

NOVEL NICKEL COMPLEXES WITH SCHIFF BASES AND α -GLYOXIMES, SYNTHESIS AND PHYSICAL-CHEMICAL STUDY

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Abstract

Nickel complexes, especially with Schiff bases gain potential interest in various areas such as catalysis, luminescent probes in analytical chemistry, dye and polymer industry, food industry, magneto-structural chemistry, agrochemistry, biological fields and several miscellaneous applications. There are numerous reports on the biological activities of Schiff base ligands and their metal complexes, including their use for DNA cleavage, enzyme modeling, and as antimicrobial, antifungal and antitumor agents [1].

In our research, new nickel complexes were synthesized with α -glyoximes, such as $[\text{Ni}(\text{Me-propyl-GlyoxH})_2(\text{imidazole})_2]$, $[\text{Ni}(\text{Me-pentyl-GlyoxH})_2(\text{diisopropyl-amine})_2]$, $[\text{Ni}((4\text{-benzyl-2-hydroxy-phenyl})\text{-Me-GlyoxH})_2]$, where GlyoxH = mono deprotonated glyoxime, and with Schiff bases, such as $[\text{Ni}(3\text{-heptanone})_2\text{A}]$, $[\text{Ni}(\text{propiophenone})_2\text{A}]$, A = ethylenediamine (en), 1,2-, 1,3-propylenediamine (1,2-pn, 1,3-pn), o-phenylene-diamine (o-fen). The Schiff bases were obtained with a simple condensation reaction between 3-heptanone or propiophenone and the corresponding diamines.

The molecular structure of our products was investigated by IR, UV–VIS spectroscopy, mass spectrometry (MS), thermoanalytical measurements (TG-DTG-DTA), and powder XRD. The biological activity was studied for a few bacteria, however, these complexes have shown no antibacterial activity so far.

Introduction

Nickel (Ni) is a naturally occurring element existing in various forms, and it is present in all compartments of the environment and, furthermore, is ubiquitous in the biosphere as its compounds and complexes. It is a silvery-white lustrous metal with a slight golden tinge. Nickel is a hard and ductile transition metal belonging to the 3d group. Nickel is one of the five ferromagnetic elements. Nickel is used in a wide variety of metallurgical processes such as electroplating and alloy production as well as in nickel cadmium batteries. Besides it plays a well defined role in the biological system and plants. It is also essential for the biosynthesis of hydrogenase, carbon monoxide dehydrogenase, and, moreover, it can be found in a number of genera of bacteria [2].

The Schiff bases are widely used as N-donor ligands in the field of coordination chemistry. Due to the attractive physicochemical properties of metal complexes, extensive studies have been carried out on complexation of Schiff bases with different metal ions, resulting broad range of utilization in various areas of science. The toxicity of Schiff base

derivatives of sulfane thiadiazole, 2-thiophene aldehydes, and salicylaldehyde, together with their some metal complexes, has been tested against insects as well [3]. In general, the C=N linkage in azomethine derivatives is an essential structural requirement for biological activity. Several azomethines have been reported to possess remarkable antibacterial, antifungal, anticancer and diuretic activities [4].

In the present paper we report the synthesis, characterization and biological evaluation of some Ni(II) complexes with Schiff bases and α -glyoximes.

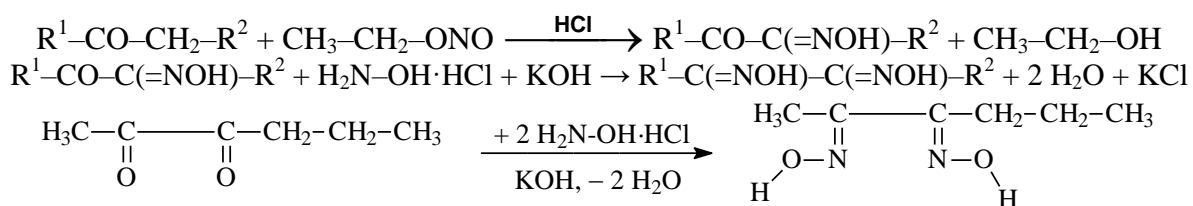
Experimental

Used materials: NiSO₄, EtOH, EtONO, 2,3-hexanedione, 4-benzyl-2-hydroxy-propionophenone, 2-octanone, hydroxylamine hydrochloride, KOH, imidazole, diisopropylamine, 3-heptanone, propionophenone, ethylenediamine, 1,2-propylene-diamine, 1,3-propylene-diamine, *ortho*-phenylene-diamine, sodium acetate.

