

Synthesis of some transition metal complexes of ligands derived from 5-phenyl-2,3-dihydro-2,3-furandione

Esvet Akbas*, Mehmet Sonmez, Metin Celebi and Furgan Aslanoglu

Department of Chemistry, Faculty of Sciences, University of Yuzuncu Yil, 65080, Van, Turkey

A series of amide ligands was prepared by the reactions of 5-phenyl-2,3-dihydro-2,3-furandione and aromatic amines. The ligands reacted with Cu(II) and Ni(II) ions to yield mononuclear complexes. The ligands and complexes were characterised by elemental analyses, mass, FTIR, UV-vis, ^1H NMR and ^{13}C NMR spectral studies, as well as magnetic moment, AAS and conductance measurements as appropriate

Keywords: furandione, transition metal complexes, amide, synthesis

Interest in substituted 2,3-dihydro-2,3-furandiones such as the 5-phenyl-,¹ 5-(β -styryl)-,² 4-benzoyl-5-phenyl-,³ 5-aryl-4-imidoyl-,⁴ 5-aryl-4-halogen-,⁵ 5-aryl-4-phenyl-,⁶ and 5-aryl-4-quinoxaliny-derivatives⁷ is because of their high reactivity and the possibility of employment as starting compounds for preparing various carbonyl compounds and heterocyclic ring systems. The reactions of substituted 2,3-dihydro-2,3-furandiones have been studied with various hydrazines,⁸⁻¹⁰ amines,¹¹⁻¹³ hydrazides,¹² carbodiimides,¹⁴ acetanilides¹⁵ and azomethines¹⁶ under different conditions. Most of these synthesised compounds in general are well known for their potential biological activities.^{8,17} When 2,3-dihydro-2,3-furandiones react with aromatic or heterocyclic amines such as aniline, *p*-toluidine, *p*-anisidine, 2-pyridylamine or 2-pyrimidylamine, aroylamides, which are β -dicarbonyl compounds, are obtained.¹⁸

The β -dicarbonyl compounds such as dibenzoylmethane, acetylaceton or acetoacetate are commonly used in organic chemistry. These compounds constitute an important ligand class in terms of their distinctive structural properties and high synthetic utility. They exist in two tautomeric forms.^{19,20} Metal complexes of β -dicarbonyl compounds are of considerable commercial interest. These metal complexes are used in the production of laser devices,²¹ as NMR shift reagents and in analytical chemistry.²²

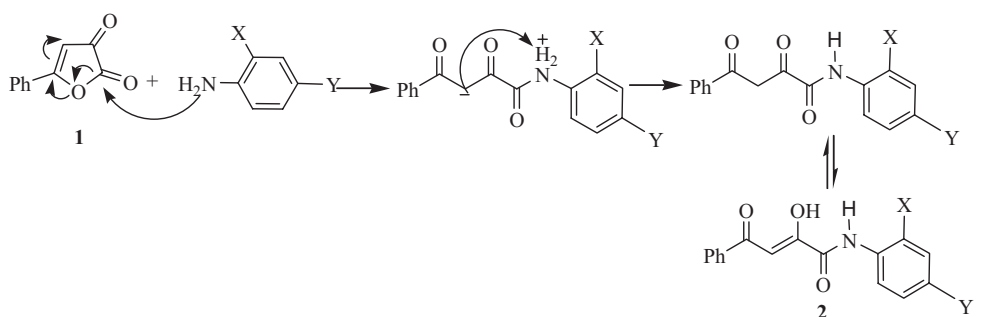
In the present work, we have synthesised methyl- (**2a**) and ethyl-2-[(2,4-dioxo-4-phenylbutanoyl)amino]benzoate (**2b**) and N-(4-nitrophenyl)-2,4-dioxo-4-phenylbutanamide (**2c**)¹¹ in good yield and we have studied their interaction with transition metals.

Result and discussion

The amide derivatives **2a–c** were prepared *via* reaction of 5-phenyl-2,3-dihydro-2,3-furandione (**1**) with aromatic amines (Scheme 1). The reactions were performed under different conditions. Reaction of furandione (**1**) and aromatic amines in absolute chloroform at room temperature for 72 h gave low yields, whereas in reactions performed in dry benzene at reflux temperature for 3 h, the same final products (**2a–c**) were obtained in good yield.

