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Three new *O*,*N*-coordinated Ni(II) complexes: Syntheses, crystal structures, and MOCVD applications



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ABSTRACT

Three new O_{N} -coordinated nickel (II) complexes, namely, Ni $(dmpda(acac)_2)$ (1), Ni $(pda)(acac)_2$ (2) and $Ni(pda)(tfac)_2$ (3) have been synthesized ($(dmpda(acac)_2 - N,N'-(2,2-dimethyl-1,3-diaminopropane)-bis-$ (2,4-pentanedioniminoato(2-), acac - 2,4-pentanedionato(-), pda - 1,3-diaminopropane, tfac - 1,1trifluoroacetylacetonato(-)) and tested as new precursors for metal-organic chemical vapor deposition (MOCVD). The structures of 1-3 were determined by single-crystal X-ray diffraction (XRD) and further characterized by IR and Raman spectroscopies. All three compounds crystallize in the triclinic space group $P\overline{1}$ with unit cell parameters of a = 9.0294(6), b = 9.2879(6), c = 10.4065(6) Å, $\alpha = 74.855(3)$, $\beta = 68.717(3), \gamma = 78.708(3)$ for 1; a = 7.6947(2), b = 10.3087(3), c = 10.7144(3) Å, $\alpha = 101.784(1), c = 10.7144(3)$ Å, $\alpha = 101.784(1), c = 10.714(1), c =$ $\beta = 95.367(1), \gamma = 106.134(1)$ for **2**; and a = 7.8931(5), b = 10.8803(8), c = 10.9438(7) Å, $\alpha = 103.283(2), c = 10.9438(7)$ Å, $\alpha = 10.9$ $\beta = 97.070(3), \gamma = 103.050(2)$ for **3**. The density functional theory (B3LYP) quantum chemical calculations have been used for detailed assignment of all intense bands in the vibrational spectra of the compounds studied. Thermal gravimetric analysis (TG/DTA) has shown that the species 1 and 3 sublime almost without decomposition, and 2 decomposes to some extent. MOCVD test experiments were carried out at low pressure (10 Torr) using 1 and 3 as precursors on Ta/Si substrates. The films have been characterized by X-ray powder diffraction, scanning electron microscopy, and energy dispersive spectroscopy were found to be primarily composed either of fcc-Ni or Ni₃C phases. The phase composition of the films strongly depends on the MOCVD conditions.

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1. Introduction

Nickel thin films are of significant interest for numerous fields of science and applications. Due to their remarkable properties, e.g., high resistance to oxidation and corrosion and low electrical resistivity, they are widely used in electronics for metallization of the ferrites and *n*-type SiC [1–3] and as selective absorbers for solar thermal energy conversion [4]. The composite Ni/CrN coatings are of wide use in the nuclear industry [5,6]; and Ni/TiO₂ [7,8], and Ni/YSZ composites [9] are interesting for catalysis and electronics. Apart from this, due to their giant magnetoresistance, the Co/Ni thin films are also employed in magnetic storage devices [10].

Among the huge variety of techniques employed for deposition of the Ni thin films (e.g., Physical Vapor Deposition, Ionized Metal PVD), Metal-Organic Chemical Vapor Deposition (MOCVD) allows to produce films and nanostructures of highly uniform thickness and composition, with conformal step coverage, minimal substrate damage and selected area growth [11]. Moreover, this method provides uniform coverage of the substrate surface in the case of non-planar device geometries. It is well known that the choice of precursor and MOCVD parameters might affect the growth process and molecular organization of thin metal films. Significant efforts have been made so far toward design of new precursors, growth methods, and, ultimately, to control the structure (e.g., molecular organization, polymorphism, and morphology) of the Ni films.

The suitable MOCVD precursors should satisfy several requirements, namely, "adequate volatility, stability, high chemical purity, sufficiently large «window» between evaporation and decomposition for the film deposition, and clean decomposition"

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[12]. Apart from this, the precursors should be nontoxic, stable in the air atmosphere, and should be easily synthesized from available reagents.

The high toxicity of a long time known nickel tetracarbonyl restricts the use of Ni(CO)₄ in the CVD applications. Several other MOCVD Ni-containing precursors have been proposed so far: Ni(η^5 -C₅H₅)₂ [13,14], Ni(*deg*)₂, Ni(*dmg*)₂ (*deg* – 3,4-hexanedionedioxime, *dmg* – 2,3-butanedionedioxime) [15]. However, applications of these complexes are also limited, mainly due to incomplete volatilization of the species. At the same time, the nickel β -diketonates [16–20] meet almost all above discussed requirements. However, these species are liable to oligomerization [21]. This usually renders the volatility of the species to be quite low [21] and therefore limits their application in MOCVD.

To overcome this obstacle, two approaches to design of Ni complexes have recently been proposed. In the framework of the first method, the oxygen atom in the ligand is replaced with nitrogen. The nickel complexes with nitrogen-containing chelating ligands turned out to exist as monomers [22-26]. At the same time, the volatility of O,N-coordinated square-planar Ni(II) complexes was higher in comparison with their 0,0-coordinated counterparts [22–26]. Moreover, the deposition of Ni films [27,28] using the Schiff base nickel complexes as precursors has been reported. The second method exploits the idea of changing of the Ni coordination number (CN) from 4 to 6 by addition of neutral diamine ligands [29-35]. For instance, the authors [32,33] have shown that the complexes Ni(diamine)(hfac)₂ could be used as MOCVD precursors for the deposition of Ni₃C films. Some of us [36] have recently found $Ni(pda)(hfac)_2$ and $Ni(pda)(thd)_2(pda-1,3-diaminopropane, hfac - 1,3-diaminopropane)$ 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato(–), thd - 2,2,6,6tetramethyl-3,5-heptanedionato(-)) to be efficient precursors for the MOCVD of Ni thin films.

