Crystal Structures of Heteronuclear Nickel(II)/Zinc(II) Doubly Oxygen Bridged Schiff-Base Complexes

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{[μ-Bis(5-chlorosalicylidene)-1,3-propanediaminato]nickel(II)}dichlorozinc(II) · 2 dmf (dmf = dimethylformamide) **1** and {[μ-bis(5-bromosalicylidene)-1,3- propanediaminato]nickel(II)}-dichlorozinc(II) · 2 dmf (dmf) **2** were synthesized and their crystal structures determined. In both structures, the Ni(II) ions have a distorted octahedral geometry involving the N_2O_2 atoms of the Schiff-base ligands and two oxygen atoms of dimethylformamide (dmf) molecules. The coordination around the Zn(II) ions is distorted tetrahedral. The Ni···Zn distances are 3.132(1) Å for **1** and 3.122(1) Å for **2**.

Key words: Hetero-Dinuclear Complex, Schiff-base, Octahedral Coordination, Tetrahedral Coordination

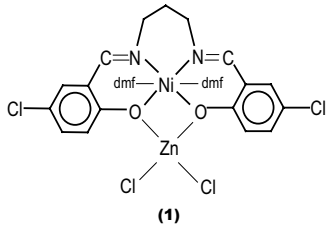
Introduction

Because of their preparative accessibility and structural variability a great number of Schiff-base complexes have been the subject to extensive studies [1]. Both homo- and heteronuclear complexes are chemical models which provide an opportunity to study experimentally and theoretically fundamental electronic processes such as electron exchange at biological metal sites. Therefore, the homo- and heteronuclear compounds are of interest to both biologists and bioinorganic chemists investigating the structure and function of the polynuclear metal centers in proteins [2]. Very recently, we studied the crystal structures of four- and six-coordinated Ni(II) and Cu(II) complexes of the tetradendate N,N′-bis(5-chloro-2-hydroxybenzylidene)-1,3-propanediamine and N,N′-bis(5-bromo-2-hydroxybenzylidene)-1,3-propanediamine Schiff-base ligands [3–6]. In this study, we report the crystal structures of the hetero-dinuclear Ni(II)/Zn(II) complexes of tetradendate N,N′- bis(5-chloro/bromo-2-hydroxybenzylidene)-1,3-propanediamine Schiff-base ligands.

Experimental Section

Preparation

Compound **1** was synthesized in two steps. At first, N,N′-bis(5-chloro-2-hydroxybenzylidene)-1,3-propanediamine (0.001 mol , 0.352 g) was dissolved in hot ethanol (50 ml) and ammonia solution (25%, 10 ml) was added with stirring. A solution of nickel(II) acetate tetrahydrate (0.001 mol,



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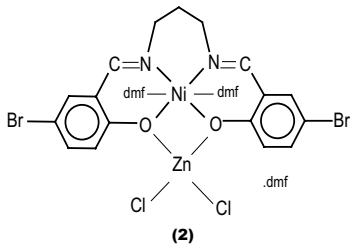

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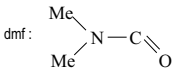

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0.248 g) in 40 ml of hot water was then added and the resulting solution set aside. After 5 h, a light green crystal powder of [N,N′-bis(5-chlorosalicylidene)-1,3-diaminopropane]nickel(II) was filtered off and dried in an oven at 343 K. In a second step, the crystal powder of the Ni(II) monomer (0.5 mmol, 0.230 g) was dissolved in 50 ml of dimethylformamide (dmf) and heated to its boiling point. To this solution, $ZnCl_2$ (0.5 mmol, 0.0683 g) in 20 ml of methanol was added and heated under reflux for 1 h. The resulting mixture was set aside for 3 d and the light green crystals which formed were filtered off and dried in air. Compound **2** was synthesized by using same procedure with the N,N′-bis(5-bromo-2-hydroxybenzylidene)-1,3-propanediamine ligand. Yield: 67%, m.p. 295 °C. – $C_{23}H_{28}Cl_4N_4O_4NiZn$ (690.4): calcd. for **1** C 40.01, H 4.06, N 8.12; found C 40.64 H 4.05 N 8.22. Yield: 69%, m.p. 292 °C. – $C_{26}H_{35}Br_2Cl_2N_5O_5NiZn$ (852.4): calcd. for **2** C 36.63, H 4.11, N 8.22; found C 37.26, H 4.10, N 8.32.

