



Dedicated to Professor Gheorghe Maria
on the occasion of his 70th anniversary

MONONUCLEAR AND BINUCLEAR NICKEL(II) COMPLEXES WITH A SCHIFF BASE LIGAND DERIVED FROM 2,3-DIHYDROXYBENZALDEHYDE**

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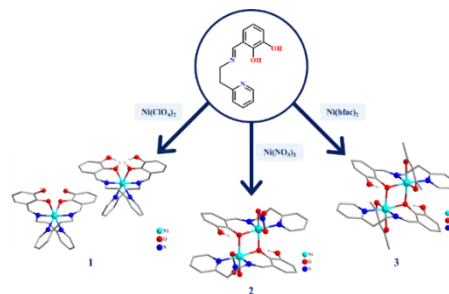
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The Schiff base (H₂L) obtained from the condensation of 2,3-dihydroxybenzaldehyde and 2-(aminoethyl)pyridine was employed as a proligand for the preparation of three new Ni(II) complexes: [Ni(HL)₂][Ni(H₂L)₂](ClO₄)₂·2C₂H₅N (**1**), [Ni₂(HL)₂(NO₃)₂] (**2**), and [Ni₂(HL)₂(hfac)₂] (**3**). All compounds have been characterized by single crystal and powder X-ray diffraction, UV-VIS, and FTIR spectroscopies. The packing diagram of each complex has been analyzed in order to identify all the supramolecular interactions involved in the crystal architecture. In the case of crystals **2** and **3** short intermolecular O···O contacts have been observed.



INTRODUCTION

Schiff bases are recognized for their versatility as ligands, leading to a plethora of coordination compounds that are promising candidates for applications in magnetism,¹ catalysis,² or biology.³ Numerous Schiff bases are derived from *o*-vanillin.⁴ A structurally related aldehyde is 2,3-dihydroxybenzaldehyde, with two vicinal phenolic groups, which represents another precursor for the synthesis of various Schiff bases and their complexes.

The majority of the nickel(II) complexes, generated by Schiff bases derived from 2,3-dihydroxybenzaldehyde, are mononuclear species.^{5–15} This observation remains valid even when the partner involved in the Schiff reaction is a monoamine (*e.g.* 2-aminophenol),⁵ a diamine (*e.g.* *o*-phenylenediamine,⁶ 2,3-diamino-2,3-dimethylbutane,⁷ 1,2-diamino-2-methylpropane⁸), an acetylhydrazide (acetic hydrazide),⁹ a semicarbazide (hydrochloric semicarbazide),¹⁰ or a thiosemicarbazide derivate (thiosemicarbazide,¹¹ 4-methyl-3-thiosemicarbazide,¹¹ 4-ethyl-3-thiosemicarbazide,^{11,12}

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etc.). Dinuclear Ni(II) complexes are obtained when a coligand, such as 1,2-bis(diphenylphosphino) ethane, is introduced in the reaction with the Schiff bases synthesized from 2,3-dihydroxybenzaldehyde and various thiosemicarbazides.¹³ On the other hand, tetranuclear Ni(II) complexes are generated starting from nickel(II) acetate,¹⁴ respectively nickel(II) nitrate,¹⁵ when the Schiff base is formed using a monoamine, 2-(2-aminophenyl) benzimidazole,¹⁴ or an aroylhydrazide, namely 2-hydroxybenzohydrazide.¹⁵ Most of these compounds have been investigated for their catalytic^{5,9,15} and biological activities.^{6,11,12,14} A tetranuclear Cu(II) compound represents the first example in the literature of a complex formed with the Schiff base obtained through the condensation of 2,3-dihydroxybenzaldehyde and 2-(aminoethyl) pyridine (H_2L).¹⁶ In a recent paper, our group described the synthesis, crystal structures, and luminescent properties of four Zn(II) complexes which were obtained from the same ligand.¹⁷ Herein, we report the synthesis and structural characterization of three new Ni(II) complexes: $[Ni(HL)_2][Ni(H_2L)_2](ClO_4)_2 \cdot 2C_2H_5N$ (**1**), $[Ni_2(HL)_2(NO_3)_2]$ (**2**), and $[Ni_2(HL)_2(hfac)_2]$ (**3**), which are also based on the aforementioned Schiff base.

RESULTS AND DISCUSSION

The new nickel(II) complexes have been obtained by reacting the Schiff base derived from 2,3-dihydroxybenzaldehyde and 2-(aminoethyl)pyridine (H_2L) with various nickel(II) precursors such as perchlorate, nitrate, and hexafluoroacetylacetonate

($hfac^-$). The crystalline phases of the synthesized complexes were verified for their purity through powder X-ray diffraction (Fig. S1). The infrared spectra for complexes **1-3** indicate the presence of the Schiff base through the band assigned to $\nu(C=N)$ vibration, located between $1630-1655\text{ cm}^{-1}$, and the band situated in the range $3450-3360\text{ cm}^{-1}$, which is due to the hydrogen bonds involving the phenolic groups. Other characteristic bands are observed for perchlorate ($\nu(ClO_4^-)$: $1099, 1062$ and 623 cm^{-1}), chelating nitrate ($\nu(N=O)$: 1483 , $\nu_a(NO_2)$: 1269 and $\nu_s(NO_2)$: 1014 cm^{-1}),¹⁸ and $hfac^-$ ($\nu(C-F)$: $1255, 1199$ and 1149 cm^{-1}) ions.