In the present contribution, we describe the X-ray structural data, and thermal properties of three new *O*,*N*-coordination Ni(II) complexes synthesized in accordance with the two approaches discussed above. Namely, Ni(*dmpda*(*acac*)₂) (**1**) is an *O*,*N*-coordinated square-planar complex (CN = 4), and the mixed-ligand compounds Ni(*pda*)(*acac*)₂ (**2**) and Ni(*pda*)(*tfac*)₂ (**3**) have CN = 6 (*dmpda*(*acac*)₂ - *N*,*N'*-(2,2-dimethyl-1,3-diaminopropane)-bis-(2,4-pentanedioniminoato(2-)), *acac* - 2,4-pentanedionato(-), *pda* - 1,3-diaminopropane, *tfac* - 1,1,1-trifluoroacetylacet-onato(-)). Furthermore, two complexes, viz., **1** and **3**, were tested as MOCVD precursors.

2. Experimental

2.1. Materials

The chemicals, liq. 1,3-diaminopropane (*pda*) (Merck, purity, >98%) and 2,2-dimethyl-1,3-diaminopropane (*dmpda*) (Merck, purity, >98%), Ni(NO₃)₂•6H₂O and NiCl₂•6H₂O (Dalchem, Russia, purity > 97%), 2,4-pentanedione (Hacac) (Dalchem, Russia, purity > 98%) and 1,1,1-trifluoro-2,4-pentanedione (H*tfac*) (Invest, Russia, purity > 98%) were used as original substances in the syntheses of Ni(II) complexes. The solvents (methanol and ethanol) were purified before the use. NiCl₂ was obtained by incineration of Ni[(NH₃)₆]Cl₂ at 200 °C for 6 h.

2.2. Element analysis and spectral characterizations of complexes

The ¹H and ¹³C NMR spectra were recorded using a Bruker AVANCE 500 spectrometer. The chemical shifts were measured relative to the chloroform signal and were recalculated relative to TMS. The infrared spectra of the compounds in polyethylene and KBr pellets were measured using a Vertex 80 FTIR spectrometer. The Raman spectra were recorded with a Triplemate SPEX spectrometer equipped with CCD spectrometric detector and a microscope attachment for back scattering experimental geometry. The 488 nm, 10 mW line of an Ar-laser was used for the spectral excitation. The differential thermal analysis (TG/DTA) was carried out by Netzsch STA 409 PC/PGin He flow (20 ml min⁻¹) with a heating rate 10 °C/min in the temperature range 25–500 °C. The samples of 1.0–3.0 mg weight were loaded in an α -alumina crucible (5 × 5 mm).

2.2.1. Synthesis of Ni(dmpda(acac)₂) (1)

The square-planar complex $Ni(dmpda(acac)_2)$ was prepared in three stages. In the first stage, the ligand $(dmpda(Hacac)_2)$ was synthesized by slow addition of *dmpda* (0.02 mol, 2.0 ml) to Hacac (0.04 mol, 4.0 ml). The ligand was purified by recrystallization from hexane. In the second stage, the methanol solution (50 ml) of $Na_2(dmpda(acac)_2)$ was prepared in reaction of $(dmpda(Hacac)_2)$ (0.01 mol, 2.661 g) with metallic sodium (0.02 mol, 0.460 g) in CH₃OH during 24 h. The third stage was carried out in inert atmosphere using the Schlenk technique. The methanol solution of Na₂(*dmpda*(*acac*)₂) was added to solid NiCl₂ (0.02 mol, 2.596 g) in methanol (50 ml). The mixture was stirred for 6 h at the boiling temperature of a solvent. The dark green solid product was dried under nitrogen for 16 h and purified by vacuum sublimation at $P = 10^{-3}$ Torr, t = 130-140 °C (yield 60%). t_{mp} : 165–167 °C, Anal. Calc. for $C_{15}H_{18}O_2N_2N_i$ ($M = 321.06 \text{ g mol}^{-1}$, Ni: 18.1%): C, 47.1; H, 7.3; N, 8.3. Found: C, 47.2; H, 7.5; N, 8.2. The nickel content in three parallel samples was: 18.0, 18.3, and 18.2%, respectively (average -18.1%). ¹H NMR (25 °C, 500 MHz, CDCl₃): $\delta = 0.82$ [s, (CH₃)₂C(CH₂)₂]. $\delta = 1.79$ [s, 2(CH₃CNH-)], $\delta = 1.84$ [s, 2(CH₃CO)], $\delta = 3.09$ [s, $(CH_3)_2C(CH_2)_2$, $\delta = 4.79$ [s, 2(CH)]; ¹³C NMR (25 °C, 125.76 MHz, CDCl₃): $\delta = 20.49$ [s, 2(CH₃CNH-)], $\delta = 23.91$ [s, (CH₃)₂C(CH₂)₂], $\delta = 25.77$ [s, 2(CH₃CO)], $\delta = 36.72$ [s, (CH₃)₂C(CH₂)₂], $\delta = 57.70$ [s, $(CH_3)_2C(CH_2)_2$, $\delta = 100.30$ [s, 2(CH)], $\delta = 164.59$ [s, $2(CO)],\delta = 175.51$ [s, 2(CNH)].