According to FTIR and ^1H NMR spectra, tautomerisation in the ligands appeared in the carbonyl groups (Scheme 2).

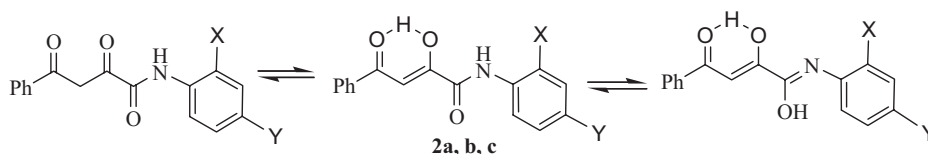
The FTIR spectrum of **2a** showed an absorption band at 3226–3220 cm^{-1} (hydroxyl function) as well as two carbonyl absorption bands at 1698 and 1584 cm^{-1} . In the ^1H NMR spectra of **2a**, the signal at δ 12.86 was a broad singlet due to the hydroxyl proton, which undergoes keto-enol tautomerisation. The keto- and enol-forms are in equilibrium, although the enol form predominates here. The resonances



X = $-\text{COOCH}_3$ (a), $-\text{COOC}_2\text{H}_5$ (b), H (c)

Y = H (a), H (b), NO_2 (c) [11]

Scheme 1



Scheme 2

* Correspondent. E-mail: esvakbas@hotmail.com

of hydroxyl protons generally occur downfield (δ ~7.5–4). If a carbonyl group in a suitable position to the hydroxyl proton is available, the absorption is downfield of the former range, at about δ ~12–10, because of intramolecular hydrogen bonding.²³ The singlets at 8.87 and 8.82 ppm are due to $\text{NH} \rightleftharpoons \text{OH}$ tautomerisation. The singlets at 7.32 and 4.00 ppm are assigned to –CH and to the methyl protons, respectively.

The ¹³C NMR spectrum of **2a** revealed signals at δ 187.53, 181.77 (C=O), and 96.02, 54.65 ppm (–CH and –CH₃ groups) (See experimental for details). Its mass spectrum showed the molecular ion peak at m/e 325.0.

The IR spectrum of **2b** showed an absorption band at 3225–3220 cm⁻¹ due to the hydroxyl function. The two carbonyl absorption bands appeared at 1698 and 1584 cm⁻¹. In the ¹H NMR spectra of **2b**, the broad singlet at δ 12.84 is assigned to the hydroxyl proton that undergoes keto-enol tautomerisation. The singlets at 8.86 and 8.82 ppm are due to the $\text{NH} \rightleftharpoons \text{OH}$ tautomerisation. The singlet at 7.31, the quartet at 4.41–4.52 and the triplet at 1.40–1.48 ppm are due to CH, OCH₂ and to the methyl protons, respectively.

The ¹³C NMR spectrum of **2b** showed signals at δ 187.51, 181.85 (C=O), 96.01, 63.73, 16.25 ppm CH, OCH₂ and CH₃ groups (see experimental for details).

The bidentate complexes of the aroylamides (**2a–c**), presented in Scheme 3, were obtained from 1/2 molar ratio reactions with metal salts and **2a–c** and have the general formulae $[\text{Co}(\text{L}_{a,b,c})_2(\text{H}_2\text{O})_2] \cdot n\text{H}_2\text{O}$ and $[\text{Ni}(\text{L}_{a,b,c})_2(\text{H}_2\text{O})_2] \cdot n\text{H}_2\text{O}$ ($\text{L}_{a,b,c}$ = ligand derived from **2a–c**). The analytical data are in a good agreement with the proposed stoichiometry of the complexes. The colours, yields, melting points, FTIR and UV-vis data of all the metal complexes are presented in Tables 2 and 3. The complexes are non-electrolytes²⁴ as shown by their molar conductivities (Λ_M) in DMF, which are in the range 14.1–26.8 S cm² mol⁻¹.

