

Ni(II) complexes of 4- and 5- nitro-substituted heteroaryl cinnamoyl derivatives

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A series of Ni(II) complexes with 4- and 5- nitro-substituted heteroaryl cinnamoyl derivatives were synthesized. All complexes were obtained with the metal to ligand ratio 1:2. The present study is focused on Ni(II) complexes of 4- and 5- nitro-substituted heteroaryl cinnamoyl derivatives (**L1-L8**), synthesized from Ni(CH₃COO)₂·4H₂O. The structures of the complexes were investigated by elemental analysis and spectroscopic UV-Vis and IR methods and one of them with Raman spectroscopy. The presence of two water molecules in the inner coordination sphere of all Ni(II) complexes was suggested.

Key words: Nitro-Substituted Heteroaryl Cinnamoyl Derivatives, Metal Complexes, IR

INTRODUCTION

2-Acetyl-1,3-indandione and its derivatives possess a wide array of important physiological activities. Some of them have antimicrobial activity [1], antiparasitical [2] and anticonvulsant effect [3]. Extensive publications and reviews, mainly from Alfimov *et al.* [4] and Chetkina *et al.* [5], focus on the study of the molecular receptors based on photochromic crown ethers and complex formation and the X-ray structure of single crystals of the 1,3-indandione and 1,3-dicyanomethyleneindan derivatives.

Recently, we reported the synthesis and structure of 2-(1-hydroxy-3-phenyl-allylidene)-2*H*-inden-1,3-dione, 2-(3-thiophene-2-yl-1-hydroxy-allylidene)-2*H*-inden-1,3-dione, 2-(3-thiophene-3-yl-1-hydroxy-allylidene)-2*H*-inden-1,3-dione, 2-(3-furane-2-yl-1-hydroxy-allylidene)-2*H*-inden-1,3-dione and their Cu(II), Cd(II), Zn(II), Co(II) and Ni(II) complexes [6] and 2-[1-hydroxy-3-phenyl-allylidene]-indan-1,3-dione, 2-[1-hydroxy-3-(4-fluoro-phenyl)-allylidene]-indan-1,3-dione, 2-[1-hydroxy-3-(4-chloro-phenyl)-allylidene]-indan-1,3-dione, 2-[1-hydroxy-3-(4-methyl-phenyl)-allylidene]-indan-1,3-dione, 2-[1-hydroxy-3-(4-cyano-phenyl)-allylidene]-indan-1,3-dione, 2-[1-hydroxy-3-(4-methoxy-phenyl)-allylidene]-indan-1,3-dione, 2-[1-hydroxy-3-(4-dimethylamino-phenyl)-allylidene]-indan-1,3-dione with Cu(II), Cd(II), Zn(II), Co(II) and Ni(II) complexes [7] and 2-(1-hydroxy-3-(4-fluoro-phenyl)-allylidene)-2*H*-

indene-1,3-dione and its Cu(II), Zn(II) and Cd(II) complexes [8].

There is no X-ray data of metal complexes with 4- and 5- nitro-substituted heteroaryl cinnamoyl derivatives in the Cambridge Structural Data Base. For this reason, the goal of current paper is to study the composition and structure of a series of metal complexes with 4- and 5- nitro-substituted heteroaryl cinnamoyl derivatives.

In the present work we describe the synthesis and reaction conditions to obtain new Ni(II) complexes of 2-[1-hydroxy-3-(thiophen-2-yl)prop-2-en-1-ylidene]-4-nitro-1*H*-indene-1,3(2*H*)-dione (**L1**), 2-[1-hydroxy-3-(thiophen-3-yl)prop-2-en-1-ylidene]-4-nitro-1*H*-indene-1,3(2*H*)-dione (**L2**), 2-[3-(furan-2-yl)-1-hydroxyprop-2-en-1-ylidene]-4-nitro-1*H*-indene-1,3(2*H*)-dione (**L3**), 2-[1-hydroxy-3-(1*H*-pyrrol-2-yl)prop-2-en-1-ylidene]-4-nitro-1*H*-indene-1,3(2*H*)-dione (**L4**), 2-[1-hydroxy-3-(thiophen-2-yl)prop-2-en-1-ylidene]-5-nitro-1*H*-indene-1,3(2*H*)-dione (**L5**), 2-[1-hydroxy-3-(thiophen-3-yl)prop-2-en-1-ylidene]-5-nitro-1*H*-indene-1,3(2*H*)-dione (**L6**), 2-[3-(furan-2-yl)-1-hydroxyprop-2-en-1-ylidene]-5-nitro-1*H*-indene-1,3(2*H*)-dione (**L7**) and 2-[1-hydroxy-3-(1*H*-pyrrol-2-yl)prop-2-en-1-ylidene]-5-nitro-1*H*-indene-1,3(2*H*)-dione (**L8**) with general formula given in Figure 1. We characterize the obtained complexes as well.

