The Crystal Structures of [N,N'-Bis(3-methoxysalicylidene)-1,3-diaminopropane]nickel(II) and -copper(II)

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Z. Naturforsch. **59b,** 228 – 232 (2004); received October 2, 2003

[N,N′′-Bis(3-methoxysalicylidene)-1,3-diaminopropane]nickel(II) dihydrate [Ni($C_{19}H_{20}N_2O_4$)·2(H_2O)] **1** and [N,N′-bis(3-methoxysalicylidene)-1,4-diaminobutane]copper(II) [Cu($C_{20}H_{22}N_2O_4$)] **2** have been synthesized and their crystal structures determined. Crystals of compound **1** are orthorhombic, space group *Pnma*, $a = 7.509(3)$, $b = 22.070(7)$, $c = 11.532(4)$ Å, $V = 1611.1(12)$ Å^3, $Z = 4$ and $D_c = 1.498$ g·cm^{-3}. The molecule **1** has mirror symmetry, but the ligand is not planar. The two parts of the Schiff base moieties are folded so as to form an angle of 21.6(1)°. The Ni atom is in a distorted octahedral geometry and coordinated by the donor atoms of the ligand in the horizontal plane and of two water molecules. Crystals of compound **2** are monoclinic, space group $P2_1/c$, $a = 9.488(1)$, $b = 21.918(3)$, $c = 8.413(1)$ Å, $\beta = 91.45(1)°$, $V = 1749.0(4)$ Å^3, $Z = 4$ and $D_c = 1.587$ g·cm^{-3}. The Cu atom is coordinated by an N_2O_2 donor set from the imine-phenol ligand in a distorted planar geometry, with the two phenolate O atoms deprotonated. The Cu–O bond lengths are 1.854(3) and 1.868(3) Å. The Cu–N bond lengths are 1.931(3) and 1.950(3) Å, the dihedral angle between the two 3-methoxysalicylidene groups is 43.4(1)°.

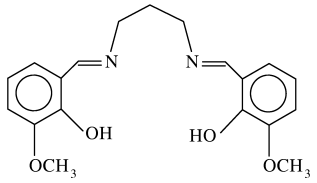
Key words: Schiff Base Complexes, Nickel(II) Complex, Copper(II) Complex, Square-Planar Coordination, Octahedral Coordination

Introduction

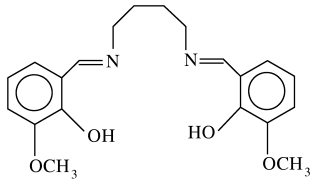
The complexes of transition metal ions with Schiff bases ligands show a diversity of structures and properties involving a number of stereochemistries and a wide range of bonding interactions [1, 2], and there is current interest in their structural, spectral, magnetochemical and electrochemical properties which are strongly dependent on the ligand structure [3, 4].

The development of a ^{62}Zn/^{62}Cu radionuclide generator increases the potential utility of Cu-labelled radio-pharmaceuticals as imaging agents in positron emission tomography (PET). ^{62}Cu – PTSM [PTSM:pyruvaldehyde bis(4-methylthiosemicarbazone)], a neutral *abd* lipophilic Cu(II) complex, has been investigated as a potential Cu tracer for imaging the heart and brain [5]. Additionally, neutral and lipophilic complexes of ^{67}Cu with a series of tetradentate Schiff base N_2O_2 ligands have also been evaluated as cerebral blood-flow imaging agents [6].

Tetradentate Schiff bases derived from 2 equivalents of an aldehyde and 1 equivalent of a variety of alkyl or aryl diamines have been known for decades. Recently, we studied the structures of four – and six – coordinate complexes with tetradentate Schiff bases: [N,N′-bis-(5-chlorosalicylidene)-1,3-diaminopropane]nickel(II) and -copper(II), and [N,N′-bis(5-bromosalicylidene)-1,3-diaminopropane]nickel(II) [7, 8]. In this paper,



(L1)



(L2)

Table 1. Crystallographic data and structure refinement.

