on the basis of **1**; d.p. 352.0–354.0°C. Anal. Calcd for $C_{20}H_{16}Br_2Cl_2N_2O_2Zn$ (%): C, 39.2; H, 2.6; N, 4.6. Found: C, 39.5; H, 2.7; N, 4.4.

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

Compound	**1**	**2**
Formula	$C_{10}H_9BrClNO$	$C_{20}H_{16}Br_2Cl_2N_2O_2Zn$
Mr	274.54	612.44
T (K)	298(2)	298(2)
Crystal shape/color	Block/yellow	Block/colorless
Crystal size (mm^3)	0.45 × 0.28 × 0.12	0.27 × 0.23 × 0.21
Crystal system	Orthorhombic	Monoclinic
Space group	*Pnma*	$P2_1/c$
a (Å)	10.024(1)	11.314(2)
b (Å)	6.822(2)	9.593(2)
c (Å)	16.331(3)	19.034(4)
β (°)	90.00	96.18(3)
V ($Å^3$)	1116.8(4)	2053.9(7)
Z	4	4
D_c ($g\,cm^{-3}$)	1.633	1.981
μ (Mo-Kα) (cm^{-1})	3.886	5.367
$F(000)$	544	1200
R_{int}	0.0495	0.0354
Measured reflections	1263	4707
Observed reflections $I \geq 2\sigma(I)$	858	3647
Min. and max. transmission	0.2737/0.6527	0.3251/0.3986
Parameters	85	262
Goodness-of-fit on F^2	1.047	1.031
R_1, wR_2 $[I \geq 2\sigma(I)]^a$	0.0375, 0.0865	0.0357, 0.0848
R_1, wR_2 (all data)^a	0.0658, 0.1054	0.0513, 0.0916
Large diff. peak and hole ($e\,Å^{-3}$)	0.573/−0.399	0.505/−0.810

$^a R_1 = F_o - F_c/F_o$, $wR_2 = [\sum w(F_o^2 - F_c^2)]/\sum w(F_o^2)^2]^{1/2}$, $w_{(I)} = [\sigma^2(F_o^2) + (0.0458(F_o^2 + 2F_c^2)/3)^2 + 0.5119(F_o^2 + 2F_c^2)/3)^{-1}]$, $w_{(2)} = [\sigma^2(F_o^2) + 0.0453(F_o^2 + 2F_c^2)/3)^2] + 0.7865(F_o^2 + 2F_c^2)/3)]^{-1}$.

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2.4. *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 the SAINT program [9], and empirical absorption corrections were performed using the SADABS program [10]. The structures were solved by direct methods and refined against F^2 by full-matrix least-squares using the SHELXTL program [11]. All of the non-hydrogen atoms were refined anisotropically. The H1 atom in **1** was located in a difference Fourier map and refined isotropically, with O–H distance restrained to 0.85(1) Å. All other H atoms were placed in geometrically ideal positions and constrained to ride on their parent atoms. The crystallographic data for the compounds are summarized in table 1. Selected bond lengths and angles are given in table 2.

3. Results and discussion

Compound **1** was yellow crystals, stable in air at room temperature, and soluble in common polar organic solvents such as DMSO, DMF, MeOH, EtOH, MeCN and Me_2CO, but insoluble in water and Et_2O. The colorless zinc complex derived from the ligand was also stable in air at room temperature, soluble in DMF, DMSO

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

1			
N1–C7	1.263(5)	N1–C8	1.422(5)
O1–C2	1.333(5)		
C2–C1–C7	119.9(4)	O1–C2–C1	122.1(3)
N1–C7–C1	122.0(4)	C7–N1–C8	121.0(4)
N1–C8–C9	116.5(3)		
2			
Zn1–O1	1.900(2)	Zn1–O2	1.819(2)
Zn1–N1	1.981(3)	Zn1–N2	2.012(2)
N1–C7	1.254(4)	N1–C8	1.439(4)
O1–C2	1.263(3)	N2–C17	1.249(4)
N2–C18	1.402(4)	O2–C12	1.279(4)
O2–Zn1–O1	111.6(2)	O2–Zn1–N1	115.0(2)
O1–Zn1–N1	98.2(2)	O2–Zn1–N2	96.6(2)
O1–Zn1–N2	118.4(2)	N1–Zn1–N2	118.0(2)

Table 3. Main IR data (cm^{-1}) for **1** and **2**.

Compound	ν(O–H)	ν(C=N)	ν(Ar–O)	ν(M–O)
1	3423w,b	1637s	1200s	
2		1618s	1182s	472m

and MeCN, insoluble in water and Et_2O, but slightly soluble in MeOH, EtOH and Me_2CO.

Bromo- and chloro-groups participate in the formation of intermolecular hydrogen bonds, so we chose these substituents for the synthesis of the ligand and the complex.

