

Dedicated to Professor Bogdan C. Simionescu  
on the occasion of his 65<sup>th</sup> anniversary

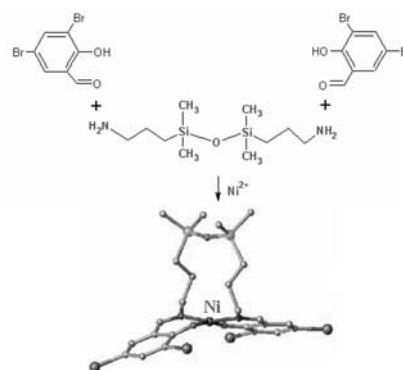
## Ni(II) AND Zn(II) COMPLEXES WITH A SALEN-TYPE LIGAND DERIVED FROM 1,3-BIS(3-AMINOPROPYL)TETRAMETHYLDISILOXANE

Alina SOROCEANU, Maria CAZACU,\* Alexandra NISTOR and Sergiu SHOVA

“Petru Poni” Institute of Macromolecular Chemistry, 41A Gr. Ghica Voda Alley, 700487 Iași, Roumania

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Two novel complexes,  $[\text{NiL}]\cdot 0.38\text{CHCl}_3$  (**1**) and  $[\text{ZnL}]\cdot 0.2\text{H}_2\text{O}$  (**2**), where **L** is a tetradentate ligand derived from condensation between 1,3-bis(3-aminopropyl)tetramethyldisiloxane and 3,5-dibromosalicylaldehyde, have been obtained by one-pot synthesis procedure consisting in the adding metal salt in the ligand forming solution. The separated complexes were characterized by X-ray single crystal diffraction and spectral (FTIR,  $^1\text{H}$  NMR, and UV-Vis) methods. The emission capacity was investigated by fluorescence spectrophotometry. Moisture sorption capacity and stability of the complexes were determined by dynamic vapor sorption analysis, while their catalytic activity was evaluated in the  $\text{H}_2\text{O}_2$  decomposition process.



### INTRODUCTION

Salen-type ligands, describing  $[\text{O}_2\text{N}_2\text{O}]$  tetradentate bis-Schiff bases,<sup>1</sup> are one of the oldest classes of ligands,<sup>2</sup> which can be easily synthesized and form complexes with almost all metal ions.<sup>2,3</sup> The salen-type Schiff base complexes of transition metals are also intensively studied in coordination chemistry. The high interest for these comes from the easiness with which they can be synthesized, their versatility and wide range of useful applications. The metallo-salens not only have played an important role in the development of modern coordination chemistry, but they can also be found at key points in the development of inorganic biochemistry,<sup>4</sup> catalysis,<sup>5</sup> magnetism, medical imag-

ing,<sup>6</sup> or more recently in molecular sensors, templating devices for syntheses, nonlinear optical (NLO) devices,<sup>4</sup> as building motifs for the construction of other functional materials,<sup>7</sup> or as sources of planar supramolecular building blocks.<sup>4</sup> Significant variations in the properties with structure are observed for these complexes.<sup>8</sup> Therefore, although there are an extremely large number of publications on salen-type metal complexes, there is still extensive research in this area, which mainly aims to diversify the range of amines and aldehydes and exploit the full potential, offered by this class of compounds. A large diversity of amine and carbonylic compounds were used to prepare salen-type ligands.<sup>9</sup> These are in general fully organic components.