	1	**2**
Sum formula	$Ni(C_{19}H_{20}N_2O_4)\cdot 2H_2O$	$Cu(C_{20}H_{22}N_2O_4)$
Color / shape	green / long prism	dark blue / prism
f_w (g·mol^{-1})	435.10	417.94
Crystal system	orthorhombic	monoclinic
Space group	*Pnma*	$P2_1/c$
a (Å)	7.509(3)	9.4880(10)
b (Å)	22.070(7)	21.918(3)
c (Å)	11.532(4)	8.4130(10)
β (°)	–	91.450(10)
V (Å^3)	1911.1(12)	1749.0(4)
Z	4	4
D_{calc} (g·cm^{-3})	1.505	1.587
μ (cm^{-1})	10.54	12.79
F(000)	906	868
θ Range for data collection	$2.50^\circ < \theta < 28.21^\circ$	$2.59^\circ < \theta < 30.95^\circ$
Index ranges	$0 \le h \le 9$	$-12 \le h \le 9$
	$0 \le k \le 27$	$-30 \le k \le 29$
	$0 \le l \le 14$	$-11 \le l \le 10$
Refls collected	2006	11770
Independent refls	2003	4613
Data / restraints / parameters	2003 / 0 / 133	2577 / 0 / 244
Final R indices $[I > 2\sigma(I)]$	$R = 0.0525$	$R = 0.0640$
	$wR = 0.1328$	$wR = 0.1425$
Largest diff. peak and hole	0.540 and −0.663 e·Å^{-3}	0.522 and −0.931 e·Å^{-3}

we report the crystal structures of a six-coordinate Ni(II) complex of N,N′-bis(3-methoxysalicylidene)-1,3-diaminopropane **(L1)** as the dihydrate and an anhydrous four-coordinate Cu(II) complex of N,N′-bis(3-methoxysalicylidene)-1,4-diaminobutane **(L2)**.

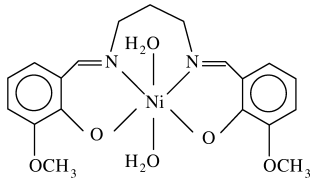
Experimental Section

Preparation

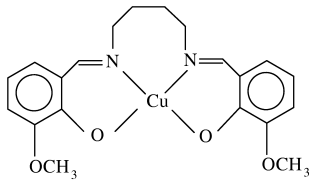
N,N′ - Bis(3-methoxysalicylidene) - 1,3 - diaminopropane **(L1)** was prepared by condensation of 20 mmol of 3-methoxysalicylaldehyde and 10 mmol of 1,3-diaminopropane in 70 ml of ethanol. The reactions mixture was stirred for 2 h. The yellow precipitate was collected by filtration and washed with cold ethanol. Then, 1 mmol of nickel(II) acetate tetrahydrate in 50 ml of pure water and 1 mmol of **(L1)** in 80 ml of methanol were mixed and heated under reflux for 30 min. Green single crystals started appearing after 2 d and were collected by filtration. Compound **2** was prepared from solutions of 0.5 mmol of copper(II) acetate monohydrate in 30 ml of methanol and 0.5 mmol of N,N′-bis(3-methoxysalicylidene)-1,4-diaminobutane **(L2)** in 50 ml of acetonitrile. The solutions were mixed and the reaction mixture heated under reflux for 30 min. Dark blue crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent at room temperature. $Ni(C_{19}H_{20}N_2O_4)\cdot 2H_2O$ (**1**): calcd. C 52.45, H 5.56, N 6.44; found C 52.90, H 5.77, N 6.65. $Cu(C_{20}H_{22}N_2O_4)$ (**2**): calcd. C 57.48, H 5.31, N 6.70; found C 57.70, H 5.51, N 6.93.

Table 2. Selected bond distances (Å) and bond angles (°) with e.s.d. in parentheses for **1** and **2**.