Description of the structures

The single crystal X-ray diffraction analysis showed that **1** crystallizes in a monoclinic space group $I2/a$ and contains a mononuclear neutral and cationic species, $[Ni(HL)_2]$ and $[Ni(H_2L)_2]^{2+}$, two perchlorate anions, and two acetonitrile molecules. The structures of the complex species in crystal **1** are presented in Fig. 1a. The Schiff base ligand acts as a chelating agent to the Ni1 ion in its monodeprotonated form (HL^-), coordinating through an iminic nitrogen, a pyridinic nitrogen, and a phenoxido oxygen atom. In its neutral form (H_2L), the ligand acts similarly to the Ni2 ion, but, in this case, the oxygen coordinated to the metal ion is a phenolic one. The tridentate coordination modes of the ligands are depicted in Figs. 1b and 1c. Each nickel ion, from the two crystallographically independent units, is surrounded by two ligand molecules, which are coordinated in a *meridional* arrangement.

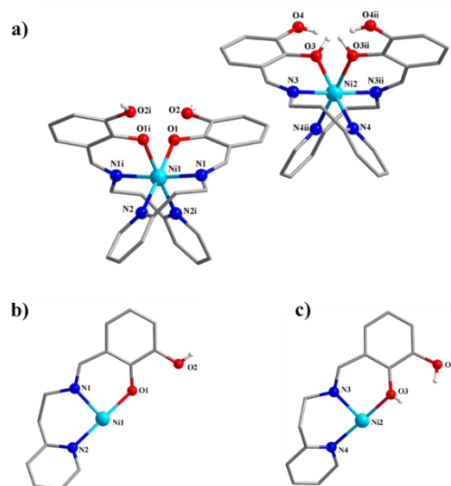


Fig. 1 – a) Perspective view of the complex species in crystal **1**; b) Coordination mode of HL^- in $[Ni(HL)_2]$ neutral species; c) Coordination mode of H_2L in $[Ni(H_2L)_2]^{2+}$. Perchlorate anions and acetonitrile molecules are omitted for clarity ($i = 1/2-x, y, 1-z$; $ii = 3/2-x, y, 1-z$)

Within the neutral unit, the two phenoxido oxygen atoms (O1 and O1i), respectively the two pyridinic nitrogen (N2 and N2i) atoms are disposed in *cis* positions, while the two iminic nitrogen atoms (N1 and N1i) are positioned *trans* to each other. The values of the O1i-Ni1-O1, N2i-Ni1-N2, and N1i-Ni1-N1 angles are equal to 82.2(1), 89.5(2), and 175.3(3)°, respectively ($i = \frac{1}{2}-x, y, 1-z$). The cationic unit displays a similar arrangement of the donor atoms, with the O3ii-Ni2-O3, N4ii-Ni2-N4, and N3ii-Ni2-N3 angles being 83.5(2), 90.9(3), and 178.1(2)°, respectively ($ii = 1-x, 1-y, 1-z$). Both Ni1

and Ni2 present a distorted octahedral geometry, a conclusion that is also validated by the SHAPE program¹⁹ (CShM ~ 0.181 for Ni1, respectively CShM ~ 0.160 for Ni2). The bond lengths of Ni1-O1_{phenoxido} (2.108(2) Å) and Ni1-N1_{iminic} (2.059(3) Å) from the neutral unit are longer than the Ni2-O3_{phenolic} (2.102(3) Å) and Ni2-N3_{iminic} (2.057(3) Å) bonds from the cationic unit. On the other hand, the bond length between Ni1-N2_{pyridine} (2.138(3) Å) is shorter compared with Ni2-N4_{pyridine} (2.161(3) Å). The crystallographic data are given in Table 1. Selected bond lengths and angles are presented in the Table 2.

Table 1

Crystallographic data, details of data collection and structure refinement parameters for compounds 1-3.