Methods:

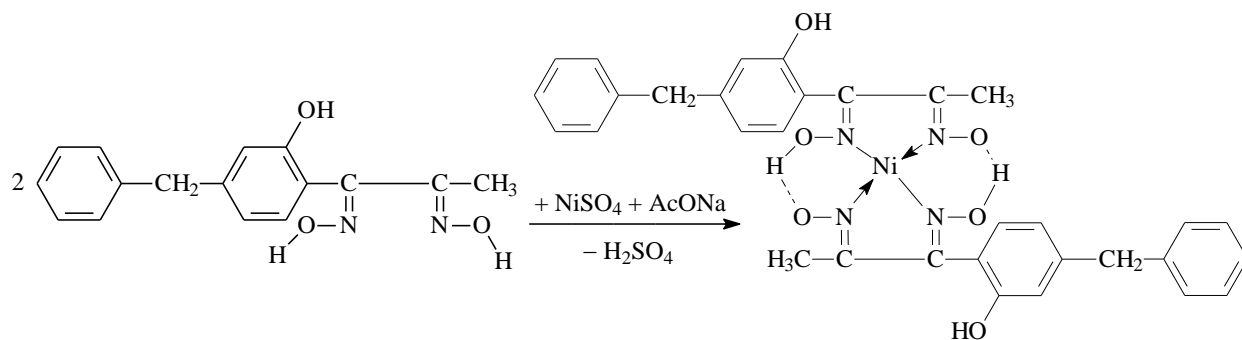
- Preparation of (4-benzyl-2-hydroxyphenyl)-Me-GlyoxH₂, Me-propyl-GlyoxH₂ and Me-pentyl-GlyoxH₂

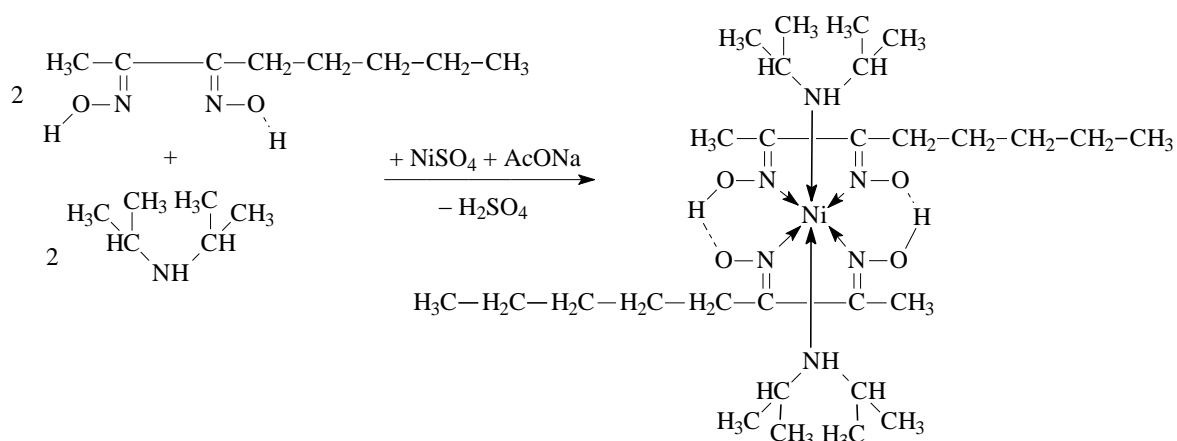
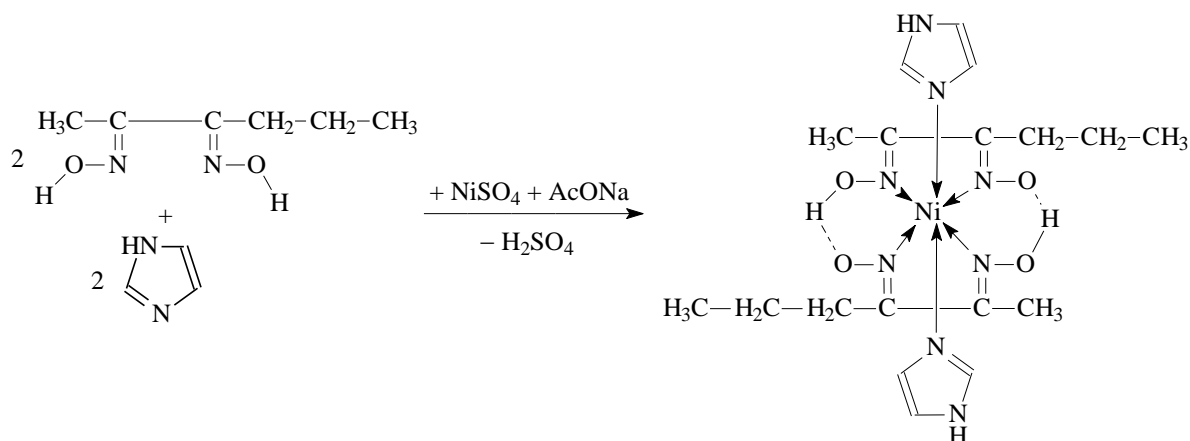
First, the (4-benzyl-2-hydroxyphenyl)-Me-dione-monoxime and Me-pentyl-dione-monoxime were prepared from 4-benzyl-2-hydroxypropionophenone and 2-octanone, respectively. The keton reactants were acidified with HCl, and, according to the isonitroso method, gaseous ethyl nitrite was bubbled into the cooled mixture. Then the obtained monoximes, and, furthermore, the 2,3-hexanedione, were reacted with hydroxylamine generated from the aqueous solution of the corresponding hydrochloride salt by addition of equimolar amount of KOH. The reaction mixture was heated for 2–3 hours, and then the precipitated product was filtered off. After recrystallization from EtOH or MeOH, it was dried on air. The reactions:



- Synthesis of [Ni(GlyoxH)₂(amine)₂] type complexes

(4-benzyl-2-hydroxyphenyl)-Me-GlyoxH₂ or Me-propyl-GlyoxH₂ or Me-pentyl-GlyoxH₂ was dissolved in EtOH, then added to the aqueous solution of NiSO₄ containing spatula tip amount of sodium acetate. In the latter case of Me-propyl-GlyoxH₂ and Me-pentyl-GlyoxH₂, imidazole and diisopropylamine, resp., were added. The mixtures were heated for 2–3 hours. After cooling the crystalline complexes were filtered, washed with EtOH–water mixture (1:1), and then dried on air. The reactions are shown below:

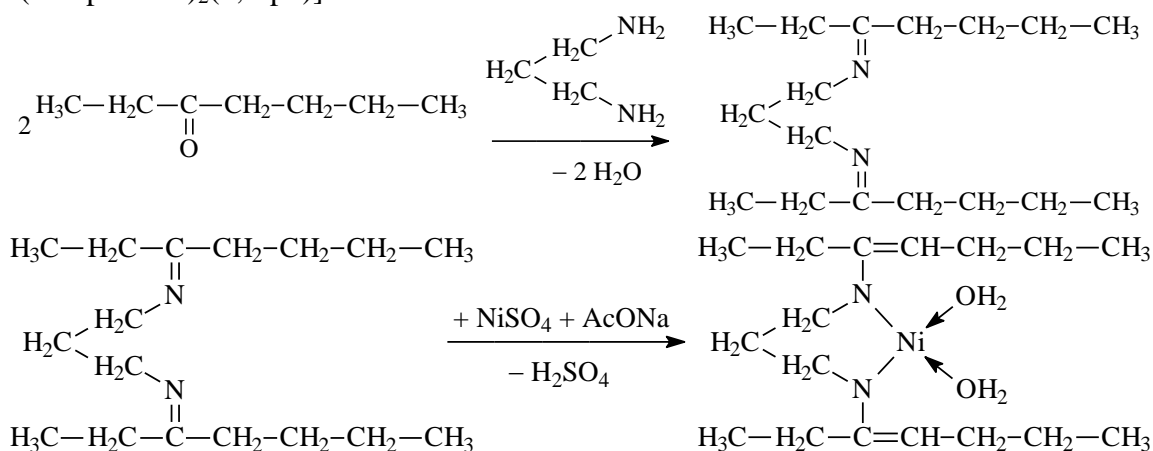




- Synthesis of $[\text{Ni}(\text{3-heptanone})_2(\text{diamine})]$, $[\text{Ni}(\text{propiophenone})_2(\text{diamine})]$ complexes