N1–Ni1	2.064(2)	N1–Cu1	1.931(3)
O1–Ni1	2.020(2)	N2–Cu1	1.950(3)
O2–Ni1	2.141(2)	O1–Cu1	1.854(3)
O3–Ni1	2.112(2)	O2–Cu1	1.868(3)
C7–N1–Ni1	124.5(2)	O1–Cu1–O2	89.50(12)
C8–N1–Ni1	119.2(2)	O1–Cu1–N1	95.40(13)
C1–O1–Ni1	127.5(1)	O2–Cu1–N1	140.0(1)
O1–Ni1–N1	88.8(1)	O1–Cu1–N2	148.5(1)
O1–Ni1–O3	91.3(1)	O2–Cu1–N2	96.2(1)
N1–Ni1–O3	89.0(1)	N1–Cu1–N2	99.8(1)
O1–Ni1–O2	91.7(1)		
N1–Ni1–O2	88.3(1)		
O3–Ni1–O2	175.9(1)		



1



2

Crystal structure determination

Crystals of **1** and **2** were mounted on an Enraf-Nonius CAD-4 diffractometer with graphite monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å) [9]. Experimental conditions are summarized in Table 1. Data reduction and corrections for absorption and decomposition were achieved using the Nonius Diffractometer Control Software [9]. The structures were solved by SHELXS-97 and refined with SHELXL-97 [10, 11]. The positions of the H atoms bonded to C atoms were calculated (C-H distance 0.96 Å) and refined using a riding model. The H atom displacement parameters were restricted to be 1.2 U_{eq} of the parent atom. Fractional atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms are deposited. Selected bond distances and bond angles for **1** and **2** are listed in Table 2. ORTEP views of the molecular structures of **1** and **2** are given

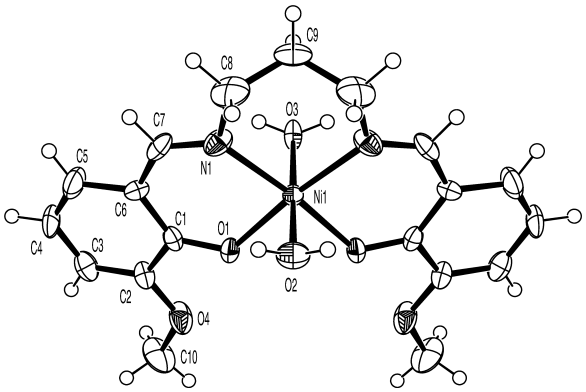


Fig. 1. The molecular structure of compound **1**. Displacement ellipsoids are plotted at the 50% probability level (Symmetry transformations used to generate equivalent atoms: x, $1/2-y$, z).

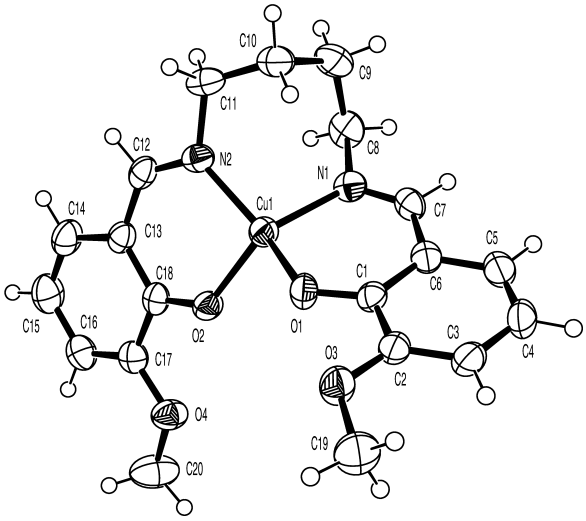


Fig. 2. The molecular structure of compound **2**. Displacement ellipsoids are plotted at the 50% probability level.

in Figures 1 and 2 and a molecule packing diagram for **1** in Fig. 3. [12, 13]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 220531 for **1** and CCDC 220532 for **2** [14].

Results and Discussion

In compound **1**, two parts of the molecule are related by the mirror plane passing through the Ni1, C9, O2 and O3 atoms (Fig. 1). The Ni(II) ion is coordinated by two imine N atoms and two phenolate O atoms of the ligand, and the coordination sphere is completed by the two water molecules. The four ligand donor atoms are planar

