



Short Note

6,6'-[[Ethane-1,2-diylbis(azaneylylidene)]bis(methaneylylidene)]bis[2-(hexyloxy)phenolato] Nickel(II)

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Abstract: Polymeric nickel complexes of salen ligands meet a wide range of applications in catalysis and electrochemistry. Because these polymers usually form very rigid films, the introduction of the conformationally flexible fragments in the corresponding monomers favors the amorphization and, thus, the mass transport. Herein we report a preparation of the hexyloxy-substituted monomeric NiSalen complex by the direct alkylation of the hydroxy-substituted complex. The resulting product was characterized by the ^1H and ^{13}C nuclear magnetic resonance (NMR), ESI-high resolution mass spectrometry (ESI-HRMS), and Fourier-transform infrared spectroscopy (FTIR). The crystal structure of the product was examined by an XRD, indicating the formation of the solvate with dichloromethane. The obtained product was found to be highly soluble in non-polar solvents, in contrast to typical NiSalens.

Keywords: nickel salen; Schiff base; crystal structure

1. Introduction

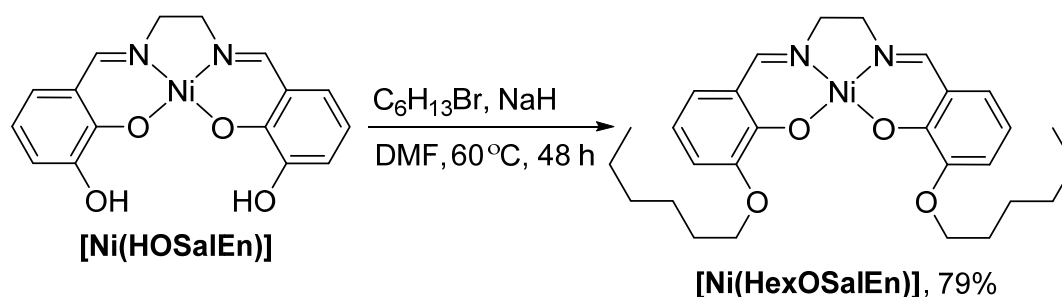
Nickel complexes of bis(salicylideneiminato) ligands (NiSalens) have attracted significant attention in the field of catalysis [1]. The most useful are the polymeric complexes of this type [2], which are considered to be the materials for electrocatalytic [3,4] and photoelectrocatalytic [5] systems, electrochemical sensors [6,7], electrochromic [8,9], and energy storage devices [10–13].

These polymeric complexes are known for unique properties, such as reversible electrochemical oxidation in a wide range of potentials, thermal stability, high redox and electronic conductivity, and high specific capacities [10,14,15]. Polymeric NiSalens met their application in Li-ion batteries as cathode active materials [16] and binders [17].

Recently, the voltage-dependent electrical resistivity of these polymers were demonstrated [18]. In order to increase the potentiorestrictive response, introduction of the conformationally flexible groups is highly required. Herein, we report the synthesis of NiSalen monomeric complex substituted with hexyloxy fragments, namely 6,6'-[[ethane-1,2-diylbis(azaneylylidene)]bis(methaneylylidene)]bis[2-(hexyloxy)phenolato] nickel(II) ([Ni(HexOSalEn)]), by the direct alkylation of the hydroxy-substituted complex [Ni(HOSalEn)]. The obtained product was characterized with nuclear magnetic resonance (NMR), high resolution mass spectrometry (HRMS), Fourier-transform infrared spectroscopy (FTIR) spectra and crystal structure.

2. Results

The [Ni(HOSalEn)] complex was subjected to an alkylation with 1-bromohexane while using different reaction conditions (Scheme 1). Attempts of alkylation using the widely used system, NaH in THF [19], failed due to the low solubility of the starting material. K_2CO_3 or Cs_2CO_3 in DMF or DMSO, which are frequently exploited for the alkylation of phenols [20], afforded the desired product in low yields (<10%). Addition of NaI had no effect on the reaction yield. Finally, NaH in DMF at 60 °C afforded the [Ni(HexOSalEn)] complex in 79% yield after 2 days.