2.2.2. Synthesis of $Ni(pda)(acac)_2$ (2)

The diamine *pda* (0.04 mol, 3.3 ml) was added to the stirred solution of NiCl₂•6H₂O (0.015 mol, 3.565 g) in C₂H₅OH (50 ml). After 2 h of stirring the Hacac (0.02 mol, 2.0 ml) was added. Then the solution was stirred for 2 h, and the light-blue solid was crystallized. The complex was dried in air and purified by vacuum sublimation at $P = 10^{-3}$ Torr, $t = 140-150 \degree$ C (yield 60%). t_{mp} : 209–212 °C, Anal. Calc. for C₁₃H₂₄O₄N₂Ni ($M = 331.05 \text{ g mol}^{-1}$, Ni: 17.7%): C, 47.1; H, 7.3; N, 8.3. Found: C, 47.2; H, 7.5; N, 8.2. The nickel content in three parallel samples was: 17.7, 17.3, and 17.4%, respectively (average - 17.5%).

2.2.3. Synthesis of $Ni(pda)(tfac)_2$ (3)

The diamine *pda* (0.04 mol, 3.3 ml) was added to the stirred solution of Ni(NO₃)₂•6H₂O (0.015 mol, 4.361 g) in C₂H₅OH (50 ml). After 30 min of stirring Htfac (0.02 mol, 3.1 ml) was added. Then the solution was stirred for 1 h, and green-blue solid was crystallized. The crystals were filtered, washed by acetone solution, dried in air, and purified by vacuum sublimation at $P = 10^{-3}$ Torr, t = 160-170 °C (yield 65%). t_{mp} : 206–208 °C, Anal. Calc. for C₁₃F₆H₁₈O₄N₂Ni ($M = 439.00 \text{ g mol}^{-1}$, Ni: 13.4%): C, 35.6; H, 4.1; N, 6.4; F, 25.8. Found: C, 36.0; H, 4.6; N, 6.4; F, 25.9. The nickel content in three parallel samples was: 13.0, 13.3, and 13.9%, respectively (average – 13.4%).

2.3. DFT computations

The IR and Raman spectra of the complexes 1-3 were calculated at the B3LYP/6-311++G(2df,p) level of theory [37,38]. The



Scheme 1. Synthesis of the ligand (dmpda(Hacac)2).

numerical integration of the exchange-correlation terms of the density functional was carried out using ultrafine grids. All calculations were performed using Gaussian 03 suite of programs. The experimental wavenumbers below 150 cm⁻¹ were not considered because of the strong mixing of collective lattice modes and internal vibrations in this range.

2.4. Single-crystal analysis

The structures of all compounds were solved by the singlecrystal X-ray diffraction analysis. Suitable single-crystals were placed on a Bruker Nonius X8 Apex 4K CCD diffractometer equipped with an X-ray source using graphite monochromated Mo-Ka radiation ($\lambda = 0.71073$ Å). The data were collected at 150 K for all structures by the standard technique [39]. Absorption corrections were made empirically using the SADABS program [39]. The structures were solved using the direct methods of the difference Fourier synthesis and were further refined by the full-matrix leastsquares method using the SHELXTL program package [40]. The positions of hydrogen atoms were calculated geometrically and refined in the framework of rigid body approximation (riding model). The crystallographic data and the details of the final refinement are given in the Supplementary Material (Table S1). The packing diagrams and ellipsoid representations were drawn using the POV-Ray engine [40,41].

2.5. Chemical vapor deposition and the properties of films

Thin films were deposited on Ta/Si substrates in an MOCVD vertical type reactor [42] at a reduced pressure value (10 Torr) using H₂ as a gas-reactant (flow 35 ml min⁻¹) and Ar (or H₂) as a gas-carrier (flow 15 ml min⁻¹). Before deposition, the substrates were washed with propanol, rinsed with distilled water, and swabbed with acetone. The MOCVD experiments were carried out using **1** as a precursor at the evaporator temperature $T_{evap} = 140 \,^{\circ}C$. The deposition temperatures were $T_s = 260-350 \,^{\circ}C$, and the deposition time was 4 h. The MOCVD experiments with precursor **3** were carried out at $T_{evap} = 120 \,^{\circ}C$, $T_s = 210-260 \,^{\circ}C$, the deposition time was 2 h. The decomposition of gaseous precursor in the reactor accompanied by the formation of black powder on the substrate surface was observed at higher deposition temperatures (>300 $^{\circ}C$).



Scheme 2. Synthesis of the Schiff base Na2(dmpda(acac)2).

The X-ray diffraction (XRD) experiments were performed at room temperature with a DRON-SEIFERT-RM4 diffractometer (CuK α radiation, a graphite monochromator in the reflected beam and a scintillation detector with amplitude discrimination). The spectra were recorded in the step-by-step mode in the angular range $2\theta = 25-65^{\circ}$.