Table 3 presents the most important FTIR spectral bands of all the metal complexes. The FTIR spectra of the complexes can be compared with those of the free ligands (**2a–c**) to determine the changes that might have taken place during the complexation. The band at 1711–1696 cm⁻¹ is characteristic of the carbonyl group present in the free ligands. The decrease in this frequency region (1693–1658 cm⁻¹) observed in all the complexes, indicates the involvement of the carbonyl oxygen atom in coordination.^{25–27}

The broad IR bands of the ligands in the range 3355–3100 cm⁻¹ may be due to OH or NH.^{25,28} The OH stretching and bending vibrational frequencies of the β -diketonate moiety of the ligands (**2a–c**) bands were seen at 3380, 3340, 3300 cm⁻¹ and 1300, 1340 and 1368 cm⁻¹ respectively. The strong bands in the FTIR spectra of the free ligands, assigned to C–O, are changed by \pm 40–60 cm⁻¹ in the spectra of the complexes. This indicates coordination through the enolic oxygen of the ligands (Scheme 3). In the spectra of all the complexes, the bands observed in the 430–506 cm⁻¹ region

may be due to M–O.^{25–27} The FTIR spectra of the complexes characterised by the appearance of a broad band in the region 3435–3595 cm⁻¹ are due to the OH frequency of water of crystallisation. This water content was also identified by the elemental analyses.

The UV-vis data for all the complexes are shown in Table 3. The spectra were recorded in DMF as solvent.

The UV-vis spectra of Ni(II) complexes recorded herein are very similar to each other and consist of two bands, one at 642–666 nm due to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\nu_1)$ and the other 404–428 nm for ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\nu_2)$, which clearly indicate the octahedral stereochemistry of the complexes.^{29,30} The magnetic behaviour of octahedral nickel(II) complexes is relatively simple. Nickel(II) has the electronic configuration 3d⁸ and thus these complexes show magnetic moments in the range expected for an octahedral field (2.8–3.2 BM).

The UV-vis spectra of all the present cobalt(II) complexes recorded herein are very similar to each other and consist of two bands, one in the 640–670 nm region and the other in the 474–510 nm region, which clearly indicate the octahedral stereochemistry of the complexes.

The magnetic measurements on the complexes reported here (4.7–5.1 BM) show that all are paramagnetic and have three unpaired electrons, indicating a high-spin octahedral configuration.³⁰

Experimental

The solvents were dried by refluxing with the appropriate drying agents and distilled before use. Melting points were determined on an Electrothermal Gallenkamp apparatus and are uncorrected. Microanalyses were performed on LECO CHNS 932 Elemental Analyser. The IR spectra were obtained in potassium bromide pellets using a Mattson 1000 FTIR spectrometer. The ¹H and ¹³C NMR spectra were recorded on Bruker Avance DPX-400 spectrometers, using TMS as an internal standard. The mass spectra (100 eV) were measured on an AGILENT 1100 MSD mass spectrometer. All experiments were followed by TLC using DC Alufolien Kieselgel 60 F 254 Merck and Camag TLC lamp (254/366 nm). The electronic spectra in the 200–900 nm range were obtained in DMSO on a Unicam UV2-100 UV/VIS spectrophotometer. Molar conductances of the ligand and their metal complexes were determined in DMSO at room temperature by using a Jenway model 4070 conductivity meter.

The atomic absorption measurements for the determination of cobalt and nickel ion were carried out using a Thermo Solar System atomic absorption spectrophotometer (AAS). For AAS, the cobalt and nickel was measured by using the following settings: flame type air-acetylene; wavelength respectively 240.7 and 232.0 nm; lamp current%75; fuel flow 0.9 l/min; burner height 12.0 mm; band pass 0.5 nm; measurement 4 second.

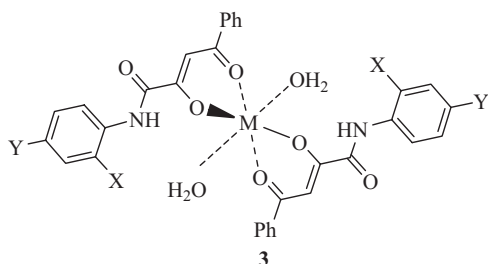
Synthesis of the organic ligands **2a–c** (LH)

General procedures for the preparation of compounds (2a–c) (a) A solution of amine derivatives (1 mmol) in absolute chloroform (5 ml) was added dropwise to a solution of furandione **1** (1 mmol) in dry chloroform (5 ml). Then the solution was stirred at room temperature for 72 h. The precipitate was filtered off and washed with dry ether and recrystallised.

