## Thermal Decomposition of New Mononuclear Ni<sup>II</sup> Complexes with ONNO Type Reduced Schiff Bases and Pseudo Halogens

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Abstract. Mononuclear nickel(II) complexes were prepared by reaction of the three ONNO type reduced Schiff bases bis-N,N-(2-hydroxybenzyl)-1,3-propanediamine (L<sup>H</sup>H<sub>2</sub>), bis-N,N-(2-hydroxybenzyl)-2,2'-dimethyl-1,3-propanediamine (LDM<sup>H</sup>H<sub>2</sub>), and bis-N,N-[1-(2-hydroxyphenyl)ethyl]-1,3-propanediamine (LAC<sup>H</sup>H<sub>2</sub>) with Ni<sup>II</sup> ions in the presence of pseudo halides (OCN<sup>-</sup>, SCN<sup>-</sup> and N<sub>3</sub><sup>-</sup>). The complexes were characterized with the use of elemental analyses, IR spectroscopy, and thermal analyses. The molecular structure of one of the complexes

was obtained by single-crystal X-ray diffraction. The obtained complexes are mononuclear, and a pseudo halide molecule is attached. One of the oxygen atoms of the ligand is in phenolate and the other was in phenol form. According to the thermogravimetry results, it was thought that the pseudo halide thermally detaches from the structure as hydropseudo halide. In azide-containing complexes an endothermic reaction was observed although the azide group usually decomposes with an exothermic reaction.

### Introduction

Complexes with ONNO type Schiff bases and +2 valence transition metal ions are known for more than 70 years [1–14]. In all complexes, two of the phenol oxygen atoms are coordinated as phenolate (Figure 1).



Figure 1. Most common complexes with ONNO type Schiff bases.

ONNO type Schiff bases are easily reduced with the help of NaBH<sub>4</sub> and turn into phenolamines [15–17]. These phenolami-

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nes are also of ONNO type and give multinuclear complexes similar to those Schiff bases [15, 17, 18]. In a previous study, a mononuclear complex was obtained by the reaction of bis-*N*,*N*-(salicylidene)-1,3-propanediamine with Ni<sup>II</sup> in DMF in the presence of N<sub>3</sub><sup>-</sup>. The most interesting feature of this complex is that one of the phenol groups was converted into phenolate, whereas the other remained intact and Ni<sup>II</sup> was neutralized by phenolate and azide groups [19]. A number of complexes were prepared with the pseudo halides N<sub>3</sub><sup>-</sup>, OCN<sup>-</sup>, and SCN<sup>-</sup>, which were characterized by thermal analyses (Figure 2). Thermogravimetry studies concerning complexes that contain azide groups and other pseudo halides have recently been reported [20–33], which showed that azide groups decompose in exothermic reactions.

Almost all complexes were obtained in crystal form but only crystals of complex **X** grew to appropriate dimensions to obtain its molecular structure with single-crystal X-ray diffraction methods. Attempts to grow single-crystals of complex **III** in DMF were unsuccessful. Recrystallization from DMSO yielded complex **X**. Complexes **I**–**X** were characterized by IR spectroscopy and elemental analyses; their thermal degradation behaviors were examined by thermogravimetric measurements.

### **Results and Discussion**

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The results of elemental analyses and important IR spectroscopic data are tabulated in Table 1. The asymmetric stretching vibrations of azide ligands,  $v_{N3}$  and  $v_{CN}$  are in good agreement with the literature [30, 33]. The molecular structure of complex **X** is shown in Figure 3 and selected bond lengths and bond angles are listed in Table 2 and Table 3, respectively. In previous studies, the X-ray diffraction models of complexes I and IV were given [19]. Complex III did not give crystals suitable





Figure 2. Formula of complexes I-X.