Complex	1	2	3
Empirical formula	C ₆₀ H ₆₀ N ₁₀ Ni ₂ O ₁₆ Cl ₂	C ₂₈ H ₂₆ N ₆ Ni ₂ O ₁₀	C ₃₈ H ₂₈ N ₄ Ni ₂ O ₈ F ₁₂
Formula weight	1365.50	723.97	1014.06
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	monoclinic	monoclinic	Triclinic
Space group	<i>I</i> 2/a	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1
a (Å)	20.9277(7)	10.4569(5)	10.5173(3)
b (Å)	13.8282(4)	11.6682(5)	11.8611(3)
c (Å)	20.2110(7)	12.0058(5)	16.8535(4)
α (°)	90	90	97.011(2)
β (°)	92.4443(4)	91.963(4)	98.980(2)
γ (°)	90	90	101.166(2)
Volume (Å ³)	5843.6(3)	1464.01(11)	2012.02(9)
Z	4	2	2
D _c (g/cm ³)	1.552	1.642	1.674
Absorption coefficient (mm ⁻¹)	0.817	1.355	1.049
<i>F</i> (000)	2832.0	744.0	1024.0
Reflections collected	17727	13687	19328
Independent reflections [<i>R</i> _{int}]	5116 [<i>R</i> _{int} = 0.0313]	3653 [<i>R</i> _{int} = 0.0326]	7040 [<i>R</i> _{int} = 0.0299]
Completeness to θ full (%)	99.2	99.5	99.6
Data/restraints/parameters	5116/1/413	3653/0/209	7040/30/688
Goodness of fit on <i>F</i> ²	1.175	1.052	1.031
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ <i>I</i>]	0.0538, 0.1438	0.0301, 0.0721	0.0290, 0.0744
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0595, 0.1465	0.0407, 0.0768	0.0360, 0.0772
Largest diff. peak/hole (eÅ ⁻³)	1.19/-0.33	0.25/-0.41	0.25/-0.31

Table 2

Selected bond distances (Å) and angles (°) for compounds 1-3.

	1	2	3
Distances (Å)			
Ni1-O	2.108(2)	Ni1-O1	2.057(2)
Ni1-O1 ⁱ	2.108(2)	Ni1-O1 ⁱ	2.079(2)
Ni1-N1 ⁱ	2.059(3)	Ni1-O3	2.111(2)
Ni1-N1	2.059(3)	Ni1-N2	2.077(2)
Ni1-N2 ⁱ	2.138(3)	Ni1-O4	2.138(2)
Ni1-N2	2.138(3)	Ni1-N1	2.017(2)
Ni2-O3 ⁱⁱ	2.102(3)		Ni1-N2
Ni2-O3	2.102(3)		Ni2-O6
Ni2-N3	2.057(3)		Ni2-O6 ⁱⁱ
Ni2-N3 ⁱⁱ	2.057(3)		Ni2-O7
Ni2-N4	2.161(3)		Ni2-O8
Ni2-N4 ⁱ	2.161(3)		Ni2-N3
			Ni2-N4

(Continuare)

1	2	3			
Angles (°)					
O1 Ni1 O1 ⁱ	82.2(1)	O1 Ni1 O1 ⁱ	82.0(1)	O1 Ni1 O1 ⁱ	82.3(1)
O1 Ni1 N2 ⁱ	94.1(1)	O1 Ni1 N2	174.4(1)	O1 Ni1 O3	87.3(1)
O1 Ni1 N2	176.3(1)	O1 Ni1 O3	89.3(1)	O1 Ni1 O4	91.5(1)
O1 ⁱ Ni1 N2 ⁱ	176.3(1)	O1 ⁱ Ni1 O3	160.5(1)	O1 Ni1 N2	173.3(1)
O1 ⁱ Ni1 N2	94.1(1)	O1 ⁱ Ni1 O4	100.8(1)	O3 Ni1 O1 ⁱ	93.8(1)
N1 ⁱ Ni1 O1 ⁱ	88.5(2)	O1 Ni1 O4	84.9(1)	O3 Ni1 O4	87.7(2)
N1 ⁱ Ni1 O1	87.9(2)	N2 Ni1 O1 ⁱ	95.9(1)	O3 Ni1 N2	89.8(1)
N1 Ni1 O1 ⁱ	87.9(2)	N2 Ni1 O3	90.9(1)	O4 Ni1 O1 ⁱ	173.5(2)
N1 Ni1 O1	88.5(2)	N2 Ni1 O4	90.3(1)	O4 Ni1 N2	94.3(2)
N1 Ni1 N1 ⁱ	175.3(3)	O3 Ni1 O4	60.9(1)	N1 Ni1 O1 ⁱ	90.4(1)
N1 Ni1 N2	91.4(2)	N1 Ni1 O1	89.8(1)	N1 Ni1 O1	88.1(1)
N1 Ni1 N2 ⁱ	91.7(2)	N1 Ni1 O1 ⁱ	95.1(2)	N1 Ni1 O3	173.3(1)
N1 ⁱ Ni1 N2	91.7(2)	N1 Ni1 N2	95.5(1)	N1 Ni1 O4	87.4(1)
N1 ⁱ Ni1 N2 ⁱ	91.4(2)	O3 Ni1 N1	102.2(1)	N1 Ni1 N2	95.2(1)
N2 ⁱ Ni1 N2	89.5(2)	N1 Ni1 O4	162.2(2)	N2 Ni1 O1 ⁱ	91.8(2)
O3 ⁱⁱ Ni2 O3	83.5(2)			O6 Ni2 O6 ⁱⁱ	79.5(1)
O3 ⁱⁱ Ni2 N4 ⁱⁱ	175.8(2)			O6 Ni2 O7	93.9(2)
O3 ⁱⁱ Ni2 N4	92.7(2)			O6 Ni2 O8	84.8(1)
O3 Ni2 N4 ⁱⁱ	92.7(2)			O6 Ni2 N3	89.2(1)
O3 Ni2 N4	175.8(2)			O6 Ni2 N4	172.2(1)
O3 Ni2 N3 ⁱⁱ	90.3(2)			O7 Ni2 O6 ⁱⁱ	173.5(1)
O3 ⁱⁱ Ni2 N3 ⁱⁱ	88.2(1)			O8 Ni2 O6 ⁱⁱ	92.5(1)
N3 Ni2 O3 ⁱⁱ	90.3(2)			O8 Ni2 O7	86.7(1)
N3 Ni2 O3	88.2(1)			O8 Ni2 N4	91.6(1)
N3 Ni2 N3 ⁱⁱ	178.1(2)			N3 Ni2 O6 ⁱⁱ	93.6(1)
N3 ⁱⁱ Ni2 N4	91.4(2)			N3 Ni2 O7	86.3(1)
N3 ⁱⁱ Ni2 N4 ⁱⁱ	89.8(2)			N3 Ni2 O8	170.5(2)
N3 Ni2 N4 ⁱⁱ	91.4(2)			N3 Ni2 N4	95.1(1)
N3 Ni2 N4	89.8(2)			N4 Ni2 O6 ⁱⁱ	93.7(1)
N4 Ni2 N4 ⁱⁱ	90.9(3)			N4 Ni2 O7	92.7(1)
$i = 0.5-x, y, 1-z; ii = 1.5-x, y, 1-z$			$i = 1-x, 1-y, 1-z$		
			$i = 2-x, 1-y, 2-z; ii = 1-x, 2-y, 1-z$		