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EXPERIMENTAL

Metal salt ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ - Fluka) and solvents used for the synthesis of the complexes were with a p.a. qualification. UV/Vis spectra of **L1-L8** and its metal complexes were measured on a Lambda 9 Perkin-Elmer UV/Vis/NIR Spectrophotometer from 200 nm to 1000 nm. The IR spectra of **L1-L8** were registered in KBr pellet on a Bruker FT-IR VERTEX 70 Spectrometer from 4000 cm^{-1} to 400 cm^{-1} at resolution 2 cm^{-1} with 25 scans. The IR spectra of the Ni(II) complexes of **L1-L8** were registered in KBr pellet on a 1750 FTIR-Perkin-Elmer Spectrophotometer.

Synthesis of Ni(II) complexes with 4- nitro-substituted heteroaryl cinnamoyl derivatives (**L1-L4**) and 5- nitro-substituted heteroaryl cinnamoyl derivatives (**L5-L8**)

0.001 mol (g) of L1-L8 in 7 cm^3 dioxane

0.0005 mol (g) of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in 10 cm^3 CH_3OH

All metal complexes were obtained after mixing methanol solutions of the $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and the corresponding ligands (**L1-L8**), dissolved in dioxane, in metal-to-ligand ratio 1:2. Non-charged complexes were formed as precipitates, which were further filtrated, repeatedly washed with H_2O , and dried over CaCl_2 for 2 weeks. It was found out that the complexes were soluble in THF and DMSO. Selected IR frequencies and elemental analyses data are presented in Tables 1, 2 and 3, respectively.

The spectral data of the compounds obtained were as follows:

4- NO_2 -substituted heteroaryl cinnamoyl derivatives and their Ni(II) complexes (**L1-L4**)

UV-Vis (DMSO) L1 $\lambda_{\text{max}} = 325 \text{ nm}, 382 \text{ nm}$

UV-Vis (DMSO) Ni(II)L1 $\lambda_{\text{max}} = 254 \text{ nm}, 395 \text{ nm}$

Raman ($\nu_{\text{max}}, \text{cm}^{-1}$) L1: 1601, 1500, 1413, 1368, 1274, 1204, 345

UV-Vis (DMSO) L2 $\lambda_{\text{max}} = 300 \text{ nm}, 377 \text{ nm}$

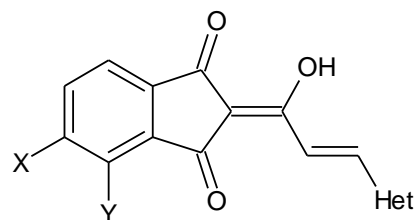
UV-Vis (DMSO) Ni(II)L2 $\lambda_{\text{max}} = 254 \text{ nm}, 313 \text{ nm}, 384 \text{ nm}$

UV-Vis (DMSO) L3 $\lambda_{\text{max}} = 325 \text{ nm}, 384 \text{ nm}$

UV-Vis (DMSO) Ni(II)L3 $\lambda_{\text{max}} = 254 \text{ nm}, 401 \text{ nm}$

Raman ($\nu_{\text{max}}, \text{cm}^{-1}$) L3: 1611, 1578, 1457, 1392, 1351, 1276, 1267, 1205, 1148, 1112, 1072, 1023, 886, 624, 400