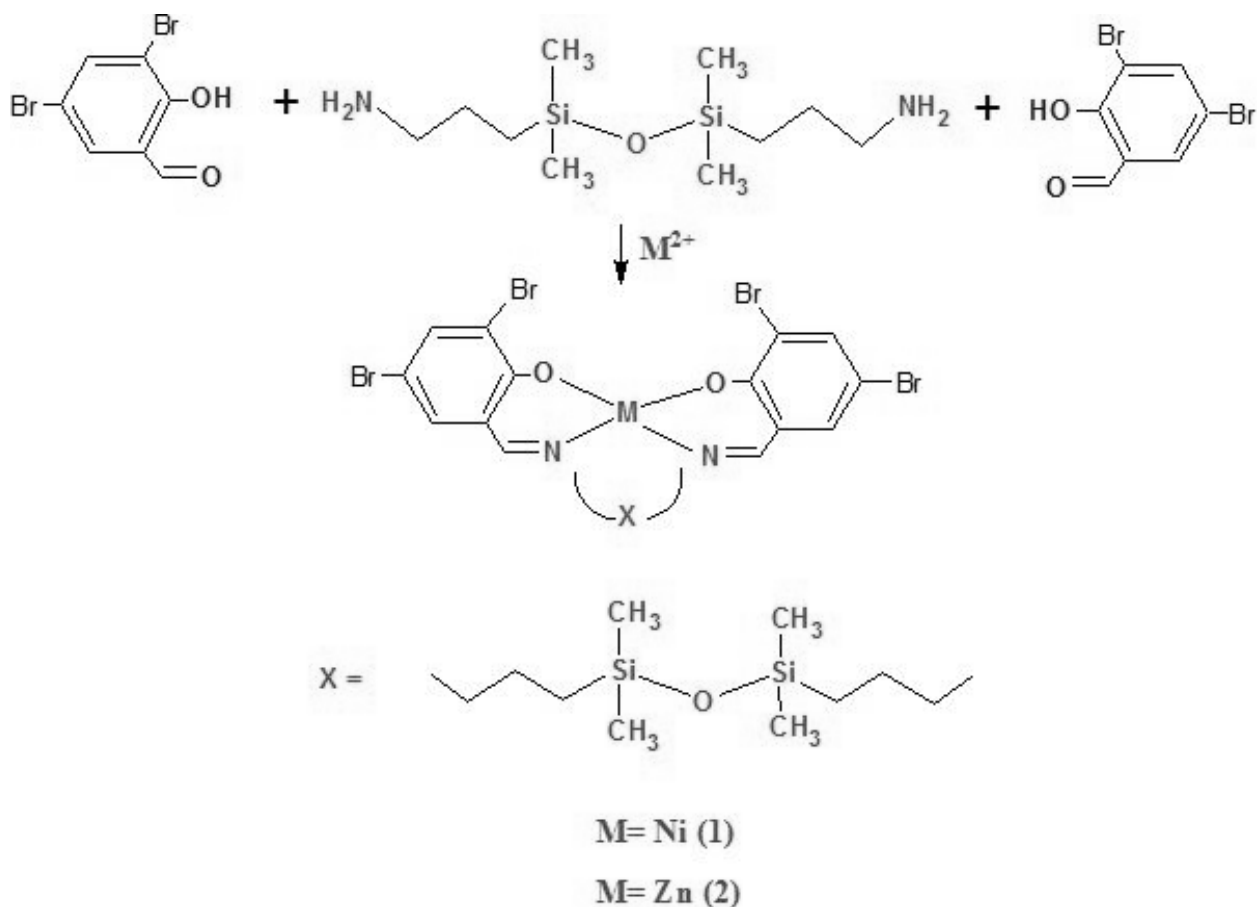
\* Corresponding author: mcazacu@icmpp.ro

Recently, we began to develop new transition metal complexes using ligands that contain flexible siloxane moiety.<sup>10-15</sup> In this paper we report about the synthesis, molecular structure and a few summary properties of nickel and zinc Schiff base complexes derived from 3,5-dibromosalicylaldehyde, and a siloxane diamine, 1,3-bis(3-aminopropyl)tetramethyldisiloxane. The main premise for this approach consists in that the introduction of the siloxane bond with its particularities (in principal the high and flexible bond angle around the O atom, ranging between 135 and 180°<sup>16</sup>) in such structure can induce major changes in the complexes behavior. It is also expected as the hydrophobic groups to improve the solubility of the complexes in common organic solvents. The biocompatibility and physiological inertness of the siloxane is an advantage in future use of the resulted derivatives in biomedical field. The presence of the siloxane moiety in the complexes might confer them conformational flexibility useful in catalysis.<sup>6</sup> This flexibility, similar to that observed in metalloproteins, is a key factor for the biomimetic activity of these

molecules.<sup>17</sup> Nickel was chosen as metal due to the special status of its complexes in coordination chemistry supported by their very interesting O<sub>2</sub>-binding reactivity, redox chemistry, unusual magnetic and structural properties, as well as their usage as catalysts for the oxidation and epoxidation reactions.<sup>4</sup> Zn(II) centred complexes have also recognized as useful in both catalytic as well as in supramolecular applications. The diversity in coordination geometries and the high reactivity that proved in certain cases makes the zinc complexes interesting units for the development of new materials with various photophysical, catalytic and sensing properties.<sup>7</sup>

## RESULTS AND DISCUSSION

Zn(II) and Ni(II) metal complexes of Schiff base derived from 1,3-bis(3-aminopropyl)tetramethyldisiloxane and 3,5-dibromosalicylaldehyde were prepared by one-pot procedure consisting in the adding the metal salt in a preheated aldehyde-amine mixture (Scheme 1).



Scheme 1 – Reaction pathway to metal complexes.