The interactions at the supramolecular level within the crystal **1** (Fig. 2) consists of hydrogen bonds established between the cationic and neutral units, leading to a dimeric assembly. Intermolecular hydrogen bonds are formed with the phenolic groups of the cationic unit serving as hydrogen bond donors and the uncoordinated phenolic oxygen (O4ⁱⁱ...O2ⁱ = 2.743(4) Å; $i = 1/2-x, y, 1-z$; $ii = 1-x, 1-y, 1-z$), respectively the phenoxido oxygen (O3ⁱⁱ...O1ⁱ =

2.605(4) Å; $i = 1/2-x, y, 1-z$, $ii = 1-x, 1-y, 1-z$) of the neutral unit acting as hydrogen bond acceptors. Moreover, the cationic unit is stabilized through a weak intramolecular hydrogen bond (O4ⁱⁱ...O3ⁱⁱ = 2.771(4) Å; $\angle O4^{ii}-H\cdots O3^{ii} = 113.3(2)^\circ$ $ii = 1-x, 1-y, 1-z$).²⁰ The perchlorate anion is involved in a hydrogen bond with the uncoordinated phenolic group of the neutral unit (O2ⁱ...O8 = 2.818(6) Å; $i = 1/2-x, y, 1-z$; $ii = 1-x, 1-y, 1-z$).

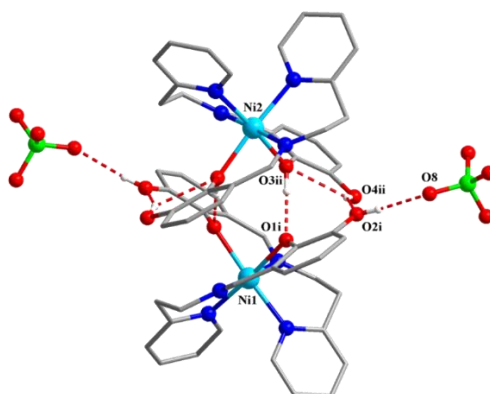


Fig. 2 – The hydrogen bonding interactions in the crystal **1**. Acetonitrile molecules are omitted for clarity ($i = 1/2-x, y, 1-z$, $ii = 1-x, 1-y, 1-z$).