X-ray structure determination

X-ray data collection was carried out on an Enraf-Nonius CAD-4 diffractometer [7] using a single crystal with dimensions 0.40 × 0.30 × 0.25 mm for **1** and 0.35 × 0.30 × 0.25 mm for **2** with a graphite monochromatized Mo-K_α radiation (λ = 0.71069 Å). Experimental conditions of **1** and **2** are summarized in Table 1. Cell constants were determined by the least-squares refinement on the setting angles of 25 carefully centered reflections. Data reduction and corrections for absorption and decomposition were achieved using the Nonius Diffractometer Control Software [7]. The structure was solved by SHELXS-97 [8] and refined with SHELXL-97 [9]. The positions of the H atoms bonded to C atoms were calculated (C–H distance 0.96 Å) and refined using a riding model, and H atom displacement parameters were restricted to be 1.2 U_{eq} of the parent atom. The relatively high residual in the difference Fourier map can be attributed to the disorder of C9 in the propanediamine chelate ring. The C9 atoms were split into C9a and C9b with site occupation factors 0.75(3) and 0.25(3) for **1** and 0.37(3) and 0.63(3) for **2**. Similar disorder was observed in the compounds including 1,3-diaminopropane [3–6]. Selected bond distances and bond angles are listed in Table 2. ORTEP views of the molecular structures of **1** and **2** are given in Figs. 1 and 2 [10]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-202943 and 202944 [11].

Results and Discussion

Compounds **1** and **2** are hetero-nuclear nickel(II)/zinc(II) doubly oxygen-bridged Schiff-base complexes. The Ni···Zn distance is 3.132(1) Å for **1** and 3.122(1) Å for **2**. In both structures, the

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

	1	**2**
Formula	$C_{23}H_{28}Cl_4N_4O_4NiZn$	$C_{26}H_{35}Br_2Cl_2N_5O_5NiZn$
f_w (g·mol^{-1})	690.37	852.39
Space group	$P2_1/c$, (No. 14)	$P2_1/c$, (No. 14)
	a = 9.354(3) Å	a = 9.341(7) Å
	b = 17.934(2) Å	b = 20.605(1) Å
	c = 19.031(2) Å	c = 18.273(3) Å
	β = 92.06(1)°	β = 91.44(3)°
Vol [Å^3]	3191.6(5)	3515.9(3)
Z	4	4
D_{calc} (g·cm^{-3})	1.437	1.610
μ [cm^{-1}]	1.709	3.682
F(000)	1408	1712
Index ranges	$-12 \le h \le 12$	$-12 \le h \le 12$
	$0 \le k \le 23$	$0 \le k \le 26$
	$0 \le l \le 24$	$0 \le l \le 23$
Reflections collected	7749	8546
Independent reflections	7318 [R(int) = 0.023]	8066[R(int) = 0.021]
Data/restraints/parameters	7318/0/344	8066/0/390
Goodness-of-fit on F^2	0.985	1.067
R Indices for all data	R = 0.060, $wR2$ = 0.123	R = 0.051, $wR2$ = 0.114
Final R indices [$I > 2\sigma(I)$]	R = 0.055, $wR2$ = 0.115	R = 0.045, $wR2$ = 0.101
Largest diff. peak and hole	0.576 and −0.483 e·Å^{-3}	0.629 and −0.595 e·Å^{-3}

Table 2. Selected bond distances [Å] and bond angles [°] for **1** and **2**.

Compound **1**		Compound **2**	
Ni1 – O1	2.029(1)	Ni1 – O1	2.044(1)
Ni1 – O2	2.032(1)	Ni1 – O2	2.024(1)
Ni1 – O3	2.104(1)	Ni1 – O3	2.124(2)
Ni1 – O4	2.117(1)	Ni1 – O4	2.115(2)
Ni1 – N1	1.994(1)	Ni1 – N1	2.017(2)
Ni1 – N2	2.007(1)	Ni1 – N2	2.022(2)
Zn1 – O1	2.005(1)	Zn1 – O1	1.988(1)
Zn1 – O2	2.015(2)	Zn1 – O2	2.007(1)
Zn1 – Cl3	2.205(2)	Zn1 – Cl1	2.216(1)
Zn1 – Cl4	2.223(1)	Zn1 – Cl2	2.193(1)
Cl3 – Zn1 – Cl4	116.97(7)	Cl1 – Zn1 – Cl2	115.21(5)
Cl3 – Zn1 – O2	116.41(8)	Cl2 – Zn1 – O2	115.12(6)
Cl4 – Zn1 – O1	115.80(4)	Cl1 – Zn1 – O1	114.54(5)
Cl4 – Zn1 – O2	110.14(4)	Cl1 – Zn1 – O2	112.95(4)
O1 – Zn1 – O2	78.80(7)	O1 – Zn1 – O2	79.41(4)
O1 – Ni1 – O2	77.86(7)	O1 – Ni1 – O2	77.64(5)
O3 – Ni1 – O4	171.22(4)	O3 – Ni1 – O4	173.28(5)
O2 – Ni1 – N1	169.07(4)	O2 – Ni1 – N1	168.66(6)
O1 – Ni1 – N2	168.43(4)	O1 – Ni1 – N2	168.33(5)
O2 – Ni1 – N2	90.58(8)	O2 – Ni1 – N2	90.90(5)
N1 – Ni1 – O1	91.23(6)	N1 – Ni1 – O1	91.02(5)
N1 – Ni1 – N2	100.34(8)	N1 – Ni1 – N2	100.42(6)
O2 – Ni1 – O4	94.71(4)	O2 – Ni1 – O4	94.71(4)
O2 – Ni1 – O3	92.33(4)	O2 – Ni1 – O3	91.56(6)
O1 – Ni1 – O3	92.91(5)	O1 – Ni1 – O3	91.91(6)
O1 – Ni1 – O4	92.69(6)	O1 – Ni1 – O4	92.70(8)
N1 – Ni1 – O3	89.07(6)	N1 – Ni1 – O3	87.52(5)
N2 – Ni1 – O3	90.59(7)	N2 – Ni1 – O3	87.71(5)
N1 – Ni1 – O4	85.97(6)	N1 – Ni1 – O4	86.55(5)
N2 – Ni1 – O4	94.19(5)	N2 – Ni1 – O4	86.98(6)