Scheme 1. Reaction conditions for the alkylation of [Ni(HOSalEn)] with hexyl bromide.

The product was purified by flash chromatography, followed by the crystallization from hexane–dichloromethane mixture. The melting point of the product comprises 172–174 °C, which is significantly lower as compared with typical NiSalen complexes, indicating an influence of the hexyloxy groups. The 1H -NMR spectrum of the resulted complex (Figure S1) shows the typical set of hexyloxy signals: 6H triplet at 0.74 ppm with $^3J_{H-H} = 6.8$ Hz, 8H multiplet at 0.93–1.13 ppm, two 4H multiplets in the ranges of 1.28–1.42 and 1.42–1.59 ppm, and smoothed triplet at 4.74 ppm, which is noticeably shifted upfield when compared with the normal position of alkoxy methylene group. Additionally, the ethylene bridge 4H singlet appears at 3.66 ppm, along with the 2H singlet of imine protons at 7.87 ppm and a set of aromatic signals, 2H triplet at 6.49 ppm, and two 2H doublets at 6.66 and 6.81 ppm, all with $^3J_{H-H} = 7.9$ Hz. ^{13}C -NMR spectrum (Figure S2) contains a set of hexyloxy peaks at 14.1, 22.6, 25.7, 27.9, 31.8, and 68.1 ppm, ethylene bridge signal at 59.0 ppm, six aryl peaks at 113.6, 115.2, 120.0, 123.5, 148.7, and 154.0 ppm, and the imine carbon signal at 163.0 ppm.

The exact mass of $[M + Na]^+$ ion, determined by ESI-HRMS (Figure S3), was found to be 547.2072 (547.2077 as calcd. for $C_{28}H_{38}N_2NiO_4Na^+$). Interestingly, no signal corresponding to an $[M + H]^+$ ion was detected, which indicates the strong binding of Na^+ in the O,O,O,O cavity of the complex. The FTIR spectrum recorded in KBr (Figure S4) contains the strong vibration at 1618 cm^{-1} , which corresponds to the C=N bond. UV-Vis spectrum in $CHCl_3$ has a typical pattern for alkoxy-substituted NiSalen, with the maxima at 349, 417, and 551 nm, and shoulders at 274 and 448 nm (Figure S5).

A single crystal of [Ni(HexOSalEn)] was obtained by layer-by-layer technique from the solution of the pure compound in dichloromethane and the upside layer of hexane. According to the crystal structure (Figure 1), the product crystallizes with CH_2Cl_2 molecule per asymmetric unit. The Ni atom shows a nearly ideal square planar configuration, with the Ni···N distances comprise 1.8468(16) and 1.8442(16) Å, Ni···O distances comprise 1.8425(13) and 1.8446(13) Å, and N-O-Ni angles comprises 176.91 and 177.57 degrees. A notable Ni–Ni interaction was found, with the Ni···Ni distance of 3.2811(5) Å.

We demonstrate the possibility for the direct alkylation of [Ni(HOSalEn)] with hexyl bromide, which provides the facile one step route to the diversity of alkoxy substituted NiSalens and the polymers obtained thereof. The obtained complex may be used further in order to synthesize the polymeric materials for energy storage and electrocatalysis.