Complex **2** crystallizes in the monoclinic space group $P2_1/n$, being a centrosymmetric dimer (Fig. 3), which consists of two $\{\text{Ni}(\text{HL})(\text{NO}_3)\}$ units that are bridged by two phenoxido oxygen atoms. The coordination environment of each nickel(II) contains two nitrogens atoms from the Schiff base ligand ($\text{Ni}-\text{N1} = 2.017(2)$ and $\text{Ni}-\text{N2} = 2.077(2)$ Å), two bridging phenoxido oxygen atoms ($\text{Ni1}-\text{O1} = 2.057(2)$ and $\text{Ni1}-\text{O1i} = 2.079(2)$ Å, $i = 1-x, 1-y, 1-z$), and two oxygen atoms from a chelating nitrate ($\text{Ni1}-\text{O3} = 2.111(2)$ and $\text{Ni1}-\text{O4} = 2.138(2)$ Å). Therefore, the geometry exhibited by the hexacoordinated nickel ions is that of a distorted octahedron, which is also confirmed by the SHAPE program ($\text{CShM} \sim 1.956$). The Schiff base is coordinated to each nickel ion in a *meridional*

orientation. The bond angles: $\text{O1}-\text{Ni}-\text{N2}$, $\text{O3}-\text{Ni}-\text{O4}$, and $\text{N1}-\text{Ni}-\text{O1i}$ have the following values: $174.4(1)$, $60.9(1)$, and $95.1(2)^\circ$, respectively ($i = 1-x, 1-y, 1-z$). The phenoxido oxygen and the pyridinic nitrogen of the same ligand are arranged in *trans* positions, while both oxygens that arise from nitrate, as well as the phenoxido oxygen of the adjacent ligand and iminic nitrogen, are found in a *cis* arrangement. The intramolecular distance between the two nickel ions is $3.0974(3)$ Å, and the angle formed between them ($\text{Ni1}-\text{O1}-\text{Ni1i}$, $i = 1-x, 1-y, 1-z$) is $97.9(1)^\circ$. The dimeric structure of the complex is stabilized through a weak²⁰ intermolecular hydrogen bond ($\text{O2}\cdots\text{O1} = 2.631(2)$ Å, $\angle\text{O2}-\text{H}\cdots\text{O1} = 115.7(1)^\circ$).

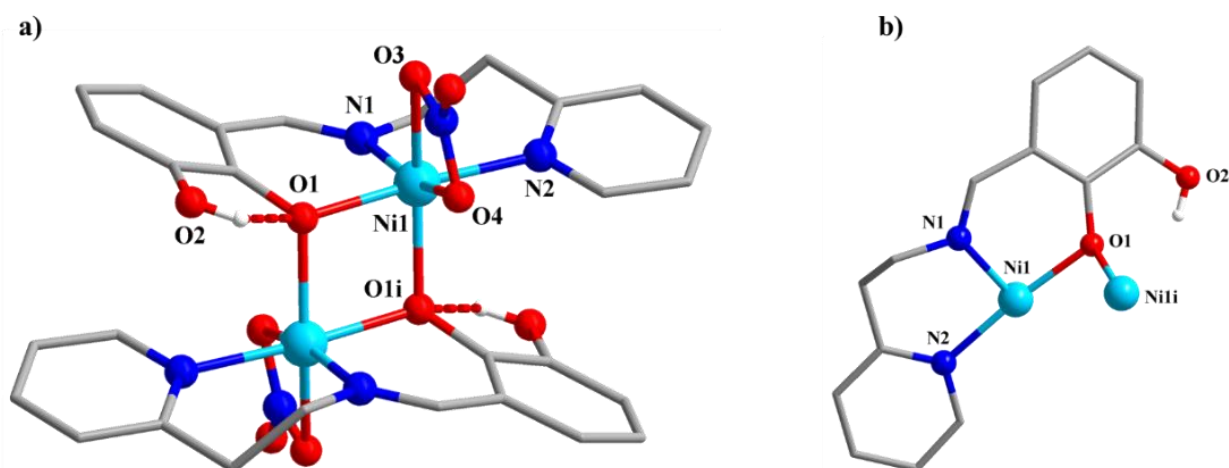


Fig. 3 – a) Perspective view of the complex **2**; b) Coordination mode of HL. Hydrogen atoms are omitted for clarity ($i = 1-x, 1-y, 1-z$).

The packing diagram of the crystal **2** reveals the formation of one-dimensional supramolecular zigzag chains that are arranged parallel to one another. Interestingly, these 1D polymeric structures are generated through the $\text{O}\cdots\text{O}$ interactions ($\text{O5}\cdots\text{O5ii} = 2.895(3)$ Å, $ii = 1-x, 2-y, 1-z$), that occur between the nitrate ligands from two neighboring binuclear units (Fig. 4). The role of these interactions in crystal packing has been previously investigated, and their values should be less than the sum of the two van der Waals radii for an oxygen atom (3.04 Å).^{21–24}