The complexes separated as crystals were first analyzed by FTIR spectroscopy and it has been found the specific absorption bands for the expected structures at:  $1620\text{ cm}^{-1}$  (CH=N),  $1250\text{ cm}^{-1}$  (Si-CH<sub>3</sub>), and  $1069\text{ cm}^{-1}$  (Si-O-Si) for the compound **1** and about in the same position  $1617\text{ cm}^{-1}$ ,  $1254\text{ cm}^{-1}$ , and  $1071\text{ cm}^{-1}$ , respectively in the compound **2**. <sup>1</sup>H NMR spectra are also consistent with the found structures (Figs. 1, 2), the proton peaks being in the appropriate ratios.

X-ray study has revealed that the compounds **1** and **2** have molecular crystal structures consisting of the neutral [ML] entities (M = Ni and Zn for **1** and **2**, respectively) and solvent molecules, H<sub>2</sub>O for **1**, and CHCl<sub>3</sub> for **2**. The final composition is in agreement with the formation of species [NiL]·0.38CHCl<sub>3</sub> (**1**) and, [ZnL]·0.2H<sub>2</sub>O (**2**). The asymmetric part of the unit cell in crystal **1** contains two identical [NiL] molecules (A and B) as crystallographic independent units, while the compound **2** crystallizes with six independent molecules [ZnL] (denoted as A, B, C, D, E and F). The bond lengths and angles for these complexes are summarized in Tables 1 and 2. As an example, the molecular structure of the components A for **1** and **2** are shown in Figs. 1 and 2, respectively.

In both complexes, the metal atoms are coordinated by the tetradentate N<sub>2</sub>O<sub>2</sub> Schiff base ligand with the formation of two six- and one twelve-membered chelate rings. The coordination geometry of each metal can be described as tetrahedrally distorted square-planar. The degree of tetrahedral distortion can be characterized by the parameter  $\tau_4$ , introduced by Houser to describe the geometry of a four-coordinate metal complex.<sup>18</sup> The value of  $\tau_4$  ranges from 1.00 for perfect tetrahedral geometry to zero for a perfect square-planar geometry. Intermediate values serve as an indication of tetrahedral distortion of square planar coordination. The  $\tau_4$  index, calculated for the investigated compounds exhibits values ranging from 0.198, 0.136 for two molecules of **1** to 0.751, 0.842, 0.740, 0.729, 0.745 and 0.772 for six independent molecules of **2**. The Si-O-Si bond angle in the dimethylsiloxane unit falls in the quite broad range between  $162.6(6) - 164.5(6)^\circ$  for **1** and  $144.4(5) - 165.6(6)^\circ$  for **2**. The variation of the Si-O-Si angle in the compounds studied indicates the lack of strict directionality of the bonds between oxygen and silicon atoms, which provides evidence for predominantly ionic nature of Si-O interactions in the disiloxane moiety.

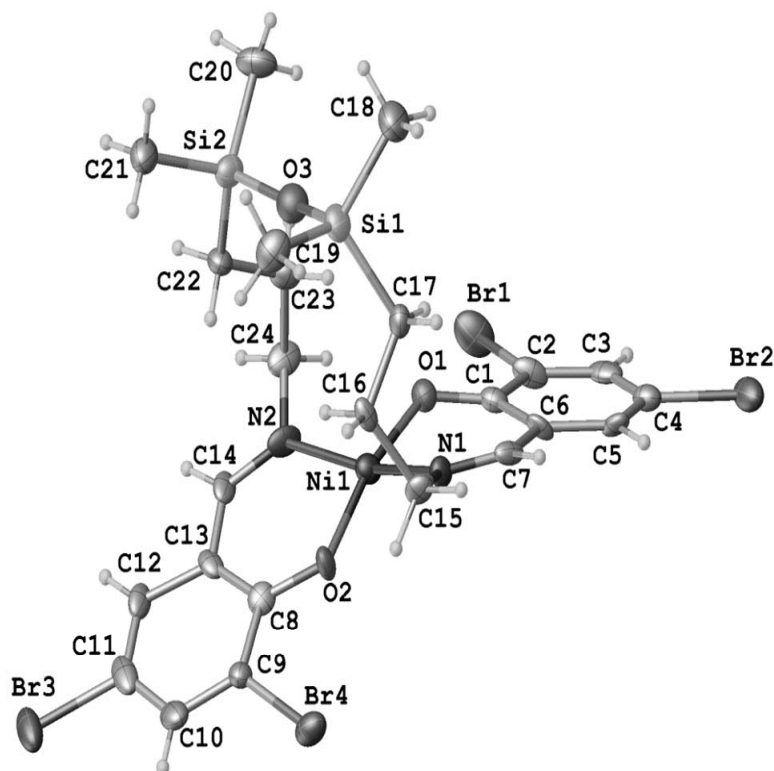


Fig. 1 – X-ray molecular structure of compound **1**. Thermal ellipsoids are drawn at 40% probability level.