The Schiff bases were prepared by the condensation reaction between 3-heptanone or propiophenone, and the corresponding diamine (ethylenediamine, 1,2-, 1,3-propylenediamine, o-phenylenediamine) in EtOH solution. The mixture was heated at 70–80 °C for 2–3 hours. The solution obtained was directly used for the synthesis of complexes by adding the aqueous solution of NiSO_4 containing slight amount of sodium-acetate. The product was filtered off, washed with EtOH–water mixture (1:1), and then dried on air.

For example, the reactions below were performed for the synthesis of $[\text{Ni}(\text{3-heptanone})_2(1,3\text{-pn})]$:



Results and discussion

Microscopic characterization and the yield of prepared complexes are presented in Table 1.

Table 1. Microscopic characterization, calculated molecular weight and the yield of prepared complexes.

Nr.	Compound	Calc. mol. weight	Yield (%)	Microscopic characterization
1.	[Ni((4-benzyl-2-HO-phenyl)-Me-GlyoxH) ₂]	625.30	63	Light brown discs
2.	[Ni(Me-propyl-GlyoxH) ₂ (imidazole) ₂]	481.17	63	Red triangle-based prisms
3.	[Ni(Me-pentyl-GlyoxH) ₂ (diisopropyl-amine) ₂]	603.51	32	Orange-red discs and triangle-based prisms
4.	[Ni(3-heptanone) ₂ (en)]	309.11	25	Greenish-blue triangle-based prisms
5.	[Ni(3-heptanone) ₂ (1,2-pn)]	323.14	15	Greenish-blue irregular microcrystals
6.	[Ni(3-heptanone) ₂ (1,3-pn)]	323.14	65	Green irregular microcrystals
7.	[Ni(3-heptanone) ₂ (o-fen)]	357.16	28	Brown triangle-based prisms
8.	[Ni(propionophenone) ₂ en]	349.09	44	Light purple triangle-based prisms
9.	[Ni(propionophenone) ₂ (1,2-pn)]	363.12	10	Light blue triangle-based prisms
10.	[Ni(propionophenone) ₂ (o-fen)]	397.14	45	Dark brown triangle-based prisms

Infrared spectroscopic study

The mid-IR spectra were recorded with a Bruker Alpha FTIR spectrometer (Platinum single reflection diamond ATR), at room temperature, in the wavenumber range of 4000–400 cm⁻¹, and the far-IR range of 650–150 cm⁻¹, respectively, on a Perkin–Elmer System 2000 FTIR spectrometer, operating with a resolution of 4 cm⁻¹. The samples were measured in solid state (in powder form) and in polyethylene pellets, respectively. The data of the most characteristic IR bands for the selected complexes are presented in Table 2.

Table 2. IR data of the selected complexes.

Comp. cm ⁻¹	1	2	3	4	5	6	7	8	9	10
ν_{O-H}	3648 w	-	3648 w	-	-	-	-	-	-	-
ν_{C-H}	2940 m	2961 m	2926 s	2970 m	2971 s	2971w	2970 s	2970 w	2970 w	2970 w
$\nu_{C=N}$	1609 s	1560vs	1560vs	1739vs	1739vs	1541vs	1738vs	1739vs	1739 s	1739 s
δ_{CH_2}	1456 m	1454 m	1458 s	1425 s	1425vs	1417vs	1457vs	1456 m	1420 s	1436 s
δ_{CH_3}	1366vs	1364 w	1366 s	1373 s	1374 m	1216 w	1374vs	1373 s	1374 m	1374 s
ν_{N-O}	1217vs	1239vs	1229vs	-	-	-	-	-	-	-
ν_{N-OH}	1191vs	1117vs	1119vs	-	-	-	-	-	-	-
τ_{O-H}	1098vs	1049 s	1049 s	1068vs	1066vs	1057vs	1092 m	1063vs	1066vs	1078vs
γ_{C-H}	616 vs	709 vs	731 vs	612 vs	612 vs	608 vs	755 s	610 vs	611 vs	743 vs
ν_{Ni-N}	488 s	516 vs	514 s	528 s	543 s	476 m	527 m	528 s	548 m	518 s

(Abbreviations: vs = very strong, s = strong, m = medium, w = weak)

Mass spectrometry

Mass spectra of the samples were recorded using electrospray ionization (ESI). In the spectra we could detect the molecular ions and some decomposition fragments.