The SEM (Scanning Electron Microscopy) and EDXS (Energy Dispersive X-ray Spectroscopy) investigations were carried out using JEOL-JSM 6700 F microscope connected with EDS-analyzer EX-2300 BU.

3. Results and discussion

3.1. Syntheses of the O,N-coordinated Ni(II) complexes 1-3

The Schiff base compounds Ni($en(acac)_2$) and Ni($pda(acac)_2$) ($en(acac)_2$) – N,N'-(1,2-diaminoethane)-bis-(2,4-pentanedioni minoato(2-)), ($pda(acac)_2$) – N,N'-(1,3-diaminopropane)-bis-(2,4pentanedioniminoato(2-)) were first prepared by reaction of hexahydrate nickel chloride with Schiff base ligands $en(Hacac)_2$, $pda(-Hacac)_2$ in acetone solution. The ligands were obtained by condensation of corresponding diamines with Hacac [43]. Note that the similar syntheses of Schiff base Ni(II) chelates in the argon atmosphere have recently been reported [27,28]. However, all our attempts to synthesize Ni($dmpda(acac)_2$) (1) using the reported methods [27,28] failed. Therefore, we modified this synthetic technique and have prepared the square-planar complex 1 in three stages.

At the first stage, the ligand $(dmpda(Hacac)_2)$ was prepared in accordance with Scheme 1. The ligand was purified by the recrystallization from hexane (note that the water solution has been used previously [43]) with the yield of 80%. The Schiff base compound Na₂ (*dmpda*(*acac*)₂) was obtained afterward according to Scheme 2. It should be noted that the sodium salt was used to prevent the formation of hydrochloric acid. Finally, the compound **1** was synthesized as shown in Scheme 3.

It is also worth mentioning that the anhydrous reagents (NiCl₂, CH_3OH) were used to avoid the destruction of the ligand $(dmpda(Hacac)_2)$. Even tiny amounts of water and mineral acids led to the decomposition of the ligand, shifted the equilibrium of Scheme 1 to the reagents [41], and therefore decreased the yield of the desirable products. It should be mentioned that the complex **1** is air-stable after a single cycle of purification and isolation.

The two other complexes Ni(pda)(acac)₂ (**2**) and Ni(pda)(tfac)₂ (**3**) were synthesized using the technique similar to the one proposed [32] to obtain the complex Ni(en)(hfac)₂ (en - 1,2-diaminoethane). Using this procedure we also synthesized such complexes as Ni(dmpda)(acac)₂ and Ni(dmpda)(hfac)₂.

3.2. Structure of the complexes 1–3

Single crystals of **1** were grown by evaporation from solution in benzene. Single crystals of **2** and **3** were grown by evaporation from



Scheme 3. Synthesis of the Ni(dmpda(acac)2) (1).

Table 1
Parameters of the MOCVD experiments and properties of films obtained.

Ni(dmpda(acac) ₂)	1	Ni(pda)(acac) ₂	2	Ni(pda)(tfac) ₂	3
Distance		Distance		Distance	
Ni(1)-O(1)	1.852(2)	Ni(1)-O(11)	2.038(1)	Ni(1)-O(11)	2.051(2)
Ni(1)-O(2)	1.856(3)	Ni(1)-O(21)	2.044(1)	Ni(1)-O(21)	2.052(2)
Ni(1)-N(1)	1.888(3)	Ni(1)-O(22)	2.058(1)	Ni(1)-O(12)	2.068(2)
Ni(1)-N(2)	1.893(3)	Ni(1)-O(12)	2.066(1)	Ni(1)-O(22)	2.071(2)
O(1)-C(1)	1.284(4)	Ni(1)-N(32)	2.089(1)	Ni(1)-N(2)	2.083(2)
O(2)-C(9)	1.293(4)	Ni(1)-N(31)	2.104(1)	Ni(1)-N(1)	2.087(2)
N(1)-C(3)	1.313(4)	O(11)-C(11)	1.257(2)	O(11)-C(11)	1.250(2)
N(1)-C(4)	1.468(5)	O(12)-C(13)	1.267(2)	O(12)-C(12)	1.272(2)
N(2)-C(6)	1.474(5)	O(21)-C(21)	1.265(2)	O(21)-C(21)	1.261(2)
N(2)-C(7)	1.320(5)	O(22)-C(22)	1.265(2)	O(22)-C(22)	1.264(2)
Angle		Angle		Angle	
O(1)-Ni(1)-O(2)	82.53(1)	O(21)-Ni(1)-O(22)	89.91(3)	O(11)-Ni(1)-O(12)	89.02(8)
N(1)-Ni(1)-N(2)	91.81(1)	O(11)-Ni(1)-O(12)	88.94(4)	O(21)-Ni(1)-O(22)	89.25(8)
O(1)-Ni(1)-N(1)	94.05(1)	N(32)-Ni(1)-N(31)	90.15(4)	N(2)-Ni(1)-N(1)	91.15(9)
O(2)-Ni(1)-N(2)	93.48(1)				

the solution mixture in acetone/ethyl acetate (molar ratio 4:1) at cooling down to 273 K.