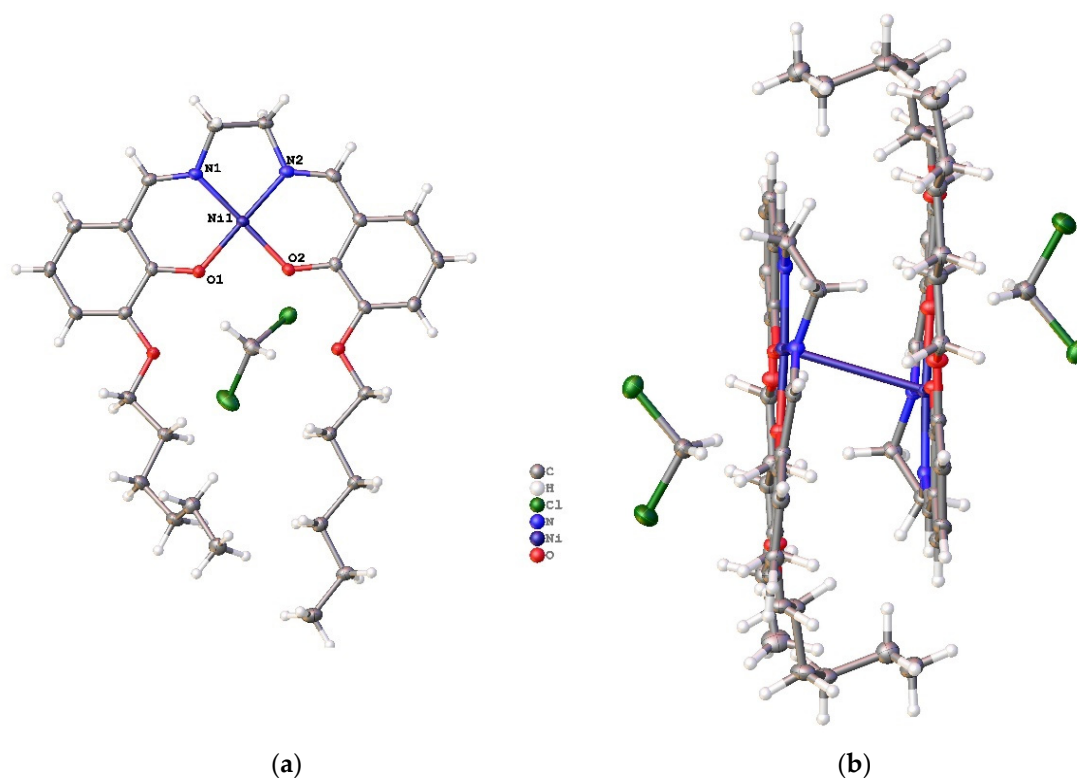


Figure 1. (a) ORTEP plot of the $[\text{Ni}(\text{HexOSalEn})]\cdot\text{CH}_2\text{Cl}_2$; (b) Ni-Ni dimer of the $[\text{Ni}(\text{HexOSalEn})]$.

3. Materials and Methods

3.1. General Considerations

Reagents of “reagent grade” purity were purchased from Sigma–Aldrich (Europe). $[\text{Ni}(\text{HOSalEn})]$ was obtained, as described in literature [21]. The Fourier transform infrared spectra were recorded on Shimadzu IRAffinity-1 FTIR spectrophotometer (Shimadzu Europa GmbH, Kyoto, Japan) in KBr pellets. UV-Vis spectra were recorded in CHCl_3 solutions on Shimadzu UV-1800 double-beam spectrophotometer (Shimadzu Europa GmbH, Kyoto, Japan) in 1 cm quartz cuvettes. ^1H and ^{13}C -NMR spectra were acquired on a Bruker Avance 400 spectrometer (Bruker Analytische Messtechnik GmbH, Rheinstetten, Germany) at 400 and 101 MHz, respectively, in CDCl_3 while using a residual solvent peak as internal standard. HRMS of the positive ions was recorded from the methanolic solution of the sample using electrospray ionization of on a Bruker micrOTOF apparatus (Bruker Analytische Messtechnik GmbH, Rheinstetten, Germany) in positive mode.

X-ray single crystal analyses were performed on Agilent Technologies «Xcalibur» diffractometer (Agilent Technology, Santa Clara, CA, USA) with monochromated $\text{Mo K}\alpha$ radiation. The temperature was kept at 100 K during data collection. The structure was solved while using Olex2 [22] and refined with the SHELXL [23] refinement package (G. Sheldrick, Gottingen, Germany) using Least Squares minimization. CCDC 2045743 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk>.