3.1. *IR spectra of 1 and 2*

The IR spectra of the Schiff-base ligand **1** and its complex **2** provide information about the metal-ligand bonding. Assignments are based on typical group frequencies. The weak and broad absorptions (table 3) at about 3423 cm^{-1} substantiate the presence of phenol in **1**. A strong absorption band at 1637 cm^{-1} in the spectra of **1** is assigned to the azomethine group, ν(C=N) [12]. This band shifts to lower wave number (1618 cm^{-1}) in the complex, attributed to coordination of the nitrogen atom of the azomethine to the zinc. The phenolic ν(Ar–O) in **1** exhibits a strong band at 1200 cm^{-1} [13]. However, in the complex, the band is at 1182 cm^{-1}, which may be assigned to the skeletal vibration related to the phenolic oxygen atom of **1**; bands are known to shift to lower frequency when the phenolic oxygen coordinates to metal ions [14–16]. Another weak band at 472 cm^{-1} for the complex can be assigned to ν(Zn–O) [17], and provides further evidence for coordination through the deprotonated phenolic oxygen atom.

3.2. *Structures of 1 and 2*

Figures 1 and 2 give perspective views of **1** and **2** together with the atomic labeling systems. The molecule of **1** possesses mirror symmetry, with atoms C1–C8, H1, H4,

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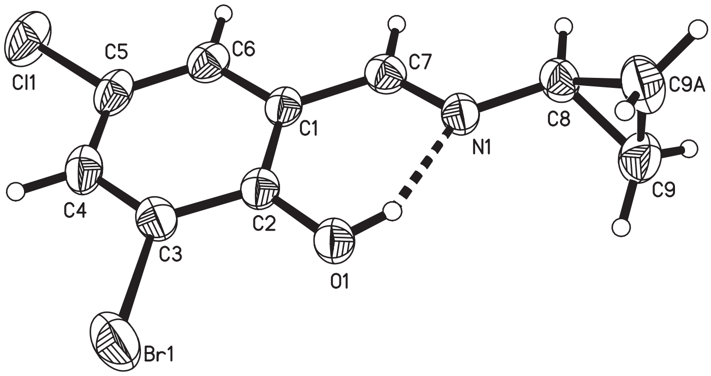

Figure 1. The structure of **1**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Intramolecular O–H···N hydrogen bond is shown as a dashed line.

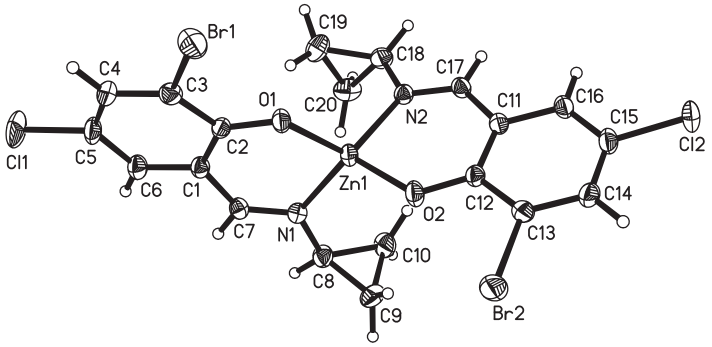

Figure 2. The structure of **2**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

H6–H8, O1, Br1, Cl1 and N1 lying on the crystallographic mirror plane. There is an intramolecular hydrogen bond of O1–H1···N1, and the dihedral angle between the phenyl and the cyclopropyl ring is 90°. Complex **2** is a mononuclear zinc(II) compound derived from **1**. The Zn atom is four-coordinate with two N and two O atoms from two deprotonated ligands of **1**. The angles subtended at Zn1 indicate a tetrahedral coordination. The two ligands in **2** are almost perpendicular to each other, which can decrease the steric effects between the molecules. In each ligand, the phenyl and the cyclopropyl ring are also nearly perpendicular, with average dihedral angle of 91.9(2)°.

The Schiff-base ligand **1** coordinates to the zinc through the deprotonated form. The bond lengths of C7=N1 and C17=N2 in **2** are shorter than that of C7=N1 in **1**, and the bond lengths of C2–O1 and C12–O2 in **2** are shorter than C2–O1 in **1** because the intramolecular hydrogen bond O1–H1 ... N1 in **1** and the H1 atom are absent when the phenolate O atom coordinates to zinc in **2**.

In the crystal structure of **1**, the molecules are linked through weak $\pi\cdots\pi$ interactions, stacking along the *b* axis (figure 3). In the crystal structure of **2**, the molecules are linked through intermolecular hydrogen bonds of C–H···Cl and C–H ··· O, forming layers parallel to the *ab* plane (figure 4).