Complex	Elemental analyse				Important IR data /cm <sup>-1</sup>												
	Expected % Found %																
	С	Ν	Н	Ni	С	Ν	Н	Ni	$\nu_{O\!-\!H}$	$\nu_{N\!-\!H}$	$\nu_{C\!-\!H} \; (Ar)$	$\nu_{C\!-\!H} \; Aliph$	v <sub>N3</sub> (OCN) (SCN)	$v_{C=O}$ (DMF)	) v <sub>C=C</sub> (Ar)	$\delta_{\mathrm{CH2}}$	$\delta_{\mathrm{C-H}}\left(\mathrm{Ar}\right)$
[NiL <sup>H</sup> ·N <sub>3</sub> ·	52.20	18.40	6.22	11.87	51.94	17.68	6.18	11.94	3370	3269	3037-3056	2861-2927	2036	1646	1598	1460	757
DMF]2·DMF (I)																	
NiL <sup>H</sup> •OCN•DMF	55.17	12.25	5.95	12.84	54.69	13.41	5.21	12.73	3497	3270	3019-3058	2863-2928	2208	1645	1597	1459	758
(II)																	
NiL <sup>H</sup> ·SCN·DMF	53.20	11.81	5.73	12.38	52.77	10.96	5.26	12.24	3491	3273	3021-3063	2866-2931	2094	1650	1598	1468	756
(III)																	
[NiLDM <sup>H</sup> ·N <sub>3</sub> ·	53.99	17.41	6.64	11.23	54.07	16.82	5.94	10.79	3501	3268	3021-3058	2860-2929	2035	1651	1601	1470	758
DMF]2·2DMF (IV)																	
NiLDM <sup>H</sup> ·OCN·	56.82	11.52	6.42	12.07	56.37	10.91	6.24	11.92	3510	3282	3024-3061	2855-2931	2194	1646	1598	1460	760
DMF (V)																	
NiLDM <sup>H</sup> ·	54.99	11.15	6.22	11.69	55.33	10.78	5.64	11.33	3504	3300	3022-3058	2864-2930	2093	1646	1599	1463	761
SCN·DMF (VI)																	
NiLAC <sup>H</sup> ·N <sub>3</sub> ·	54.35	17.29	6.42	12.07	53.89	16.86	5.89	12.01	3449	3260	3018-3049	2865-2924	2027	1649	1600	1469	757
DMF (VII)																	
NiLAC <sup>H</sup> •OCN•	56.82	11.52	6.42	12.07	56.43	11.36	6.04	11.57	3469	3266	3017-3051	2865-2931	2189	1647	1598	1465	757
DMF (VIII)																	
NiLAC <sup>H</sup> ·SCN·	54.99	11.15	6.22	11.69	54.51	10.59	5.78	11.51	3475	3264	3018-3052	2864-2932	2082	1650	1598	1490	758
DMF (IX)																	
[NiL <sup>H</sup> ·SCN·	50.03	10.14	6.02	10.63	49.59	10.24	5.76	10.46	3416	3270	3028-3057	2848-2939	2088	1651	1601	1478	757
DMFJ·DMSO (X)																	

for XRD analysis in DMF. It was recrystallized from DMSO and crystals suitable for XRD analysis as a result of the solvatization of a DMSO molecule with the complex were obtained. This new complex was described as compound **X**.

Elemental analyses and the molecular structure of the complex show that Ni<sup>II</sup> has mononuclear and octahedral coordina-



Figure 3. Molecular structure of NiL<sup>H</sup>·SCN·DMF·DMSO (X).

Table 2. Selected	l bond	lenghts /A	A of	complex	Χ.
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N1–Ni	2.107(4)	
N2-Ni	2.101(5)	
N3–Ni	2.034(6)	
Ni-O1	2.046(4)	
Ni-O2	2.061(3)	
Ni-O3	2.134(4)	
C18-N3	1.148(7)	
C18-S1	1.632(8)	
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tion spheres similar to those reported in literature. As seen from the data listed in Table 4, the coordination sphere around Ni<sup>II</sup> is an almost ideal octahedron with no significant deformation. The lengths of the coordinative bonds around Ni<sup>II</sup> are 2.034, 2.046, 2.061, 2.101, 2.107, and 2.134 Å and the bond angles are approximately 90 °. Only the N2–Ni–O3 and, N1–Ni–O3 angles were found to amount 82.99 and 85.62 °. The N3–Ni–O3, O2–Ni–N1 and O1–Ni–N2 angles were observed to amount 176.70, 174.51, and 173.02 °, respectively, and deviate only slightly from the ideal value of 180 °.