UV-Vis (DMSO) L4 $\lambda_{\text{max}} = 285 \text{ nm}, 333 \text{ nm}, 455 \text{ nm}, 488 \text{ nm}$



X = H, Y = NO_2 (**L1-L4**); X = NO_2 , Y = H (**L5-L8**)

L1-L4: 4-nitro-substituted heteroaryl cinnamoyl derivatives

L5-L8: 5-nitro-substituted heteroaryl cinnamoyl derivatives

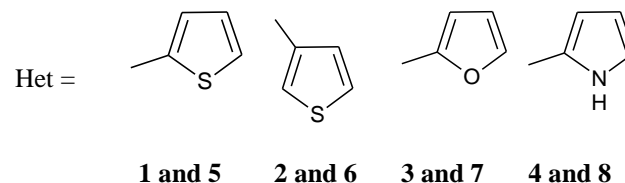


Figure 1. General formula of **L1-L8**

5- NO_2 -substituted heteroaryl cinnamoyl derivatives and their Ni(II) complexes (**L5-L8**)

UV-Vis (DMSO) L5 $\lambda_{\text{max}} = 278 \text{ nm}, 387 \text{ nm}, 394 \text{ nm}$
UV-Vis (DMSO) Ni(II) L5 $\lambda_{\text{max}} = 255 \text{ nm}, 323 \text{ nm}, 387 \text{ nm}$

Raman ($\nu_{\text{max}}, \text{cm}^{-1}$) Ni(II)L5: 1686, 1645, 1610, 1588, 1484, 1412, 1362, 1345, 1275, 1215, 1062, 1046

UV-Vis (DMSO) L6 $\lambda_{\text{max}} = 282 \text{ nm}, 360 \text{ nm}, 427 \text{ nm}$

UV-Vis (DMSO) Ni(II)L6 $\lambda_{\text{max}} = 255 \text{ nm}, 307 \text{ nm}, 385 \text{ nm}$

UV-Vis (DMSO) L7 $\lambda_{\text{max}} = 320 \text{ nm}, 378 \text{ nm}, 452 \text{ nm}$

UV-Vis (DMSO) Ni(II)L7 $\lambda_{\text{max}} = 254 \text{ nm}, 322 \text{ nm}, 390 \text{ nm}$

UV-Vis (DMSO) L8 $\lambda_{\text{max}} = 286 \text{ nm}, 338 \text{ nm}, 460 \text{ nm}$

The resulting complexes are light brown to dark brown crystalline substances with melting points above 370°C. The yields were as follows: NiL1 – 45 %; NiL2 - 40 % NiL3 - 53 %; NiL4 - 33 %; NiL5 - 61 %; NiL6 - 52 %; NiL7 - 67 %; NiL8 - 42%.

RESULTS AND DISCUSSION

Complexation with Ni(II) were conducted using metal salt, namely $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ at molar ratio M:L = 1:2. Neutral complexes were synthesized and isolated as brown or black precipitates, respectively. All complexes were investigated by means of elemental analysis, UV-Vis and IR spectroscopy. The elemental analysis data show metal-to-ligand ratio 1:2 and presence of two water molecules for all Ni(II) complexes. The data from the absorption spectra of the free ligands **L1-L8** and their Ni(II) complexes in DMSO are listed in the experimental part. In the UV/Vis spectra of the all metal complexes, one new maximum appeared at 254 nm. Selected IR frequencies and elemental

analyses data are listed in Tables 2, 3 and 1, respectively.

Table 1. Elemental analysis data of the Ni(II) complexes with 4- and 5- nitro-substituted heteroaryl cinnamoyl derivatives

Compound	C %		H %		N %		S %		Ni %	
	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found
NiL1	51.43	51.06	2.70	2.78	3.75	3.66	8.58	8.43	7.85	7.59
NiL2	51.43	51.17	2.70	2.81	3.75	3.58	8.58	8.41	7.85	7.66
NiL3	53.54	53.43	3.07	2.89	3.90	3.74	-	-	8.18	7.97
NiL4	53.89	53.77	3.11	3.00	7.86	7.79	-	-	8.23	8.09
NiL5	51.43	51.11	2.70	2.84	3.75	3.63	8.58	8.37	7.85	7.61
NiL6	51.43	51.01	2.70	2.67	3.75	3.58	8.548	8.44	7.85	7.57
NiL7	53.54	53.33	3.07	2.91	3.90	3.78	-	-	8.18	8.00
NiL8	53.89	53.62	3.11	3.02	7.86	7.67	-	-	8.23	8.11

Table 2. Selected IR frequencies for Ni(II) complexes with 4-NO₂-substituted heteroaryl cinnamoyl derivatives.