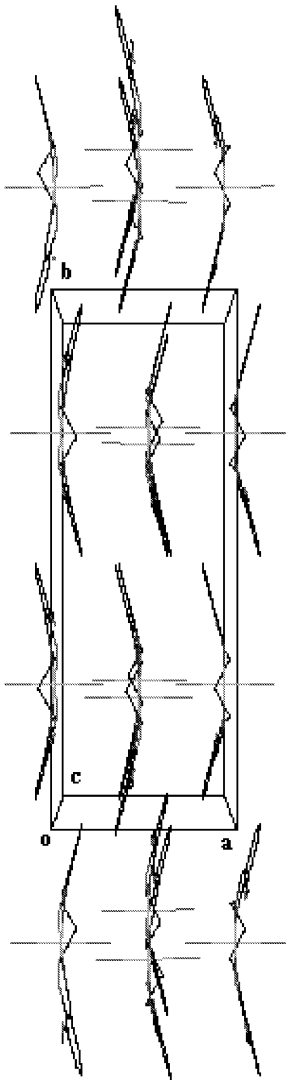


Fig. 3. Unit cell packing diagram for **1**.

with the Ni1 atom 0.002(3) Å above the basal plane N1, O1, $N1^{i}$ and $O1^{i}$ [symmetry code: (i) x, 1/2-y, z]. The angle O3–Ni1–O2 175.9(2)° indicates that the Ni atom is coordinated by two oxygen atoms in the axial positions, the Ni(II) ion thus showing a distorted octahedral geometry. Compound **1** is isostructural with [N,N′-bis(5-chlorosalicylidene)-1,3 diaminopropane]nickel(II) dihydrate [$Ni(C_{17}H_{14}N_2O_2Cl_2).2(H_2O)$] [7]. The Ni–N and Ni–O distances in **1** are 2.064(2) and 2.065(2) Å, respectively, in good agreement with the values found in other nickel complexes with similar ligands (Table 3) [7, 15, 16]. The average distance between Ni and the O atoms of the water molecules in **1** is 2.127(2) Å.

In the solid state, planar nickel(II) Schiff base complex have been found to appear in a "stepped" centrosymmetric

Table 3. Selected interatomic distances (Å) and angles (°) for other nickel complexes similar to **1**.

Compound	*n*	Ni1 – N1	Ni1 – O1	O1– Ni1 – N1	ϕ^{i}
a	4	1.850(6)	1.838(7)	94.6(3)	11.5(3)
b	4	1.871(8)	1.866(6)	91.2(3)	6.1(1)
c	4	1.839(2)	1.852(2)	93.3(1)	4.8
d	4	1.901(4)	1.845(3)	92.3(2)	8.9(1)
e	5	2.034(5)	2.030(4)	89.5(2)	38.6(4)
f	4	1.958(2)	1.910(2)	93.2(2)	38.7(1)
g	6	2.053(4)	2.037(3)	88.3(1)	29.1(1)
h	4	1.959(4)	1.908(3)	93.4(1)	29.3(2)
1	6	2.064(2)	2.020(2)	88.8(1)	21.6(1)

[a] $[Ni(C_{20}H_{14}N_2O_2)]$ (Radha, Seshasayee, Ramalingam, Aravamudan [15]); [b] $[Ni(C_{25}H_{20}N_2O_2)]$ (Akhtar, Drew [21]); [c] $[Ni(C_{24}H_{18}N_2O)_2]$ (Akhtar [29]); [d] $[Ni(C_{17}H_{16}N_2O_2)]$ (Drew, Prasad, Sharma [24]); [e] $[Ni(C_{17}H_{16}N_2O_2).(H_2O)]$ (Elerman, Kabak, Atakol [30]); [f] $[Ni(C_{17}H_{14}N_2O_2Cl_2)]$ (Elmali, Zeyrek, Elerman, Durlu [7]); [g] $[Ni(C_{17}H_{14}N_2O_2Cl_2)\cdot 2(H_2O)]$ (Elmali, Zeyrek, Elerman, Durlu [7]); [h] $[Ni(C_{17}H_{14}Br_2N_2O_2)]$ (Elmali, Zeyrek, Elerman, Svoboda [8]); [i] ϕ the dihedral angle between the two planes defined by Schiff base moieties; [n] Coordination number of Ni atom.

conformation [16, 17 – 19]. Due to the non-planarity of the chelate rings in solution, two chiral "umbrella" conformations are also possible. Also, the non-planar free-ligand molecule [20] on coordination to Ni may assume a more planar form. In compound **1**, the greatest deviation from the coordination planes Ni1, N1, O1, N1^{i} and O1^{i} [symmetry code: ^{i} (*x*, 1/2-*y*, *z*)] is only 0.003(1) Å. The maximum deviation from the plane defined by atoms O1, N1, C1 – C9 and C10 being 0.533(3) Å for the C9 in **1**, indicates a chair conformation. However, the whole molecule is not planar since the two halves are folded with respect to one another. The least-squares planes through each half of the molecule are inclined at an angle of 21.6(1)°, forming a shallow umbrella form as reported in other similar structures [7, 15].