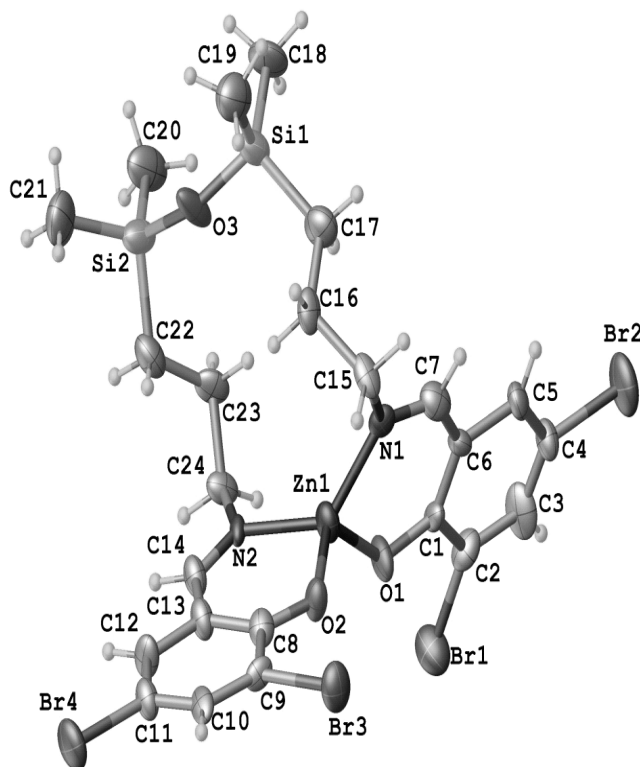


Fig. 2 – X-ray molecular structure of compound **2**. Thermal ellipsoids are drawn at 50% probability level.

Table 1

The selected bond lengths (Å) and angles (°) for the complexes **1** and **2**

	<b>1 (M = Ni)</b>		<b>2 (M = Zn)</b>					
	<b>A</b>	<b>B</b>	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>	<b>E</b>	<b>F</b>
M1–O1	1.851(7)	1.845(7)	1.924(8)	1.930(8)	1.928(9)	1.934(8)	1.917(9)	1.919(9)
M1–O2	1.829(7)	1.851(7)	1.928(9)	1.910(9)	1.930(9)	1.918(9)	1.927(9)	1.87(1)
M1–N1	1.893(8)	1.895(9)	1.97(1)	2.00(1)	1.98(1)	1.98(1)	1.98(1)	2.01(1)
M1–N2	1.928(9)	1.873(8)	1.993(9)	2.00(1)	1.98(1)	1.99(1)	2.00(1)	2.01(1)
Si2–O3	1.637(9)	1.621(8)	1.636(9)	1.63(1)	1.62(1)	1.59(1)	1.61(1)	1.60(1)
Si1–O3	1.606(9)	1.621(8)	1.616(9)	1.64(1)	1.60(1)	1.61(1)	1.61(1)	1.57(1)
O1–M1–O2	166.2(3)	170.8(3)	120.6(4)	126.5(4)	118.8(4)	116.8(4)	122.3(4)	119.6(4)
O1–M1–N1	91.7(3)	91.7(4)	95.8(4)	95.8(4)	97.1(4)	97.7(4)	93.4(6)	98.1(5)
O2–M1–N1	86.6(4)	88.1(4)	106.3(4)	106.8(4)	103.6(4)	112.9(4)	106.5(5)	108.5(5)
O1–M1–N2	90.6(4)	88.2(3)	107.8(4)	105.5(4)	105.0(5)	109.0(4)	108.2(5)	103.5(5)
O2–M1–N2	94.6(4)	93.4(3)	95.5(4)	97.3(5)	96.3(5)	97.4(5)	96.3(5)	97.8(5)
N1–M1–N2	165.0(4)	170.6(4)	133.5(4)	128.4(5)	138.2(5)	124.4(5)	133.2(5)	131.3(5)
Si2–O3–Si1	162.6(6)	164.5(6)	153.5(6)	144.4(6)	154.6(7)	165.2(1)	157.0(1)	165.6(8)

Fig. 3 shows the electronic absorption and emission spectra for **1** and **2** in DMSO. The complex **1** is characterized by three intense absorptions at 342, 398, and 426 nm, while the Zn complex, **2**, shows a moderate absorption band at 336 nm and a very high absorption at 426 nm. Both complexes excited at 426 nm show fluorescence emission at the same wavelength, 510 nm, but this effect is much more intense in the case of Zn complex, **2**.