Thermoanalytical measurements (TG-DTG-DTA)

Thermal measurements were performed with a 951 TG and 910 DSC calorimeter (DuPont Instruments), in Ar or N₂ at a heating rate of 10 Kmin⁻¹ (sample mass of 4–10 mg).

In the case of [Ni(GlyoxH)₂(amine)₂] type complexes the first decomposition steps are belonging to the leaving amine groups up to 300 °C. Subsequently, the decomposition of glyoxime groups takes place which is accompanied by big exothermic peaks. This behavior

can be explained with the presence of oxygen in the molecule. In the case of Schiff bases, first heptanone and propiophenone parts, respectively, are leaving, afterwards the diamine moieties eliminate. Two examples are presented in the figure. The general decomposition mechanisms:

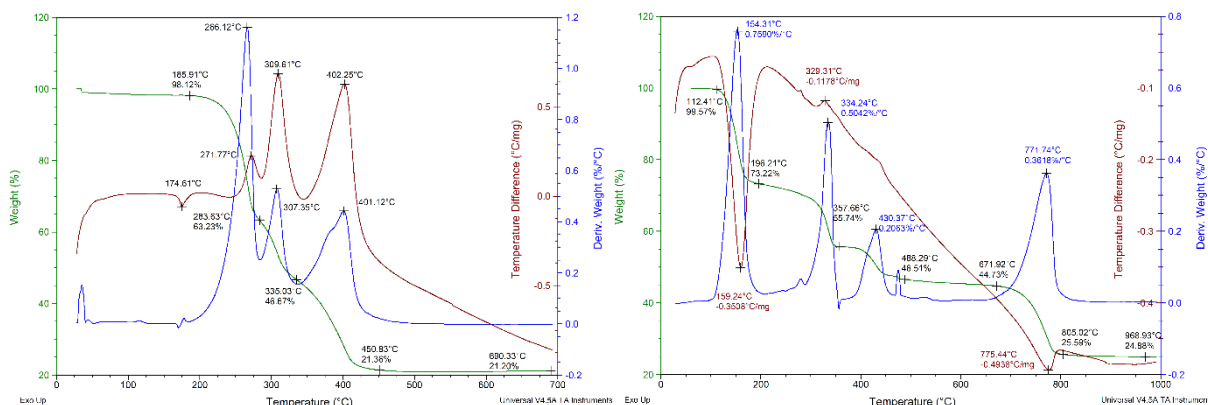
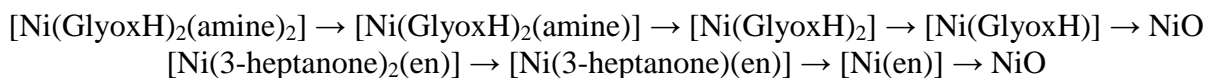


Figure. Thermal decomposition of $[\text{Ni}(\text{Me-propyl-GlyoxH})_2(\text{imidazole})_2]$ and $[\text{Ni}(\text{3-heptanone})_2(\text{en})]$

Powder X-ray diffraction measurements

The crystal structure of the complexes was studied with powder XRD measurements, carried out on a PANalytical X'pert Pro MPD X-ray diffractometer. As being new compounds their diffractograms are not deposited in the Cambridge database.

UV-VIS spectroscopy

The electronic spectra were recorded with Jasco V-670 Spectrophotometer in 10% EtOH/water solutions containing substrate in 10^{-4} mol/dm³ concentration. Using Sørensen buffer solutions the electronic spectra were also recorded as a function of pH, and then the acidity constants were calculated too.

Conclusion

In this work new nickel complexes were synthesized and their physico-chemical properties were studied. Decomposition mechanism was determined with the thermoanalytical method.

Acknowledgement

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References

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