The compound 1 has an isolated molecular structure. Selected structural parameters (bond distances and angles) of 1 are listed in Table 1. The molecular unit consists of Ni^{2+} cation and one ligand. The slightly distorted square (trapezoid) first coordination sphere of the Ni atom is formed by two N atoms of dmpda and, correspondingly, two O atoms of acac moieties (Fig. 1). Note that the Ni-O and Ni–N bond lengths are in the range of 1.852–1.893 Å (Table 1, first column) typical for low-spin nickel complexes (e.g., Ni(en(a- $(cac)_2$), Ni $(en(pacac)_2)$, and Ni $(en(tfac)_2)$ (pacac = 6,6-dimethyl-3,5hexanedionato(-))) [44–46]. It is worth mentioning the Ni²⁺ low-spin planar complexes are usually red (e.g., Ni(en(acac)₂) and Ni(en(tfac)₂) [44,46]) or yellow [47]. In contrast to this, the crystals of **1** are green. This fact might originate from the noticeable tetrahedral distortion of 1: the dihedral angle between O–Ni–O and N– Ni–N planes is ~15° (Fig. 1(a)) (cf. 1.5° and 2.4° for Ni($en(acac)_2$) and Ni(*en*(*tfac*)₂), respectively).

The packing of molecules in the crystals of **1** (Fig. 1(b)) is due to weak van der Waals contacts, e.g., the H^{...}H interactions. Therefore, the terminal groups of organic ligands retain the ability to rotate almost freely. It is also worth mentioning that in contrast to the case of **1**, the molecules of Ni(*en*(*pacac*)₂), Ni(*en*(*tfac*)₂), and Ni(*en*(*acac*)₂) stack above each other at a distance of *b*/2 forming the columns parallel to the *b* axis [44–46]. The shortest distance Ni–Ni in the neighboring complexes of **1** is 5.34 Å (cf. 4.65 Å in Ni(*en*(*acac*)₂) [44]). Similar to the case of **1**, the octahedral complexes **2** and **3** have the isolated molecular structures with very similar packing modes (Figs. 2 and 3).

The molecular units of **2** and **3** consist of Ni²⁺ cation, one 1,3diaminopropane and two β -diketonate ligands RC(O)CHC(O)CH₃ (**2**: R = CH₃, **3**: R = CF₃). The slightly distorted octahedral coordination sphere of the nickel cation is formed by two N atoms of *pda* and four O atoms of *acac/tfac* moieties, correspondingly (Figs. 2(a) and 3(a)). The average values of Ni–O and Ni–N bond lengths in **2** and **3** (2.06 and 2.09 Å) are typical of *high-spin* nickel complexes [29–36]. The chelate angles O–Ni–O and N–Ni–O are close to 90° for both complexes **2** and **3** (Table 1). In this case, the ligands (*pda* and *acac/tfac*) form the six-membered chelate rings.

The $-CH_3$ and $-CF_3$ groups in the one of *tfac* ligands in **3** may share two positions (Fig. 3(a)). This disorder results in the coexistence of *trans*- and *cis*-isomers (the *trans/cis* concentration ratio is 2:1) in the crystalline form of **3**. Similarly to the case of **1**, the packing of molecules in the crystals of **2** and **3** (Figs. 2(b) and 3(b)) is due to van der Waals contacts. Again, the terminal groups of organic ligands are able to rotate almost freely. Moreover, there are three symmetrically independent intermolecular hydrogen bonds N–H...O in the crystal structure of **2** (Fig. 2(b)). These H-bonds link molecules of **2** to infinite double chains along the direction [001] (Fig. 2(b)). The shortest distance Ni–Ni in the neighboring complexes of **2** is 5.17 Å (cf. 5.34 Å in **1**). Similarly to the case of **2**, the intermolecular H-bonds were also observed in the crystal structure of **3** (Fig. 3(b)).

It is instructive to compare the most important structural parameters of the species **1**, **2**, and **3**. Note that in accordance with the crystal field theory, the Ni²⁺ center adopts the low-spin state (singlet) in the planar coordination complexes, and the high-spin state (triplet) in the octahedral environment. As seen from Figs. 1-3



Fig. 1. (a) The formula unit of 1 as 50% probability thermal ellipsoids; (b) Packing diagram of the 1 molecules viewed along the b axis.



Fig. 2. (a)The formula unit of 2 as 50% probability thermal ellipsoids; (b) Hydrogen bonding pattern in the crystals of 2 (for clarity, the H atoms are omitted).

and Table 1, the Ni–O and Ni–N bond lengths in the planar complex 1 are ~0.2 Å shorter than those in 2 and 3 (octahedral coordination). Therefore, this difference is mainly due to the change of the spin state of Ni²⁺ in the complexes 1 and 2/3. On the other hand, the C–O distances in 1 are only slightly longer (0.02–0.03 Å) than their counterparts in 2 and 3. Contrary to the case of 1, the crystal unit cell of 3 is comprised of pairs, and the molecules of 2 form infinite double chains (Figs. 2 and 3). These facts might explain the high values of the melting points of 2 and 3 (recall that t_{mp} of 2/3 are in the range 205–210 °C, while t_{mp} of 1 is 165–167 °C).

3.3. Spectroscopic characterization

The complexes **1**–**3** were characterized by vibrational spectroscopy methods. The experimental IR spectra of **1**, **2**, and **3** are presented in Fig. 4.