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<b>Table 3.</b> Selected bond angles /° of complex X.				
N3-Ni-O1	92.61(19)			
N3-Ni-O2	90.17(18)			
O1-Ni-O2	87.14(15)			
N3–Ni–N2	93.80(2)			
O1-Ni-N2	173.02(18)			
O2-Ni-N2	89.96(17)			
N3–Ni–N1	94.90(2)			
O1-Ni-N1	90.41(16)			
O2-Ni-N1	174.51(18)			
N2-Ni-N1	91.92(18)			
N3–Ni–O3	176.70(2)			
01-Ni-O3	90.63(16)			
O2-Ni-O3	89.49(15)			
N2-Ni-O3	82.99(18)			
N1–Ni–O3	85.62(17)			
N3-C18-S1	179.00(7)			

Table 4. Crystallographic data of complex X.

Chemical formula	C <sub>23</sub> H <sub>34</sub> N <sub>4</sub> NiO <sub>4</sub> S <sub>2</sub>
Formula mass	553.37
Temperature /K	293
Wavelength /Å	0.71073 Mo-K <sub>a</sub>
Crystal system, space group	Monoclinic, $I2/a$
Unit cell dimensions /Å, °	
a	18.7698 (2)
b	11.8211 (2)
С	24.5208 (16)
β	109.923 (4)
Volume /Å <sup>3</sup>	5115.3 (3)
Ζ	8
Calculated density /g·cm <sup>-3</sup>	1.437
Absorption coefficient /mm <sup>-1</sup>	0.958
<i>F</i> (000)	2336
Crystal size /mm	$0.30 \times 0.25 \times 0.20$
$\theta_{\rm max}$ /°	24.02
$\theta_{\min}$ /°	2.07
Index range	$0 \le h \le 21$
	$0 \le k \le 13$
	$-28 \le l \le 26$
Number of reflections used	3966
Number of parameters	290
R <sub>int</sub>	0.0286
R	0.0545
$R_{ m w}$	0.1247
Goodness of fit	1.012
$\Delta \rho_{\min}, \Delta \rho_{\max} / e \cdot A^{-3}$	-0.712, 1.037

The most interesting phenomenon observed is the fact that one of the phenol groups of the ligand is coordinated as phenolate and the other remains in phenol form. The 2+ charge of Ni<sup>II</sup> is neutralized by the negative charges of phenolate and pseudo halide. The hydrogen atom of the phenol group has a very strong tendency to form hydrogen bonds and phenol hydrogen atoms form hydrogen bonds with phenolate groups of neighboring molecules. The characteristics of this hydrogen bond are shown in Table 5. Under these circumstances, two complex molecules are bonded to each other with two hydrogen bonds through a dimerization process (Figure 4). As seen in Table 5, there is an intramolecular hydrogen bond formed between hydrogen attached to amine nitrogen atoms and oxygen atoms of the phenol group. However, the bond angle amounts 102.93 °, which is far from the expected value. Therefore, this is not a real hydrogen bond formation. It can be described as agnostic interaction [37].

Table 5. Hydrogen bonding parameters for complex X.

D–H•••A	D–H	Н•••А	D•••A	D–H•••A
O2–H2(B)•••O1	0.93 Å	1.52 Å	2.412(5) Å	158 °



Figure 4. Dimerization of two molecules of complex  ${\bf X}$  by hydrogen bonding.