The moisture sorption, very important for the stability and further applications of the compounds, was studied by recording sorption-desorption

isotherms in dynamic regime. For this, the samples were dried at 25 °C in flowing nitrogen (250 mL/min) until the constant weight at RH < 1 %. Then, the relative humidity (RH) was gradual increased from 0 to 90%, in 10% humidity steps, each step having a pre-established equilibrium time between 10 and 15 minutes so as the sorption equilibrium to be achieved every time. Thus sorption isotherms were traced. When the RH decreased, desorption curves were registered. The obtained isotherms at room temperature are presented in Fig. 4.

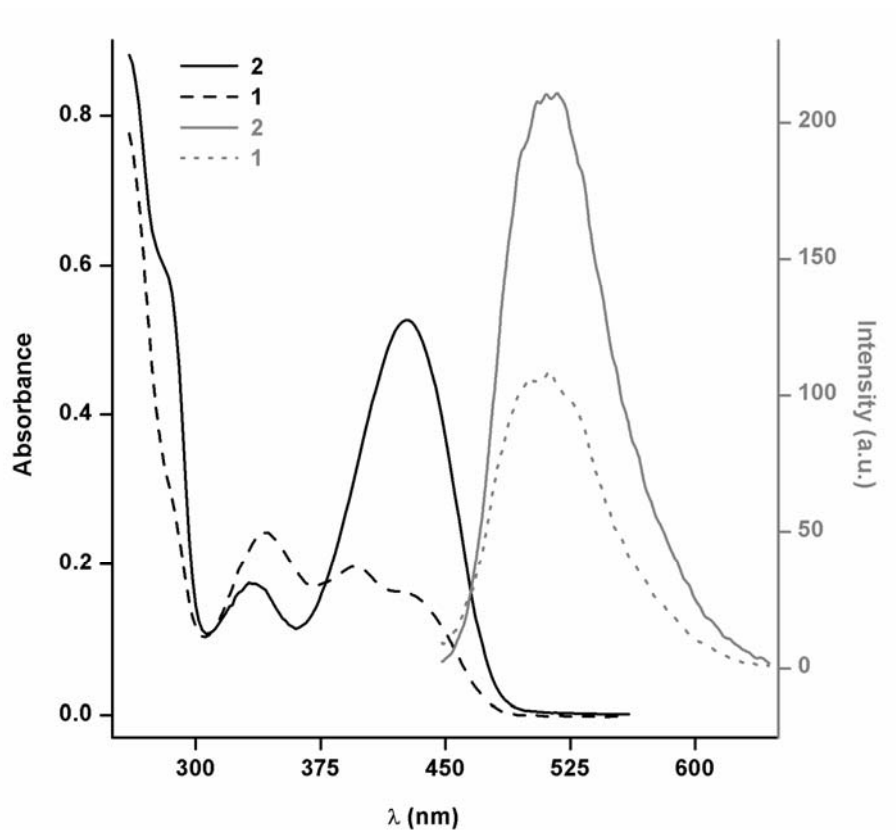


Fig. 3 – Absorption (left) and emission (right) spectra for Ni (1) and Zn (2) Schiff base complexes in DMSO solution.