The Far-IR and Raman spectra of the species studied are available in the Supplementary Material (Figures S1 and S2, respectively). In order to obtain comprehensive data and assign clearly all intensive bands in the vibrational spectra of 1-3, in the present study we combined the experimentally measured IR and Raman spectra and quantum chemical (DFT) calculations. The fully optimized geometries of the complexes (B3LYP/6-311++G(2df,p)) are also given in the Supplementary Material (Table S2). The

calculated bond lengths and angles of **1–3** are in good agreement with the corresponding experimental values. These results confirm the reliability of theoretical methods employed in the present work.

The calculated IR spectra of **1–3** are also presented in Fig. 4 (red curves). The assignment of experimental bands was primarily based on the calculated spectra of the complexes and on the IR intensity data. The comparison of experimental and calculated frequencies of the most intensive vibrations in the IR and Raman spectra and their assignments are presented in Tables (Supporting Information S3–S5). The experimentally measured vibrational frequencies of the molecules are in good agreement with the DFT theoretical predictions. The RMS difference between the calculated and experimental IR frequencies is about 15 cm⁻¹.

It is seen from Fig. 4 that the experimental IR and Raman spectra of the complexes are rather complex. Most parts of the intense peaks represent actually the mixture of several closely lying broadened vibrational modes. The most intensive bands in the predicted IR spectra of **1** and **2** compounds corresponding to C=C and C=O stretching vibrations of the diketonate cycle are located at 1520 and 1587 cm⁻¹ for **1** and at 1513 and 1603 cm⁻¹ for **2** (Fig. 4(a) and 4(b), Tables S3, S4), respectively. Due to the presence of CF₃ electron-withdrawing substituents in **3**, these bands are shifted to 1602 and 1632 cm⁻¹, correspondingly (Fig. 4(c)). Another intensive



Fig. 3. (a) The formula unit of 3 as 50% probability thermal ellipsoids; (b) Packing diagram of the 3 molecules viewed along the a axis.



Fig. 4. Experimental (black) and calculated (B3LYP/6-311++G(2df,p), red) IR spectra of (a) Ni(*dmpda*(*acac*)2) (1), (b) Ni(*pda*)(*acac*)2 (2), and (c) Ni(*pda*)(*tfac*)2 (3).

group of bands in the IR spectrum of **3** lies in the spectral range from 1160 to 1196 cm⁻¹ (Fig. 4(c)). These peaks are mainly attributed to C_{β} –F stretching vibrations with some contribution of the diketonate cycle deformation (Table S5). The intensive bands in the



Fig. 5. Thermogravimetry curves (heating rate -10 °C/min) for Ni(*dmpda*(*acac*)2) (**1**, green), Ni(*pda*)(*acac*)2 (**2**, red), Ni(*pda*)(*tfac*)2 (**3**, blue), Ni(*pda*)(*hfac*)2 (black).34 Ni(*pda*)(*thd*)2 (brown)0.34.

Table 2



Fig. 6. XRD patterns of the Ni films deposited from **3** at $T_s = 210 \bigcirc C(a)$, 230 $\bigcirc C(b)$, 260 $\bigcirc C$; Ar gas-carrier (*c*), 260 $\bigcirc C$; H₂ gas-carrier (*d*).

spectra of **1** and **2** were also located in the spectral region 1390– 1460 cm⁻¹ (Fig. 4(a) and 4(b), Tables S3 and S4). The main contributions to the corresponding normal modes are $\delta(HC_{\beta}H)$ of methyl substituents.

It is worth to be mentioned that the spectral regions corresponding to Ni–O and Ni–N stretching vibrations differ noticeably for compounds 1 and 2/3. This fact is due to different coordination patterns of the Ni atom. In the case of 1, the planar square coordination sphere of the metal center is formed by the two N atoms of dmpda and two O atoms of acac ligands (Fig. 1). On the contrary, the Ni centers in 2 and 3 have slightly distorted octahedral coordination (Figs. 2 and 3). Therefore, the Ni-O and Ni-N stretching modes in 1 overlap and appear at the same wavenumbers in the experimental spectra (468, 474, 688, 695 cm^{-1} , Fig. 4(a), Table S3). In the case of 2 and 3, the positions of Ni–O and Ni–N stretching modes are different. For instance, the modes with a maximal contribution of v(Ni-N) are observed at 319 and 376 cm⁻¹ in the IR spectrum of **2**, while v(Ni-O) is located at 414 cm⁻¹ and contributes to some other bands listed in Table S4. The Ni–O and Ni–N stretching vibrations in the spectra of **1** are mainly located at higher wavenumbers than those of 2 and 3. This is not surprising because, as discussed above, the Ni-O and Ni-N distances in 1 are ~ 0.2 Å shorter than their counterparts in 2 and **3** (Table 1).