Table 6 lists the thermogravimetric data of complexes I-X. Figure 5 shows the TG and DTA curves of complex NiL<sup>H</sup>·N<sub>3</sub>·DMF (I). This complex is reported in literature. Two units of NiL<sup>H</sup>·N<sub>3</sub>·DMF form a dimer with one DMF solvate molecule. Four endothermic reaction steps are observed in the TG and DTA curves of this complex. The first reaction is the breakage of the solvatized DMF molecule from the (NiL<sup>H</sup>·N<sub>3</sub>)<sub>2</sub>·DMF dimer. The theoretical mass of DMF is 7.38 %, whereas the experimental mass loss is  $6.50 \pm 0.44$  %. The second weight loss step amounts  $8.75 \pm 0.14$  %. This is probably due to dissociation of HN<sub>3</sub> from the complex. Azides are known to be explosive and can easily turn into nitrogen. The explosion reaction of azide is highly exothermic [38]. However, the reaction observed here is endothermic and cannot be the explosion reaction of azide. HN<sub>3</sub> is a liquid compound at room temperature and their salts are stable up to ~200 °C [39]. In the NiL<sup>H</sup>·N<sub>3</sub>·DMF octahedral unit one phenol group of the ligand  $L^{H}$  is in phenolate and the other is in phenol state.

The azide group coordinative bonded to hydrogen of this phenol group thermally detaches from the structure as  $HN_3$ . In the remaining part of the molecule  $Ni^{II}$  is coordinated between two amine nitrogen atoms and two phenolate oxygen atoms of the  $L^H$  molecule and oxygen atoms of the DMF group. The third weight loss step is related to the removal of DMF from the remaining part of the complex. The expected and experi-



Table 6. Thermoanalytical data of complex	kes I–X.
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Complex	1st Thermal Reaction: Dissociat	2 <sup>nd</sup> Thermal Reaction: Degradation of the complex				Residue NiO	
	Temp. range /°C	Expected mass loss /%	Found mass loss /%	Temp. range /°C	Found mass loss /%	Expected /%	Found /%
[NiL <sup>H</sup> ·N <sub>3</sub> ·DMF] <sub>2</sub> ·DMF (I) <sup>a)</sup>	126–240, DTG: 127, 166, 207	30.83	29.76 ± 0.52	240-430	21.70	15.10	14.48 ± 1.18
NiL <sup>H</sup> •OCN•DMF (II)	118–230, DTG: 190	25.36	$25.28\pm0.14$	270-440	24.60	16.34	$15.12\pm2.05$
NiL <sup>H</sup> ·SCN·DMF (III)	138-202, DTG: 198	27.83	$26.56 \pm 0.46$	210-380	15.30	15.75	$14.24\pm1.22$
$[NiLDM^{H}\cdot N_{3}\cdot DMF]_{2}\cdot 2DMF (IV)$	184–294, DTG: 231	41.44	$42.31 \pm 1.17$	190-440	13.90	11.54	$10.92 \pm 1.09$
NiLDM <sup>H</sup> .OCN.DMF (V)	175–265, DTG: 235	23.85	$23.09\pm0.30$	270-445	36.04	15.34	$14.71\pm1.16$
NiLDM <sup>H</sup> ·SCN·DMF (VI)	165–266, DTG: 221	26.28	$26.65 \pm 1.20$	275-430	13.60	14.87	$15.04\pm0.52$
NiLAC <sup>H</sup> ·N <sub>3</sub> ·DMF (VII)	165-268, DTG: 232	23.85	$22.42\pm0.35$	245-420	18.60	15.36	$16.22\pm1.46$
NiLAC <sup>H</sup> •OCN•DMF (VIII)	172-250, DTG: 214	23.85	$23.36\pm0.27$	250-430	47.80	15.35	$16.06\pm0.94$
NiLAC <sup>H</sup> ·SCN·DMF (IX)	149-230, DTG: 192	26.29	$25.93 \pm 1.14$	235-445	36.90	14.87	$14.33\pm1.16$
[NiL <sup>H</sup> ·SCN·DMF]·DMSO (X)	146-228, DTG: 219	38.03	$36.45 \pm 0.24$	240-395	28.60	13.53	$12.79\pm0.83$