The packing diagram for **1** is shown in Fig. 3 as a projection along the *c* axis. The molecules parallel to *a* are stacked with each Ni atom almost directly above the other. The closest Ni…Ni distance is 5.080 Å and there is from a geometrical point of view an infinite Ni…Ni…Ni chain along the *a* axis, as in the isostructural [N,N′-bis(5-chlorosalicylidene)-1,3diaminopropane]nickel(II) dehydrate [7], and similar to [N,N′-*o*-phenylenedisalicylideneaminato]nickel(II) [15], N,N′-propylenebis[(2-hydroxy - 1 - naphthyl)methaniminato]nickel(II) [21], bis(di methyl gly oxi mato)nickel(II) and bis (N,methylsalicyl ideneiminato)copper(II) [16].

In compound **2**, the Cu atom is coordinated by two imine N atoms and two phenolate O atoms in a distorted square planar coordination geometry. The atom with the greatest deviation from the coordination plane Cu1, N1, O1, N2 and O2 is O2 at −0.632(2) Å. The unique halves of the Schiff base ligand are reasonably planar, with the maximum deviation from the plane defined by toms N1, N2, O1, O2 (distorted coordination plane) and C8, C9, C10, C11 (6-7-6 chelate ring structure) being 0.283(3) Å for C10. However, the whole molecule is not planar since the two halves are twisted with respect to one another. The dihedral angle between the two 3-methoxysalicylidene groups is 43.4(1)°. The Cu–O bond lengths are 1.854(3) and 1.868(3) Å for Cu1–O1 and Cu2–O2, respectively, while the Cu–N bond lengths are 1.931(3) for Cu1–N1 and 1.950(3) Å for Cu1–N2, respectively. These values are 1.857 – 1.960 Å for Cu–O and 1.938 – 2.000 Å for Cu–N in similar Schiff base compounds [8, 15, 21 – 28] (Table 4).

The four donor atoms in complex **2** are coplanar with the Cu atom 0.053(1) Å above the best coordination plane (basal plane) N1, O1, N2 and O2. N1 and O2 are on the same side of the plane as Cu at distances of – 0.536(2) and – 0.632(2) Å, respectively, while N2 and O1 are on the opposite side at distances of 0.499(2) and 0.617(2) Å, respectively. The puckering resulting from the butyl group is significantly different from that of a normal square plane in, for examples, [N,N′-bis(salicylidene)-1,2 diiminoethane]copper(II), Cu(sal_2en), with an ethyl backbone [27]. In the case of Cu(sal_2en), the ethylene bridge allows essentially planar coordination about the copper centre, resulting in a dihedral angle of approximately 0°. However, the presence of butyl substituents prevents the putrescine backbone from attaining a similar conformation resulting in a dihedral averaging 43.4(1)° for compound **2**. The dihedral angle [43.4(1)°] in the compound **2** is significantly larger than the dihedral angle [21.6(1)°] of compound **1**. An alternative way of expressing the conformational variance is to note the expansion of the N–C–N angles [99.8(1)°] from 90°and the compression of both trans- O–Cu–N angles [140.0(1) and 148.5(1)°] from 180°. As a result, the dihedral angle between the two planes defined by Cu, O1, N1 and Cu, O2, N2 is 48.6(1)° which is larger than in N,N′-bis(salicylidene)-2,2′ diiminobenzidine]copper(II) [37°], an analogue with a similar 6-7-6 chelate ring structure [23, 28].

Acknowledgements

This work was supported by the Scientific Research Project Fund of University of Ankara under grant number 2002-07-45-004.

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