3.4. Thermal behavior and volatility of the complexes 1–3

The thermogravimetry (TG) curves (heating rate 10 °C/min) for **1–3** in He (for the sake of comparison, the same data for the species

Selected bond lengths (Angstroms) and angles (degrees) for compounds 1–3.							
	No	Deposition conditions	Composition (major component, XRD data)	Average crystallite size (nm)	EDS, Ni , at%, C , at%, O , at%		
(3)	a b	$T_{evap} = 120 \ ^{\circ}C, T_{s} = 210 \ ^{\circ}C \ (Ar, 2 h)$ $T_{evap} = 120 \ ^{\circ}C, T_{s} = 230 \ ^{\circ}C \ (H_{2}, 2 h)$	fcc-Ni Ni ₃ C, <i>fcc</i> -Ni (traces)	10 45	Ni - 87.2, C - 10.5, O - 2.3 Ni - 68.4, C - 25.3, O - 6.3		
(1)	C d f g	$T_{evap} = 120 °C, T_s = 260 °C (Ar, 2 h)$ $T_{evap} = 120 °C, T_s = 260 °C (H_2, 2 h)$ $T_{evap} = 140 °C, T_s = 260 °C (Ar, 4 h)$ $T_{evap} = 140 °C, T_s = 300 °C (Ar, 4 h)$ $T_{evap} = 140 °C, T_s = 350 °C (Ar, 4 h)$	Ni₃C, fcc-Ni (traces) Ni₃C fcc-Ni, Ni₃C (traces) fcc-Ni, Ni₃C (traces) fcc-Ni	80 20 20 60 90	$ \begin{split} \mathbf{Ni} &- 42.2, \ \mathbf{C} - 45.7, \ \mathbf{O} - 12.1 \\ \mathbf{Ni} &- 18.1, \ \mathbf{C} - 77.6, \ \mathbf{O} - 4.3 \\ \mathbf{Ni} &- 76.9, \ \mathbf{C} - 15.4, \ \mathbf{O} - 7.7 \\ \mathbf{Ni} &- 80.8, \ \mathbf{C} - 13.6, \ \mathbf{O} - 5.6 \\ \mathbf{Ni} &- 90.7, \ \mathbf{C} - 8.9, \ \mathbf{O} - 0.4 \end{split} $		



Fig. 7. XRD patterns of the Ni films deposited from 1 at $T_s = 260 \text{ } \odot \text{C}$ (*e*), 300 $\odot \text{C}$ (*f*), and 350 $\odot \text{C}$ (*g*).

Ni(*pda*)(*hfac*)₂, Ni(*pda*)(*thd*)₂ [36] are also given) are shown in Fig. 5. In the row of Ni(*pda*)(β -diketonate)₂ (β -diketonate = *thd*, *acac*, *tfac*, *hfac*), the most volatile complex is Ni(*pda*)(*hfac*)₂ (Fig. 5, black curve). This fact can be attributed to the strong repulsion between the CF₃ groups in the crystal structure of Ni(*pda*)(*hfac*)₂. Earlier we found that the introduction of CF₃ groups led to the increase of volatility of several β -diketonate derivatives [48–50]. The temperatures of 50% mass loss are: Ni(*pda*)(*hfac*)₂–187 °C; Ni(*pda*)(*tfac*)₂ (**3**) - 222 °C; Ni(*pda*)(*thd*)₂-227 °C; Ni(*pda*)(*acac*)₂ (**2**) - 258 °C; and Ni(*dmpda*(*acac*)₂) (**1**) - 273 °C.

It would be instructive to compare the thermal behavior of **1** with the reported data on some nickel iminoketonates: the temperatures of 50% mass loss (at the heating rate 10 °C/min) are 232 °C for Ni(*i*-acac)₂ (*i*-acac - 2-imino-4-pentanonate) [51]; 273 °C for Ni(*dmpda*(acac)₂) (**1**), 300 °C for Ni(*thd*)₂ [7], 325 °C for Ni(*tha*)₂ (*tha* - 2,2,6,6-tetramethyl-3imino-5-heptanonate) [24] and 371 °C for [Ni(acac)₂]₃ [51]. It is seen that the complex **1** has a moderate volatility in comparison with the above mentioned nickel iminoketonates. However, among various *O*,*N*-coordinated nickel complexes with CN = 4, the Schiff base compounds are more volatile in comparison with other nickel chelates, e.g., *bis*(*N*-*R*-salicylaldimine) nickel(II) [23,27,28].

It is seen from Fig. 5 that **1** and **3** sublime (the mass loss asymptotes are 99% and 98%, respectively, Fig. 5) without decomposition under experimental conditions. At the same time, complex **2** decomposes to some extent upon sublimation (the complete mass loss was 89%, Fig. 5). Therefore, the complexes **1** and **3** can be further considered as MOCVD precursors.

3.5. MOCVD experiments and characterization of the films

As mentioned in the previous section, **1** and **3** were tested as precursors for MOCVD process. Evaporation temperatures for both complexes were chosen using the TG data discussed above (cf. Fig. 5 and the related discussion). The substrate temperatures were chosen on the basis of the results obtained in our previous experiments [36]. To study the influence of a carrier gas on the purity of Ni films deposited from **3**, some samples (viz., *c* and *d*, Table 2) were



Fig. 8. Scanning electron microscopy images of the samples deposited from 3 (a, b, c, d) and from. 1 (samples e, f, g).

obtained using only H_2 as a gas-carrier. The deposition conditions and the properties of films are summarized in Table 2.

The X-ray diffraction (XRD) technique was employed to study the structure of the deposited films. The XRD patterns of the samples deposited from 3 are presented in Fig. 6. The single-phase *fcc*-Ni (face centered cubic, ICDD PDF card 4–850) film was prepared from the precursor **3** at $T_s = 210$ °C using Ar as a gas-carrier (sample a, Table 2). The diffraction pattern of the sample *b* indicates the presence of the two phases. The peaks at ~45° and ~52° (Fig. 6) belong to *fcc*-Ni, and the peaks at ~39°, 42°, and 59° belong to Ni₃C (ICDD PDF card 72-1467) or *hcp*-Ni (hexagonal closest packed, ICDD PDF card 45-1027). The positions of the reflexes which belong to the second phase are slightly different form the reported standards.