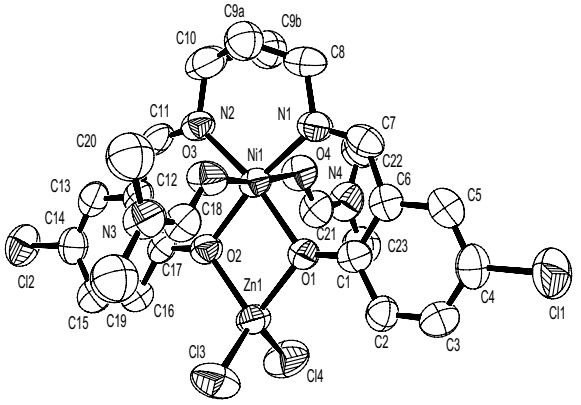

Fig. 1. The molecular structure and atomic labelling scheme of **1**. Displacement ellipsoids are plotted at the 50% probability level. Hydrogen atoms are omitted for clarity.

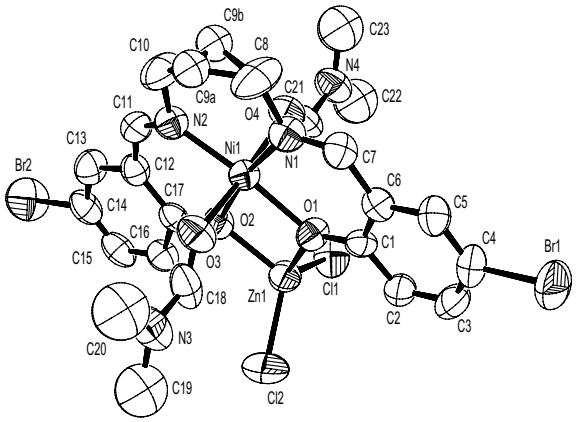

Fig. 2. The molecular structure and atomic labelling scheme of **2**. Displacement ellipsoids are plotted at the 50% probability level. Hydrogen atoms and also the dmf solvate are omitted for clarity.

Ni(II) ion is coordinated by two imine N atoms and two phenol O atoms. The coordination sphere is completed by the oxygen atoms of two dmf molecules. The atoms with the greatest deviation from the coordination plane Ni1, N1, O1, N2 and O2 are O2 at 0.008(1) Å for **1** and O1 at 0.021(1) for **2**. The deviations of Ni1 from the N_2O_2 least-squares plane are only 0.003(1) Å for **1** and 0.019(1) Å for **2**. The angles O3 – Ni1 – O4 (171.22(4)° for **1** and 173.28(5)° for **2**) indicate that the Ni(II) ions are coordinated by two oxygen atoms of dmf molecules at slightly distorted axial positions. The Ni(II) ions are in a distorted octahedral geometry. The N1 – Ni1 – O2 and N2 – Ni1 – O1 angles are 169.07(4)° and 168.43(3)° for **1** and 168.66(6)° and 168.33(5)° for **2**. In the NiN_2O_2 plane, average Ni – N distances are 2.001(1) Å for **1** and 2.020(1) Å for **2**, the average Ni – O distances 2.031(1) Å for **1** and 2.034(1) Å for **2**, and the axial bond distances Ni1 – O3 and Ni1 – O4 are 2.104(1) and 2.117(1) Å for **1** and 2.124(2) and 2.115(2) Å for **2**.

The Zn(II) ions have a distorted tetrahedral coordination, which is common for zinc(II) and copper(II) complexes [12]. The average Zn – O and Zn – Cl bond lengths are 2.010(1) and 2.214(1) Å for **1** and 1.998(1) and 2.205(1) Å for **2**, respectively. The bridging planes containing Ni1, O1, Zn1, O2 are planar for **1** and **2**.

In both structures, the unique half of the Schiff-base ligands of the compounds **1** and **2** are reason-

ably planar. However, the whole ligands are not exactly planar since the two halves of the Schiff-base ligands are twisted with respect to one another. The least-squares planes through each half of the molecules are inclined at an angle of 13.9(1)° in **1** and 10.8(1)° in **2**. The atoms Ni1, N1 C8, C9 (disordered), C10 and N2 form a six-membered chelate ring of chair conformation.

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