a) In [NiL<sup>H</sup>·N<sub>3</sub>·DMF]<sub>2</sub>·DMF. 1<sup>st</sup> Thermal Reaction: Dissociation of solvated DMF at 119–146 °C Expected: 7.38 % Found:  $6.50 \pm 0.44$  %. 2<sup>nd</sup> Thermal Reaction: Loss of HN<sub>3</sub> at 149–185 °C Expected: 8.69 % Found: 8.75 ± 0.14 %. 3<sup>rd</sup> Thermal Reaction: Loss of DMF at 185–234 °C Expected: 14.76 % Found: 14.78 ± 0.94 %. 4<sup>th</sup> Thermal Reaction: Degradation of NiL at 280–345 °C. Degradation range of NiL 314–360 °C DTG: 340 °C. Degradation range of NiLDM<sup>H</sup> 337–421 °C DTG: 390 °C.



Figure 5. TG and DTA curves for NiL<sup>H</sup>·N<sub>3</sub>·DMF (I).

mentally found mass losses are 14.76 % and 14.78  $\pm$  0.94 %, which nearly similar. The total mass loss expected from the first three thermal reactions is 30.83 % and the experimentally found value is 29.76  $\pm$  0.52 %. The fourth weight loss is the decomposition of the NiL<sup>H</sup> molecule, which takes place in a non-uniform manner. In other complexes thermal HSCN formation such as HN<sub>3</sub> is not clearly observed. Figure 6 illustrates the TG and DTA curves of complexes **II**, **III**, **V**, and **IX**. In these TG and DTA curves the formation of HN<sub>3</sub>, HOCN and HSCN and the loss of coordinative DMF appears as a single endothermic reaction.

## **Experimental Section**

#### General

<sup>1</sup>H-NMR spectra were obtained with a Bruker DPX FT NMR (500 MHz) spectrometer (SiMe<sub>4</sub> as internal standard and 85 % H<sub>3</sub>PO<sub>4</sub> as an external standard). The concentration of solute molecules was 150 mg in 1.0 mL CDCl<sub>3</sub>.

#### **Preparation of Ligands**

 $L^{H}H_{2}$ ,  $LDM^{H}H_{2}$ , and  $LAC^{H}H_{2}$  were obtained the reduction of corresponding Schiff base. Bis-*N*,*N*(salicylidene)-1,3-propanediamine (1.410 g, 0.005 mol), bis-*N*,*N*(salicylidene)-2,2'-dimethyl-1,3-propanediamine (1.540 g, 0.005 mol), or bis-*N*,*N*(2-hydroxyacetophenylidine)-1,3-propanediamine (1.540 g, 0.005 mol) was dissolved in MeOH (50 mL) under heating. Solid NaBH<sub>4</sub> was slowly added to this solution. Twice the volume of ice was added to yield a colorless solution, which was left to stand for one day. The colorless precipitate was filtered off and dried in air.

<sup>1</sup>**H** NMR (L<sup>H</sup>H<sub>2</sub>): δ = 6.67–6.73 and 7.03–7.09 (H<sub>Ar</sub>), 2.48–2.65 (H<sub>CH2</sub>, neighbor to nitrogen), 1.58–1.69 (H<sub>CH2</sub>, methylene), 3.75–2.86 (H<sub>CH2</sub>, benzyl), 4.75 (H<sub>N-H</sub>). (LDM<sup>H</sup>H<sub>2</sub>): δ = 6.72–6.77 and 7.12–7.18 (H<sub>Ar</sub>), 3.88–4.34 (H<sub>CH2</sub>, benzyl), 2.38–2.54 (H<sub>CH2</sub>, neighbor to nitrogen), 0.98–1.22 (H<sub>CH3</sub>), 5.26 (H<sub>N-H</sub>). (LAC<sup>H</sup>H<sub>2</sub>): δ = 6.66–6.82, 7.15–7.26, and 7.48–7.59 (H<sub>Ar</sub>), 1.52–1.68 (H<sub>CH2</sub>, methylene), 2.32–2.40 (H<sub>CH2</sub>, neighbor to nitrogen), 3.68–3.78 (H<sub>C-H</sub>, benzyl), 2.14–2.28 (H<sub>CH3</sub>), 5.31 (H<sub>N-H</sub>).