The structure of complex **3** (Fig. 5) closely resembles that of the complex **2**. A notable difference is that it crystallizes in a triclinic space group $P-1$, and it comprises two centrosymmetric dimers that are crystallographically independent. The chelating Schiff base ligand is coordinated to

each nickel ion, occupying *meridional* positions. Additionally, the coordination sphere of the each metallic ion is completed by two oxygens that arise from the chelating hexafluoroacetylacetonato anion, as well as by a phenoxido oxygen that comes from the ligand coordinated to the other nickel ion. Using the SHAPE program, the coordination geometry of the hexacoordinated Ni1 and Ni2 ions can be described as a distorted octahedral ($\text{CShM} \sim 0.319$ for Ni1 and $\text{CShM} \sim 0.480$ for Ni2). The intramolecular distances between the two nickel ions are $3.127(1)$ Å for $\text{Ni1}-\text{Ni1i}$ ($i = 2-x, 1-y, 2-z$), and $3.191(1)$ Å for $\text{Ni2}-\text{Ni2ii}$ ($ii = 1-x, 2-y, 1-z$). The values for the $\text{Ni1}-\text{O1}-\text{Ni1i}$ and $\text{Ni2}-\text{O6}-\text{Ni2ii}$ angles are equal to $97.6(2)$ and $100.4(1)^\circ$, respectively ($i = 2-x, 1-y, 2-z$; $ii = 1-x, 2-y, 1-z$). Other bond lengths and angles are presented in Table 2.

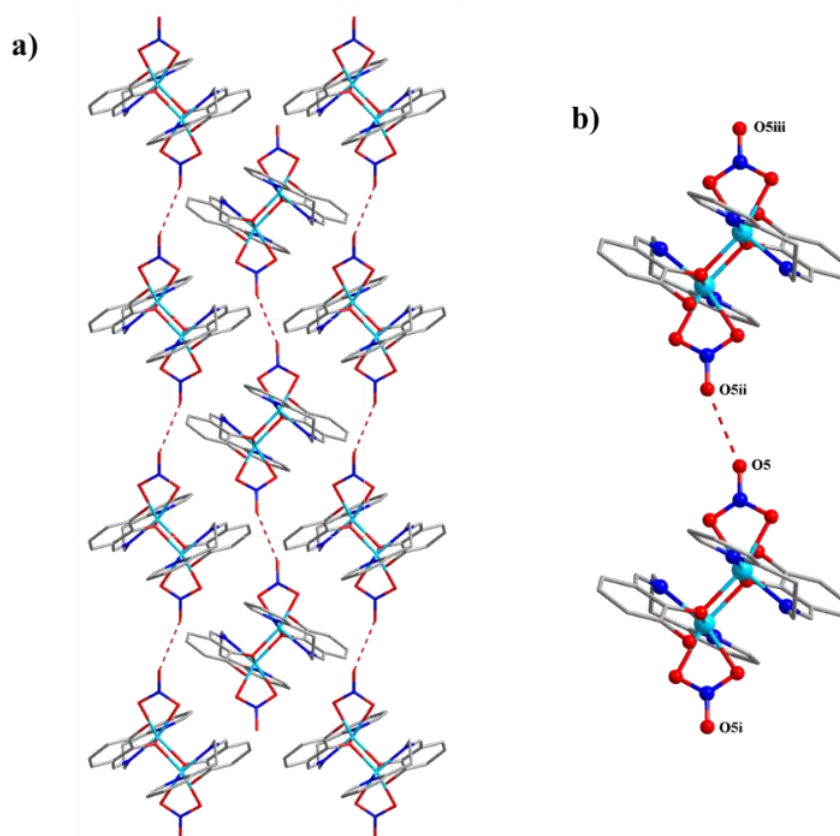


Fig. 4 – a) The packing diagram for crystal **2** (view along the crystallographic *c*-axis); b) Detail of the packing diagram for crystal **2**, showing intermolecular O \cdots O interactions (red dotted lines). Hydrogen atoms are omitted for clarity ($i = 1-x, 1-y, 1-z$; $ii = 1-x, 2-y, 1-z$, $iii = x, 1 + y, z$).

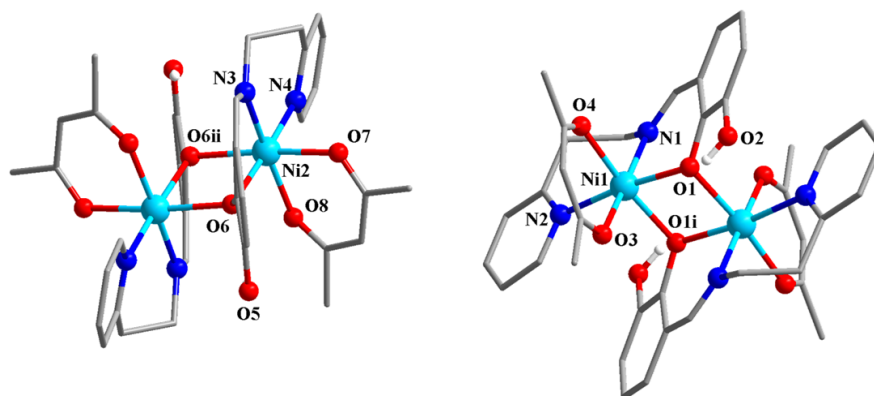


Fig. 5 – Perspective view of crystallographically independent binuclear species in crystal **3**. Hydrogen and fluorine atoms are omitted for clarity ($i = 2-x, 1-y, 2-z$; $ii = 1-x, 2-y, 1-z$).