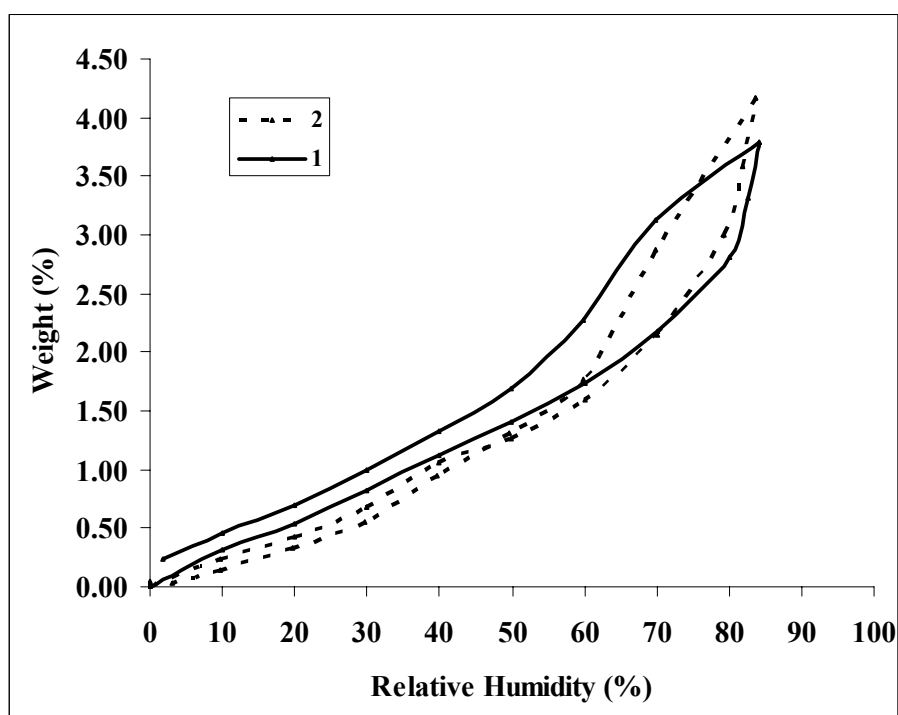


Fig. 4 – Water vapor sorption-desorption isotherms registered in dynamic regime.

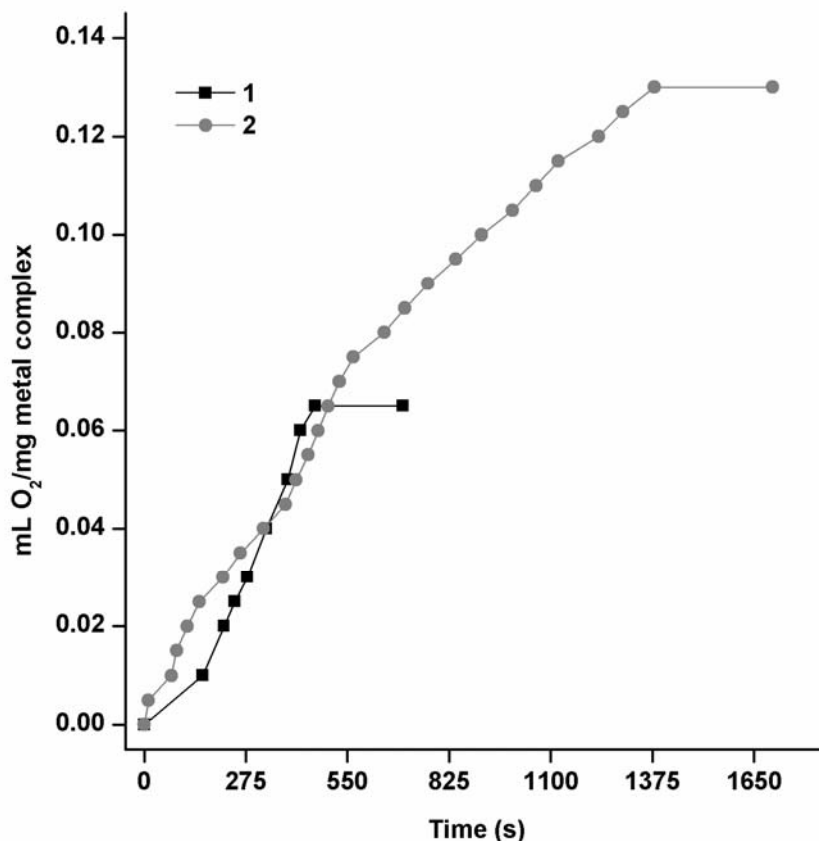


Fig. 5 – Oxygen volume released in dependence on time.

The two samples have absorbed similar amounts of water vapours, 3.8 (**1**) and 4.2 (**2**) % indicating, as expected, a hydrophobic material. This character is mainly conferred by the presence of the tetramethyldisiloxane moiety. While in the case of the sample **2** this process is completely reversible, the compound **1** retains a small amount (about 0.2 %) of water after desorption in the chosen working conditions. Since the two compounds have very similar chemical compositions and crystal structures, this difference in the moisture behaviour could be assigned to presence of different solvate molecules in the crystals (**1** and **2**). The isotherms show slight hysteresis over the entire humidity range, indicating that the desorption process is slower than sorption.

The catalytic activity of the obtained metal complexes evaluated in the model reaction of the hydrogen peroxide decomposition reveals a better activity of the Zn-based complex (Fig. 5).

## EXPERIMENTAL

### Materials

1,3-Bis(3-aminopropyl)tetramethyldisiloxane, (AP<sub>0</sub>), supplied by Fluka (b.p.=142°C/11.5 mmHg,  $d_4^{20} = 0.905$ ) was used as

received. 3,5-Dibromosalicylaldehyde, 98%, m.p. 82-83.5 °C, Zinc nitrate hexahydrate, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99.999%, and Nickel nitrate hexahydrate, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99.999%, were purchased from Sigma-Aldrich.