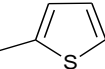
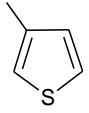
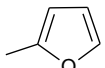
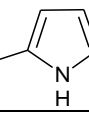
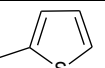
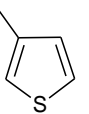
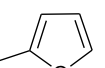
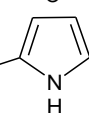
No	VOH	VNH	V _{ar}	VC=O	VC=O'	VC=C	VC=C(Het)	V _{as} NO ₂	V _s NO ₂	δ _{OH}	V=CH	V ₂ -Thiophen	V ₃ -Thiophen
NiL1 	3251		3065	1674	1631	1613	1577	1532	1352	1275	961	824	-
NiL2 	3270		3058	1667	1619	1582	1571	1533	1349	1248	961	-	785
NiL3 	3363		3057	1674	1635	1619	1582	1538	1351	1264	961	-	-
NiL4 	3276	3221	3058	1674	1630	1614	1588	1532	1343	1256	961	-	-

Table 3. Selected IR frequencies for Ni(II) complexes with 5-NO₂-substituted heteroaryl cinnamoyl derivatives.

No	VOH	VNH	V _{ar}	VC=O	VC=O'	VC=C	VC=C(Het)	V _{as} NO ₂	V _s NO ₂	δ _{OH}	V=CH	V ₂ -Thiophen	V ₃ -Thiophen
NiL5 	3272		3085	1692	1627	1613	1570	1528	1342	1255	977	839	-
NiL6 	3098		3064	1713	1625	1612	1578	1544	1338	1240	985	-	799
NiL7 	3325		3061	1693	1635	1614	1577	1528	1342	1257	982	-	-
NiL8 	3275	3225	3060	1694	1630	1613	1589	1528	1343	1255	988	-	-

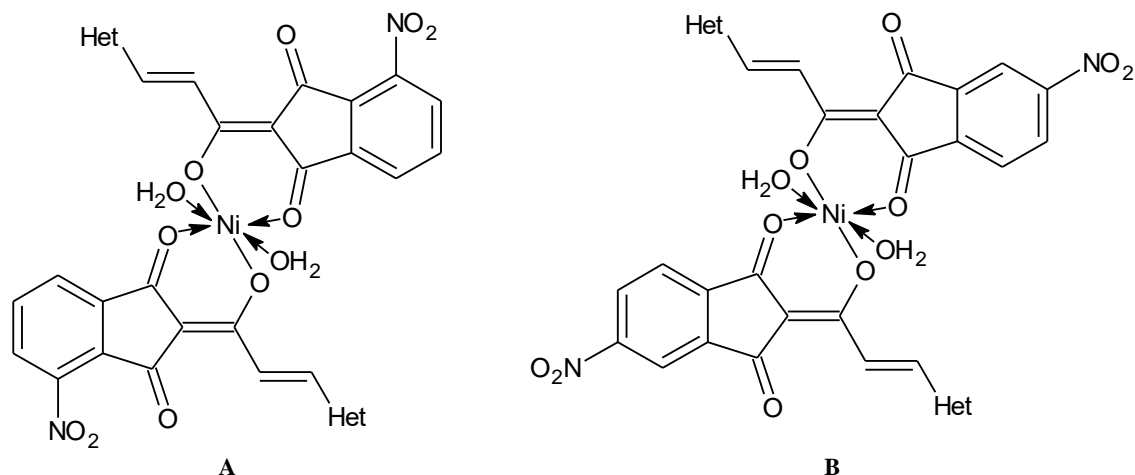


Figure 2. Suggested structures of the Ni(II)L1- Ni(II)L4 (A) and Ni(II)L5 – Ni(II)L8 (B) complexes