Regarding supramolecular interactions within crystal **3** (Fig. 6), short F \cdots F contacts between different CF₃ groups of the hfac⁻ anions are observed (F11Bii \cdots F4B = 2.842(15) Å, $ii = 1 + x, y, z$). It is important to note that the three fluorine atoms from every CF₃ group are disordered over six crystallographic positions, each having an occupancy of 0.5. Furthermore, C-H \cdots F interactions occur between the fluorine atom of the CF₃ group of the hfac⁻ anion and the C-H bonds of the benzene ring

(C5-H5A \cdots F9Ai = 2.555(10) Å, C5i-H5Ai \cdots F9A = 2.551(10) Å, $i = 2-x, 2-y, 1-z$). These type of interactions are specific for compounds that features fluorine atoms.^{25,26} Figure 6 also reveals the presence of O \cdots O interactions between the phenolic oxygen atoms of two vicinal molecules (O2 \cdots O2iii = 2.891(2) Å, $iii = 3-x, 1-y, 2-z$). Similar to the crystal **2**, intramolecular hydrogen bonds are established between phenolic and phenoxido oxygen atoms (O2 \cdots O1 = 2.658(2) Å, O5 \cdots O6 = 2.619(2) Å).

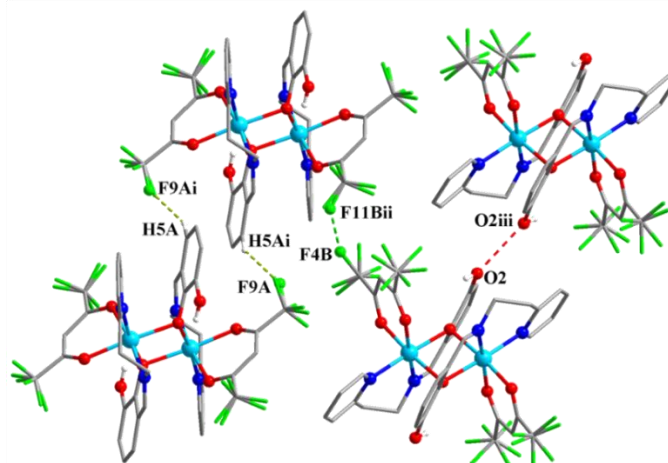


Fig. 6 – The supramolecular interactions within the crystal **3**, O...O interactions (red dotted lines) and C-H...F and F...F interactions (green dotted lines). Hydrogen atoms are omitted for clarity ($i = 2-x, 2-y, 1-z$; $ii = 1+x, y, z$; $iii = 3-x, 1-y, 2-z$).

The electronic spectra of complexes **1-3** show the characteristic *d-d* bands of (pseudo)octahedral nickel(II) chromophores. These bands are identified at 905–920 nm, 550–610 nm, and 370–390 nm arising from the ${}^3A_2 \rightarrow {}^3T_2$ (ν_1), ${}^3A_2 \rightarrow {}^3T_1$ (3F) (ν_2), and ${}^3A_2 \rightarrow {}^3T_1$ (3P) (ν_3) transitions, respectively, assuming the *O* point group. As shown in Fig. 7, the

band due to the ν_1 transition is splitted because of the low symmetry, into two components located between 1125–1145 nm. The forbidden transition (${}^3A_2 \rightarrow {}^1E$) band is identified for complexes **2** and **3** at 787 and 779 nm, respectively.²⁷ Additionally, the bands in the range 215–330 nm are attributed to the $\pi-\pi^*$ and $n-\pi^*$ electronic transitions of the Schiff base ligand.

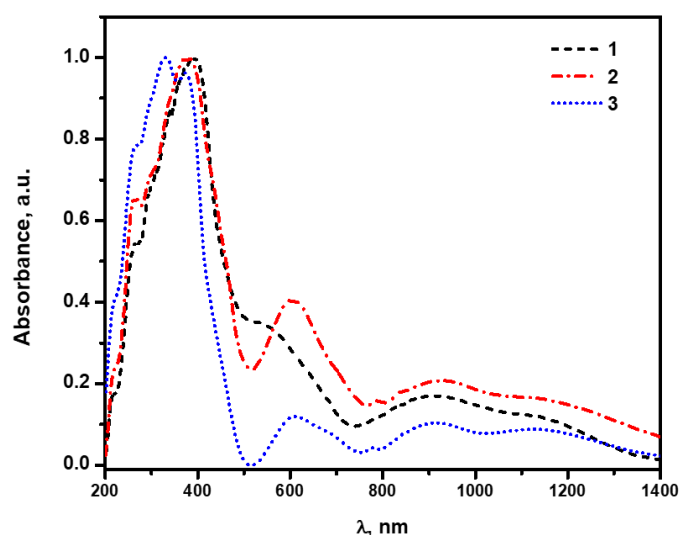


Fig. 7 – The electronic spectra of complexes **1-3**.