The Schiff bases were prepared from the corresponding aldehyde and amine compounds in EtOH. Bis-N,N(salicylidene)-1,3-propanediamine, bis-N,N(salicylidene)-2,2'-dimethyl-1,3-propanediamine was prepared from salicylaldehyde and 2,2'-dimethyl-1,3-propanediamine and bis-N,N(2-hydroxyacetophenylidine)-1,3-propanediamine was prepared from 2-hydroxyacetophenone and 1,3-propanediamine.

#### Preparation of the Complexes

The Ligand ( $L^{H}H_{2}$ ,  $LDM^{H}H_{2}$  or  $LAC^{H}H_{2}$ ) (0.001 mol) was dissolved in DMF (40 mL) whilst heating. Afterwards, a solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (0.237 g) in hot MeOH (20 mL) and a solution of the sodium pseudo halide salt (0.002 mol) in hot water (5 mL) was added. The resulting mixture was left to stand for 1–5 days and the precipitated crystals were filtered off and dried in air.

#### Preparation of Complex X for XRD Studies

All complexes were obtained as blue crystals. However, the crystals were not big enough for XRD studies. Therefore, the complex



**Figure 6.** TG and DTA curves for (a) NiL<sup>H</sup>·OCN·DMF (II), (b) NiL<sup>H</sup>·SCN·DMF (III), (c) NiLDM<sup>H</sup>·OCN·DMF (V), and (d) NiLAC<sup>H</sup>·SCN·DMF (IX).

 $\rm NiL^{H}$ -SCN-DMF (III) (200 mg) was dissolved in DMSO (10 mL) whilst heating. DMF (10 mL) was added and the final mixture was left to stand for 5–6 days. The resulting crystals were filtered off and used for XRD studies.

The C, H, and N analyses of the complexes were carried out with a Leco 932 CHNS analyzer. Ni analysis was performed with a GBC Avanta PM Model AAS apparatus.

Thermogravimetric analyses were performed with a Shimadzu DTG-60 H apparatus under N<sub>2</sub> atmosphere in Pt pans. The TG and DTA curves were taken between 30 °C and 750 °C at a heating rate of 10 °C min<sup>-1</sup>. The pans were cleaned with oxygen at 750 °C.

А blue prismatic crystal with approximate dimensions  $0.20 \times 0.25 \times 0.30$  mm was attached to a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer [34]. X-ray diffraction data of single crystal were collected at room temperature with graphite monochromated Mo- $K_a$  radiation. The cell parameters were determined from a least-squares refinement of 25 centered reflections. Cell refinement was carried out using CAD4 EXPRESS [34]. During data collection, three standard reflections were periodically measured every 120 minutes and showed no significant intensity variation. With  $\omega/2\theta$  scan mode 2052 unique reflections having  $I \ge 2\sigma(I)$  were measured in the range of 2.07  $\leq \theta \leq$  24.02°. Data reduction was carried out using SHELXL97 [35]. The structure was solved by direct methods using SHELX97 [35] in the WinGX package [36] and refined by full-matrix least-square method on  $F^2$  using SHELXL97 [35]. All non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were included at calculated position using a riding model with  $U_{eq} = 1.2 U_{iso}$  (C, N). Selected crystallographic data are given in Table 4, selected bond lengths and angles are given in Table 2 and Table 3, respectively.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC-751983 for complex **X**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2, 1EZ, UK (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk or http:// www.ccdc.cam.ac.uk).

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