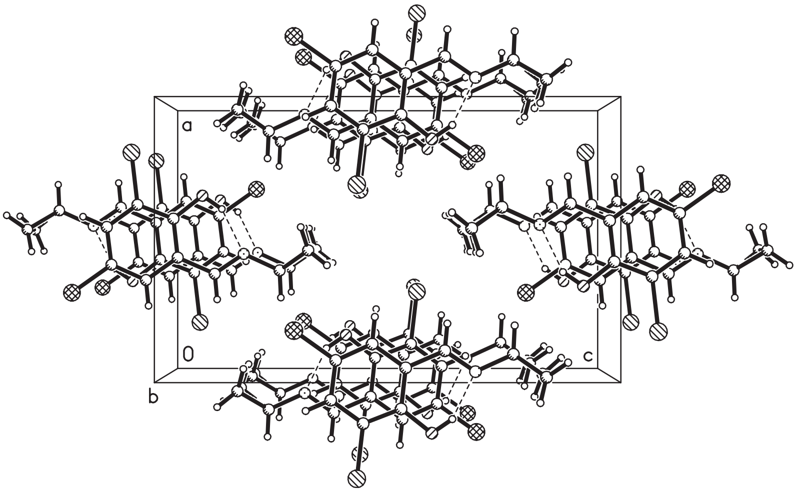

Figure 3. The crystal packing of **1** viewed along the *b* axis. Intramolecular O–H···N hydrogen bonds are shown as dashed lines.

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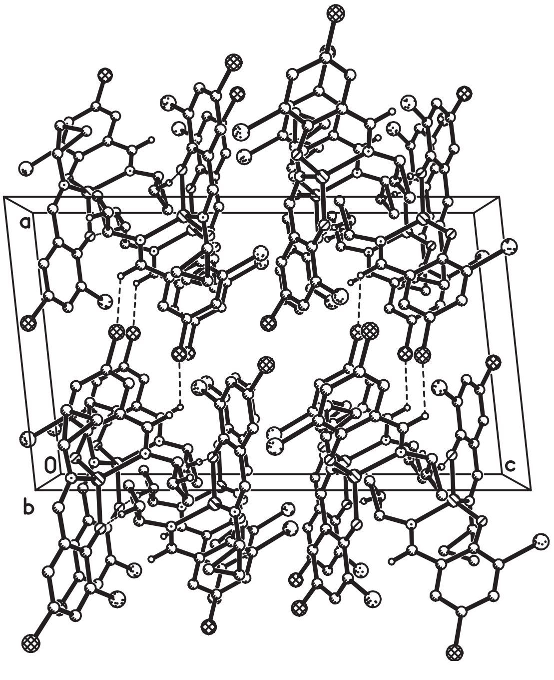

Figure 4. The crystal packing of **2** viewed along the *b* axis. Intermolecular C–H···Cl and C–H···O hydrogen bonds are shown as dashed lines.

Supplementary material

Crystallographic data for **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 638096 and 645739. Copies of these data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: +44 1223 336033.

References

[1] R.D. Archer, B. Wang. *Inorg. Chem.*, **29**, 39 (1990).
[2] S.C. Bhatia, J.M. Bindlish, A.R. Saini, P.C. Jain. *J. Chem. Soc., Dalton Trans.*, 1773 (1981).
[3] S. Chang, L. Jones, C.M. Wang, L.M. Henling, R.H. Grubbs. *Organometallics*, **17**, 3460 (1998).
[4] P.S. Dixit, K. Srinivasan. *Inorg. Chem.*, **27**, 4507 (1988).
[5] D.P. Kessissoglou, W.M. Butler, V.L. Pecoraro. *Inorg. Chem.*, **26**, 495 (1987).
[6] H. Miyasaka, N. Matsumoto, H. Ōkawa, N. Re, E. Gallo, C. Floriani. *J. Am. Chem. Soc.*, **118**, 981 (1996).
[7] R. Ramnauth, S. Al-Juaid, M. Motevalli, B.C. Parkin, A.C. Sullivan. *Inorg. Chem.*, **43**, 4072 (2004).
[8] I. Bertini, H.B. Gray, S.J. Lippard, J.S. Valentine. *Bioinorganic Chemistry*, University Science Books, Mills Valley, CA, USA (1994).
[9] Bruker, *SMART (Version 5.628) and SAINT (Version 6.02)*, Bruker AXS Inc., Madison, Wisconsin, USA (1998).
[10] G.M. Sheldrick. *SADABS Program for Empirical Absorption Correction of Area Detector*, University of Göttingen, Germany (1996).
[11] G.M. Sheldrick. *SHELXTL V5.1 Software Reference Manual*, Bruker AXS, Inc., Madison, Wisconsin, USA (1997).
[12] J.E. Kovacic. *Spectrochim. Acta*, **A23**, 183 (1963).
[13] G.C. Percy, D.A. Thornton. *J. Inorg. Nucl. Chem.*, **34**, 3357 (1972).
[14] C. Fukuhara, E. Asato, T. Shimoji, K. Katsura, M. Mori, K. Matsumoto, S. Ooi. *J. Chem. Soc., Dalton Trans.*, 1305 (1987).
[15] G.E. Batley, D.P. Graddon. *Aust. J. Chem.*, **20**, 877 (1967).
[16] T. Tokki, Y. Muto, K. Imai, H.B. Janassen. *J. Inorg. Nucl. Chem.*, **35**, 1539 (1973).
[17] M.M. Bekheit, K.M. Ibrahim. *Synth. React. Inorg. Met.-Org. Chem.*, **16**, 1135 (1986).

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