EXPERIMENTAL

All chemical substances were purchased from commercial suppliers and utilized without any additional purification processes.

Synthesis of $[\text{Ni}(\text{HL})_2][\text{Ni}(\text{H}_2\text{L})_2](\text{ClO}_4)_2 \cdot (\text{ACN})_2$ (**1**)

To a 10 mL solution of 2,3-dihydroxybenzaldehyde (0.1 mmol; 0.0138 g) in acetonitrile, 2-(aminoethyl) pyridine (0.1 mmol; 12 μL) was added. After one

hour, the *in situ* prepared Schiff base was mixed with 10 mL acetonitrile solution of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, and stirring continued for another hour. The final green solution was filtered, and within one week green block crystals have been obtained. Yield: 16,2%; IR (KBr, cm^{-1}): 3360m, 2927w, 1633s, 1604m, 1446m, 1413m, 1363w, 1284m, 1215w, 1099s, 1062m, 1022w, 985w, 850w, 775m, 731m, 623m, 568w, 541w, 499w, 433w.

Synthesis of $[\text{Ni}_2(\text{HL})_2(\text{NO}_3)_2]$ (**2**)

The synthesis of complex **2** followed a procedure that is similar to that of complex **1**, with the use of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ instead of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, while isopropanol has served as a solvent. The final green solution was filtered and layered with diethylether. The green block crystals appeared in two weeks. Yield: 37,65%; IR (KBr, cm^{-1}): 3423s, 3039w, 2927w, 2862w, 1631s, 1606m, 1570w, 1483s, 1462s, 1400m, 1385m, 1282s, 1269s, 1230m, 1145w, 1107w, 1064w, 1014w, 964w, 856m, 769m, 748m, 623w, 594w, 568w, 540m, 430w.

Synthesis of $[\text{Ni}_2(\text{HL})_2(\text{hfac})_2]$ (**3**)

A 10 mL dichloromethane solution of the Schiff base, prepared in a manner comparable to that for complex **1**, was added to a 20 mL boiling solution of $\text{Ni}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}$ in heptane. The resulting green solution was filtered and the next day elongated green plate-like crystals had emerged. Yield: 39,4%; IR (KBr, cm^{-1}): 3450w, 3392w, 2925w, 1651s, 1608m, 1548m, 1519m, 1462m, 1402w, 1340w, 1255s, 1199m, 1149s, 972w, 856w, 790m, 744m, 669m, 582m, 543m, 426w.

Crystal structure determination and refinement

The crystallographic data for compounds **1-3** were collected on a Rigaku XtaLAB Synergy, Single source at offset/far, HyPix diffractometer equipped with a graphite-monochromated Mo K α radiation source ($\lambda = 0.71073\text{\AA}$). The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction.²⁸ The structures were solved by direct methods and refined by full-matrix least squares techniques based on F^2 , using SHELXT and SHELXL-2015/2018 crystallographic software packages.²⁹ The non-H atoms were refined anisotropically and the hydrogen atoms were refined using riding constrains. A summary of the crystallographic data and the structure refinement is given in Table 1, while selected bond lengths and angles are shown in Table 2. CCDC reference numbers: 2428712 (crystal **1**); 2428713 (crystal **2**); 2428714 (crystal **3**).

Physical measurements

The FT-IR spectra were recorded using KBr pellets on a Bruker Tensor 27 spectrophotometer with a range between 4000 and 400 cm^{-1} . The electronic spectra were obtained from solid state samples utilizing the diffuse reflectance technique with Spectralon as the standard, on a Jasco V670

spectrophotometer. The X-ray powder diffraction measurements were conducted over a 5–35° (2 θ) range on a Proto AXRD benchtop using Cu-K α radiation with a wavelength of 1.54059 \AA .

CONCLUSIONS

Three new nickel(II) complexes have been obtained utilizing a tetradentate Schiff base ligand derived from 2,3-dihydroxybenzaldehyde and 2-(aminoethyl)pyridine. The use of three distinct nickel(II) precursors generates different nuclearities of the resulting complexes. Starting from nickel(II) perchlorate, two mononuclear species (cationic and neutral) are formed and co-crystallize. When nickel(II) nitrate and nickel(II) hexafluoroacetylacetonate are employed, dinuclear, centrosymmetric complexes are assembled. In all cases, the UV-Vis spectra indicate (pseudo)octahedral geometries of the nickel(II) ion, in line with the single crystal X-ray diffraction measurements.

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