### Measurements

Fourier transform infrared (FT-IR) spectra were recorded using a Bruker Vertex 70 FT-IR spectrometer. Analyses were performed in the transmission mode in the range 400–4000 cm<sup>-1</sup> at room temperature with a resolution of 2 cm<sup>-1</sup> and accumulation of 32 scans. The samples were incorporated in dry KBr and measured as pellets. <sup>1</sup>H NMR spectra were acquired in CDCl<sub>3</sub> at 25°C with a Bruker Avance DRX 400 MHz spectrometer operating at 400.13 MHz. Chemical shifts are reported in ppm and are referenced to chloroform  $\delta^1\text{H} = 7.26$  ppm. Dynamic water vapor sorption (DVS) capacity of the samples was determined in the relative humidity (RH) range 0–90 % by using the fully automated gravimetric analyzer IGAsorp produced by Hiden Analytical, Warrington (UK). UV-VIS absorption spectra were recorded on spectrophotometer Shimadzu UV-1700 using quartz cuvettes of 1 cm. Fluorescence spectra were obtained by using a Perkin Elmer LS55 luminescence spectrometer in solution.

### X-ray Crystallography

Crystallographic measurements for **1** and **2** were carried out with an Oxford-Diffraction XCALIBUR E CCD diffractometer equipped with graphite-monochromated Mo- $K_{\alpha}$  radiation. The crystals were placed at 40 mm from the

CCD detector. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction.<sup>19</sup> All structures were solved by direct methods using SHELXS-97<sup>20</sup> and refined by full-matrix least-squares on  $F_o^2$  with SHELXL-97.<sup>20</sup> All atomic displacements for non-hydrogen, non-disordered atoms were refined using an anisotropic model. One of the 3-aminopropyl fragments in structure **1**, as well as the solvate molecules in both structures presented too large thermal ellipsoids, so that disordered models, in combination with the available tools (PART, DFIX, and SADI) of SHELXL97 were applied in order to better fit the electron density. The combined anisotropic/isotropic refinement has been used for these non-H atoms. All H atoms attached to carbon were introduced in idealized positions ( $d_{CH} = 0.96 \text{ \AA}$ ) using the riding model with their isotropic displacement parameters fixed at 120% of their riding atom. Positional parameters of the H attached to O atoms were obtained from difference Fourier syntheses and verified by the geometric parameters of the corresponding hydrogen bonds. The main crystallographic data together with refinement details are summarized in Table 2.

CCDC-902503 (**1**) and CCDC-902504 (**2**) contain the supplementary crystallographic data for this contribution. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](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 [deposit@ccdc.ca.ac.uk](mailto:deposit@ccdc.ca.ac.uk)).

*Catalytic test:* 20 mg complex were added into 50 mL NaOH 4N solution and stirred for 15 min, after which 15 mL

$H_2O_2$  (15%) was added and the stirring continued. The evolved  $O_2$  volume was measured from time to time (within 1-2 minutes).

### Procedure

#### Synthesis of Ni(II) complex, **1**

2.021 g (7.22 mmol) of 3,5-dibromosalicylaldehyde was dissolved in 20 mL solvent mixture 1:1 methanol-methylene chloride. This solution was poured over a mixture of 0.897 g (1 mL, 3.61 mmol) 1,3-bis(3-aminopropyl)tetramethyldisiloxane and 20 mL solvent mixture 1:1 methanol-methylene chloride. The resulted mixture was heated for 3 h at 70 °C. 1.163g (3.99 mmol)  $Ni(NO_3)_2 \cdot 6H_2O$  dissolved in 10 mL methanol, was then added over this solution, with stirring at room temperature. Small crystals of good quality were formed immediately. These were separated by filtration, washed with methanol and dried in air. Crystals yield: 0.6 g, 26.6 %. Calcd.  $C_{24.38}H_{30.13}NiBr_4Cl_{1.13}N_2O_3Si_2$  ( $M_r$  873.54 g/mol), %: C, 33.49; H, 3.45; N, 3.21. Found, %: C, 33.91; H, 3.85; N, 3.90. IR spectrum (KBr pellet), selected bands,  $\nu_{max}$ : 3067w  $\nu$ (C-H aromatic), 2937m, 2922m  $\nu$ (C-H from Si-CH<sub>3</sub>), 1620s  $\nu$ (C=N), 1582m  $\nu$ (aromatic ring), 1441vs  $\nu$ (CH<sub>2</sub>), 1318s  $\nu$ (CH<sub>3</sub>), 1250s  $\nu$ (Si-CH<sub>3</sub>), 1069s  $\nu$ (Si-O-Si), 747s  $\nu$ (Me-O), 494w  $\nu$ (Me→N).