In order to evaluate the mode of coordination of the ligand to the metal ions, the IR spectra of the ligands **L1-L8**, as well as of their Ni(II) complexes were recorded. In the IR-spectrum of the pure ligands **L1-L8** a band of -OH group was observed between 3502-3438 cm^{-1} . The vibrational frequencies for the OH group are absent in the spectra of the complexes. Thereby, the free ligands coordinate as bidentate monoanion forming 6-membered chelate ring with the metal ion. Based on the obtained results it is suggested that the composition of the complexes is $[\text{M}(\text{L})_2 \cdot 2\text{H}_2\text{O}]$. Based on the experimental data, the most probable structure for the Ni(II) complexes was suggested with deprotonated OH group of 4- and 5-nitro-cinnamoyl derivatives. Based on previous studies on the structure of metal complexes of 2-acetyl-1,3-indandione [9-11], it is supposed that the Ni(II) complexes contain at least two water molecules, axially coordinated to the metal center. It is seen that nitro complexes exhibit $\nu_a(\text{NO}_2)$ and $\nu_s(\text{NO}_2)$ in the 1470–1370 and 1340–1320 cm^{-1} regions, respectively. Thus $\nu_a(\text{NO}_2)$ shifts markedly to a higher frequency, whereas $\nu_s(\text{NO}_2)$ changes very little on coordination [12]. The most probable structures of the all complexes was suggested and depicted in Figure 2.

It was not possible to measure Raman spectra of the free ligands **L2**, **L5**, **L6**, **L7** and **L8** and their metal complexes - the sample burned even at 1 mW laser power. Only the Raman spectra of the free ligands **L1**, **L3** and Ni(II)L5 complex were measured. In the Raman spectrum of **L1** and **L3** the band at 1601 cm^{-1} and 1611 cm^{-1} can be attributed to stretching vibrations of C=C. In the Raman spectrum of Ni(II)L5 complex the band of the carbonyl group appears at 1686 cm^{-1} . In the same spectrum the band of the NO_2 group appears at 1345 cm^{-1} . In the IR spectrum of Ni(II)L5 complex the

same band was observed at 1342 cm^{-1} . The band in the Raman spectrum of **L1** and **L3** at 1368 cm^{-1} and 1351 cm^{-1} was observed at 1357 and 1355 cm^{-1} in the IR spectrum were for stretching vibrations of NO_2 group, respectively.

The ligands coordinate in a bidentate way as monoanions after deprotonation of the enolic OH group. This is confirmed by the IR data of the metal complexes, which are compared with those of the free ligands and presented in Table 2 and 3. The IR data of the 4- and 5-nitro-substituted heteroaryl cinnamoyl derivatives are presented in a previous work of ours [13].

CONCLUSIONS

The synthesis of eight new Ni(II) complexes with 4- and 5- nitro-substituted heteroaryl cinnamoyl derivatives have been described. A series of non-charged complexes with Ni(II) was isolated and analyzed by elemental analyses, UV-Vis and IR spectroscopy. For the Ni(II) complexes a octahedral structure was proposed.

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КОМПЛЕКСИ НА Ni(II) С 4- И 5- НИТРО-ЗАМЕСТЕНИ ХЕТЕРОАРИЛ ЦИНАМОИЛНИ ПРОИЗВОДНИ

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(Резюме)

Целта на настоящата разработка е получаването на нови комплекси на Ni(II) с 4- и 5- нитро-заместени хетероарил цинамоилни производни с потенциално биологично действие. Структурата на получените осем метални комплекси е изследвана с елементарен анализ и UV-Vis, ИЧ-спектроскопски методи (за един от тях и с Раманова спектроскопия). Въз основа на получените експериментални резултати считаме, че най-вероятно лигандите са координирани бидентатно, като моноанион след депротониране на енолната -ОН група. Предполага се октаедрична геометрия на металния център с 2 органични лигандни молекули и 2 молекули вода координирани към Ni(II).

Ключови думи: 4- и 5- нитро-заместени хетероарилни цинамоилни производни, метални комплекси, ИЧ