Note that the EXAFS data suggest direct Ni–C coordination in the samples deposited from related compounds Ni(*pda*)(*thd*)₂, and Ni(*pda*)(*hfac*)₂ [36]. Therefore, we suppose this phase to be a solid solution NiC_x formed on the basis of Ni₃C crystal lattice. The increase of the deposition temperature from 210 to 260 °C leads to increasing of the reflex intensity of NiC_x phase in the samples deposited from precursor **3** (samples *a*–*d*, Table 2). It is also worth mentioning that the formation of NiC_x phase was observed in the case of the films prepared from similar octahedral coordinated precursors Ni(*en*)(*CF*₃*COO*)₂, Ni(*pda*)(*thd*)₂, and Ni(*pda*)(*hfac*)₂ [33,36].

On the basis of the XRD data (Fig. 7), the films deposited from precursor **1** at the surface temperatures 260 and 300 °C (samples *e* and *f*, Table 1) were found to be comprised of *fcc*-Ni (face centered cubic, ICDD PDF card 4-850) phase with the reflexes at $2\Theta = 44.3^{\circ}$ (111), 51.9° (200), and of the tiny amounts of another phase, probably, Ni₃C (ICDD PDF card 72-1467) with reflexes at $2\Theta = 39.5^{\circ}$ (110), 41.8° (006), 44.9° (113), 59.0° (116). In contrast to the case of **3**, the increase of the deposition temperature from 210 to 260 °C leads to increasing of the reflex intensity of *fcc*-Ni, and the single-phase *fcc*-Ni film was obtained from **1** at $T_s = 350$ °C (sample *g*, Table 2, Fig. 7).

To get deeper insight into the structure of the deposited films, the Scanning Electron Microscopy (SEM) technique was applied. The SEM images of the samples a-g are shown in Fig. 8. According to the SEM data (Fig. 8, Table 2), the size of grains increases upon the rise of substrate temperature (with the only exception of the sample *d*). The grain size of the samples deposited from **1** and **3** vary from 30 to 120 nm and from 20 to 150 nm, respectively (Fig. 8, Table 2). In the case of the sample *d*, the grains of 20–30 nm merged to agglomerates with the average size of 300 nm (Fig. 8).

Furthermore, the Energy Dispersive X-ray Spectroscopy (EDXS) has shown that the samples deposited from both precursors **1** and **3** consist only of Ni, C, and O (Table 2). It is seen from Table 2 that in the case of **1** the percentage of carbon decreases almost two times from ca. 15.4 at.% to 8.9 at.% upon the increase of the deposition temperature ($260-350 \degree C$). The opposite tendency was observed in the case of **3**: the content of carbon rises sharply from ca. 10.5 at. % (the deposition temperature $-210\degree C$) to 77.6 at. % ($260\degree C$, correspondingly).

Moreover, the use of argon as a gas-carrier instead of hydrogen leads to decrease of the percentage of carbon from 77.6 at % (Table 2, sample *d*) to 45.7 at.% (sample *c*). At the same time, the oxygen content increases from 4.3 at % (sample *d*) to 12.1 at % (sample *c*). The presence of oxygen impurities in the samples is typical of all nickel-containing films due to oxidation of nickel surface by the oxygen from air or precursors. The comparison of the films obtained from both precursors has shown (Table 2) that the samples deposited from **1** are less contaminated by carbon and oxygen impurities.

4. Conclusion

In the present contribution, we have studied syntheses, structure, and thermal properties of the three novel nickel complexes, namely, Ni($dmpda(acac)_2$) (1), Ni(pda)(acac)₂ (2) and Ni(pda)(tfac)₂ (3). The species 1 has been synthesized for the first time. The crystal structures of compounds 1–3 have been determined by singlecrystal X-ray diffraction. All species turned out to form molecular crystals. The elementary unit of 1 is comprised of isolated molecules, while the molecules of 2 form infinite double chains, and the molecules of 3 form H-bonded pairs.

Thermogravimetry revealed that the octahedral complexes **2** and **3** are more volatile in comparison with **1**. At the same time, **1** is more volatile in comparison with ketoiminate and β -diketonate nickel complexes synthesized before [36]. The compounds **1** and **3** turned out to be suitable for MOCVD applications, since they can be sublimed into the gas phase without decomposition in the solid state. On the contrary, *ca.* 10% wt. of compound **2** left in the solid phase after the complete sublimation of the sample.

The **1** and **3** were tested as MOCVD precursors, and the singlephase *fcc*-Ni films were formed on Ta/Si substrates under particular conditions. The comparison of the nickel films obtained from **1** and **3** revealed that the best quality of samples is achieved with the use of precursor **1**. The obtained data are useful for further optimization of deposition conditions of *fcc*-Ni films with required composition and morphology.

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Appendix A. Supplementary material

CCDC 882751, 892458 and 892459 contain the supplementary crystallographic data for (1), (2) and (3), respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/services/ structure_deposit/.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.05.001.

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