<sup>1</sup>H-NMR (DMSO, 400.13 MHz,  $\delta$ , ppm): 8.53 (-CH=N-), 8.09, 7.89, (aromatic H), 3.63-3.58 (=N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si), 1.69-1.64 (=N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si), 0.55-0.52 (=N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si), 0.12 ((CH<sub>3</sub>)<sub>2</sub>Si<). Intensity ratio: 1:2:1:1:1:6.

Table 2

Crystallographic data, details of data collection and structure refinement parameters for **1** and **2**

	<b>1</b>	<b>2</b>
Empirical formula	$C_{24.38}H_{30.13}NiBr_4Cl_{1.13}N_2O_3Si_2$	$C_{24}H_{30.4}ZnBr_4N_2O_3Si_2$
Formula weight	873.54	839.44
Temperature/K	200.0	250.0
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
$a$ , (Å)	20.7546(18)	17.173(3)
$b$ , (Å)	12.7127(10)	18.944(2)
$c$ , (Å)	26.704(2)	33.075(4)
$\alpha$ , (°)	90.00	74.958(12)
$\beta$ , (°)	110.171(10)	85.179(13)
$\gamma$ , (°)	90.00	68.592(14)
$V$ , (Å <sup>3</sup> )	6613.5(10)	9674(2)
$Z$	8	12
$D_{calc}$ (g/cm <sup>3</sup> )	1.755	1.729
$\mu$ , (mm <sup>-1</sup> )	5.611	5.820
Crystal size (mm)	0.2 × 0.2 × 0.10	0.15 × 0.15 × 0.10
$\theta_{min}$ , $\theta_{max}$ (°)	5.84 to 52°	5.94 to 50.1°
Reflections collected/unique	35108/12948 [ $R_{int}=0.1155$ ]	102480/34171 [ $R_{int}=0.1916$ ]
$R_1^a(I > 2\sigma(I))$	0.0809	0.0996
$wR_2^b(I > 2\sigma(I))$	0.1577	0.1374
GOF	0.912	0.914
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e/Å <sup>3</sup> )	2.43/-1.68	1.07/-0.86

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ , <sup>b</sup>  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ .

<sup>c</sup> GOF =  $\{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$ , where  $n$  is the number of reflections and  $p$  is the total number of parameters refined.

*Synthesis of Zn(II) complex, 2*

A solution containing 1 ml of 1,3-bis(3-aminopropyl)tetramethyldisiloxane (0.897 g, 3.61 mmol) in 20 mL solvent mixture 1:1 methanol-methylene chloride was added under stirring at room temperature to the solution of 3,5-dibromosalicylaldehyde (2.021 g, 7.22 mmol) in 20 mL solvent mixture 1:1 methanol-methylene chloride. The mixture was stirred at 70 °C for 3 h. Then, the orange solution was added to a solution of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.189 g, 3.99 mmol) in 10 mL methanol. The mixture was stirred at room temperature for 10 min. A clear yellow solution generated prismatic crystals of good quality after 3-4 h at room temperature. These were separated by filtration, washed with methanol and dried in air. Crystals yield: 0.3 g, 9.90 %. Calcd for C<sub>24</sub>H<sub>30.42</sub>Br<sub>4</sub>N<sub>2</sub>Zn<sub>1</sub>O<sub>3.21</sub>Si<sub>2</sub> (M<sub>r</sub> 839.19 g/mol), %: C, 34.32; H, 3.62; N, 3.34. Found, %: C, 34.10; H, 3.50; N, 3.40. IR spectrum (KBr pellet), selected bands, ν<sub>max</sub>: 2930 m ν(C-H from Si-CH<sub>3</sub>), 1617vs ν(C=N), 1506m ν(aromatic ring), 1443vs ν(CH<sub>2</sub>), 1386s ν(CH<sub>3</sub>), 1254s ν(Si-CH<sub>3</sub>), 1071s ν(Si-O-Si), 840s ν(Si-CH<sub>3</sub>), 707s ν(Me-O), 482w ν(Me→N).

<sup>1</sup>H-NMR (DMSO, 400.13 MHz, δ, ppm): 8.33 (-CH=N-), 7.69-7.66, 7.51-7.40 (aromatic H), 3.27-3.30 (=N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si), 1.49 (=N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si), 0.26 (=N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si), 0.03 ((CH<sub>3</sub>)<sub>2</sub>Si<). Intensity ratio: 1:2:1:1:1:6.

**CONCLUSIONS**

The reaction between 1,3-bis(3-aminopropyl)tetramethyldisiloxane, 3,5-dibromosalicylaldehyde and nickel or zinc salts resulted in the formation of the two derived complexes with similar molecular structures. The further investigation of the synthesized complexes revealed difference in their behaviour. Thus, nickel complex proved to be catalytically less active as compared with zinc derivative while the last is more fluorescent and moisture stable.

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