3.2. Synthesis of 6,6'-[[Ethane-1,2-diy]bis(azaneylylidene)]bis(methaneylylidene)]bis[2-(hexyloxy)phenolato] Nickel(II)

To a stirred suspension of $[\text{Ni}(\text{HOSalEn})]$ (179 mg, 0.5 mmol) in 5 mL of dry DMF, NaH (60% susp. in oil, 44 mg, 1.1 mmol) was added in one portion under Ar, and then the mixture was stirred at 60 °C for 1 h. At this point, 1-bromohexane (155 μL , 182 mg, 1.1 mmol) was added in one portion, and the reaction mixture was stirred at 60 °C for 48 h under Ar. The reaction mixture was cooled to RT and

then poured in 50 mL of H₂O with 200 µL of AcOH. Sticky precipitate was collected by decantation, washed with water, and dried at 50 °C on air. The dried residue was refluxed in hexane, cooled to RT, filtered, and washed with hexane. The obtained precipitate was purified on a short chromatographic column (SiO₂, DCM → DCM + 2% MeOH), evaporated, and crystallized while using layer-by-layer crystallization technique from 5 mL of DCM layered with 25 mL of hexane to obtain a desired product as brown crystalline solid (207 mg, 0.395 mmol, 79%).

M.p. 172–174 °C (hexane-DCM). ¹H-NMR (400 MHz, CDCl₃) δ, ppm: 7.87 (s, 2H, imine), 6.81 (d, *J* = 7.9 Hz, 2H, Ar), 6.66 (d, *J* = 7.9 Hz, 2H, Ar), 6.49 (t, *J* = 7.9 Hz, 2H, Ar), 4.83–4.63 (m, 4H, -OCH₂-), 3.66 (s, 4H, bridge), 1.42–1.59 (m, 4H, alkyl), 1.28–1.42 (m, 4H, alkyl), 0.93–1.13 (m, 8H, alkyl), 0.74 (t, *J* = 6.8 Hz, 6H, -CH₃). ¹³C-NMR (101 MHz, CDCl₃) δ, ppm: 163.0 (imine), 154.0 (Ar), 148.7 (Ar), 123.5 (Ar), 120.0 (Ar), 115.2 (Ar), 113.6 (Ar), 68.1 (-OCH₂-), 59.0 (bridge), 31.8 (alkyl), 27.9 (alkyl), 25.7 (alkyl), 22.6 (alkyl), 14.1 (-CH₃). FTIR (KBr) $\tilde{\nu}$, cm⁻¹: 3003, 2932 (C-H), 1618, 1601 (C=N), 1552 (C=C), 737 (Ni-O). UV-Vis (CHCl₃, 5.8·10⁻⁵ M) λ_{max}, nm (log ε): 274 (sh.), 349 (4.058), 417 (3.872), 448 (sh.), 551 (3.145). HRMS (ESI) *m/z* [M + Na]⁺ calcd for C₂₈H₃₈N₂NiO₄Na⁺ 547.2077, found 547.2072. Crystal Data for C₂₉H₄₀Cl₂N₂NiO₄ (*M* = 610.24 g/mol): triclinic, space group P-1 (no. 2), *a* = 7.6002(3) Å, *b* = 13.6714(5) Å, *c* = 14.7436(5) Å, α = 97.065(3)°, β = 101.868(3)°, γ = 93.363(3)°, *V* = 1482.24(10) Å³, *Z* = 2, *T* = 100.01(10) K, μ(MoKα) = 0.871 mm⁻¹, *D*_{calc} = 1.367 g/cm³, 11,770 reflections measured (5.498° ≤ 2θ ≤ 56.996°), 6749 unique (*R*_{int} = 0.0225, *R*_{sigma} = 0.0421), which were used in all calculations. The final *R*₁ was 0.0355 (*I* > 2σ(*I*)) and *wR*₂ was 0.0833 (all data).

Supplementary Materials: The following are available online, ¹H and ¹³C-NMR spectra, HRMS, FTIR and UV-Vis spectra, and the crystallographic data for [Ni(HOSalEn)] in crystallographic information file (CIF) format. CCDC 2045743 also contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

Author Contributions: Conceptualization: D.A.L. and O.V.L.; synthesis: D.A.L. and A.S.B.; crystallography: D.A.L.; manuscript preparation: D.A.L. and O.V.L. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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