(b) A solution of amine derivative (1 mmol) and furandione **1** (1 mmol) was refluxed in dry benzene (10 ml) for 3 h and the solvent was evaporated. Then the precipitate was treated with dry ether to give a crude solid that was recrystallised to give compounds **2a–c**.

Methyl 2-[(2,4-dioxo-4-phenylbutanoyl)amino]benzoate (2a): The compound **2a** was obtained according to general procedure (a) in yield 0.1186 g (36.5%), and according to general procedure (b) in yield 0.2448 g (75.3%), m.p. 168–169°C (2-propanol). Mass spectrum (100 eV) for C₁₈H₁₅NO₅: m/e : 327.1 (3.0%), 326.0 (19.8%), 325.0(100.0%), 323.2, 294.0, 276.0, 248.0, 221.0, 180.0, 179.0, 177.9, 175.9, 152.0, 150.9, 146.9, 145.9, 129.9, 119.9, 118.9, 104.8, 89.9, 76.9, 68.9, 50.9. The characteristic FTIR, ¹H NMR and ¹³C NMR spectra data are presented in Table 1.

Ethyl 2-[(2,4-dioxo-4-phenylbutanoyl)amino]benzoate (2b): The compound **2b** was obtained according to general procedure (a) in yield 0.1195 g (35.3%), and according to general procedure (b) in yield 0.2529 g (75.5%), m.p. 135–136°C (ethanol). Elemental



M=Ni (**a, b, c**), Co (**d, e, f**); X=–COOCH₃ (**a, d**), H (**b, e**), –COOC₂H₅ (**c, f**); Y=H (**a, c, d, f**), NO₂ (**b, e**)

Scheme 3

Table 1 FTIR, ¹H NMR and ¹³C NMR spectra of compounds **2a,b** in CDCl₃: (values, ppm; J (Hz))

Comp.	IR(KBr)	¹ H NMR	¹³ C NMR
2a	3226–3220 cm ⁻¹ (C=O ⇌ OH and NH ⇌ OH, exchangeable); 2994 cm ⁻¹ (CH _{aliph}); 1698, 1584 cm ⁻¹ (C=O).	12.86 (1H, bs, -OH, C=O ⇌ OH); 8.87 and 8.82 (1H, s, NH, NH ⇌ OH); 7.32 (1H, s, -CH); 7.15–8.14 (9H _{arom} , m); 4.00 (1H, s, CH ₃).	187.53 and 181.77 (C=O); 170.24, 162.05, 141.97, 136.83, 135.00, 135.46, 133.18, 130.84, 128.88, 125.70, 122.52, 110.34; 96.02 (-CH-); 54.65 (-CH ₃).
2b	3225–3220 cm ⁻¹ (C=O ⇌ OH and NH ⇌ OH, exchangeable); 2993 cm ⁻¹ (CH _{aliph}); 1696, 1585 cm ⁻¹ (C=O).	12.84 (1H, bs, -OH, C=O ⇌ OH); 8.86 and 8.82 (1H, s, NH, NH ⇌ OH); 7.31 (1H, s, CH); 7.14–8.14 (9H _{arom} , m); 4.41–4.52 (2H, q, -OCH ₂ , J = 7.1); 1.40–1.48 (3H, t, CH ₃ , J = 7.1).	187.51 and 181.85 (C=O); 169.76, 162.02, 141.95, 136.49, 135.78, 135.45, 133.20, 130.84, 129.67, 125.66, 122.49, 118.66; 96.01 (-CH-); 63.73(-OCH ₂); 16.25 (CH ₃).

Table 2 Analytical and physical data for the complexes

Compd	Colour	M.p. /°C	Yield /%	μ _{eff} [B.M.]	Found (Calcd.)/%				Λ _M (S cm ² mol ⁻¹)
					C	H	N	M	
(3a) [Ni(MEB) ₂ (H ₂ O) ₂].H ₂ O C ₃₆ H ₃₄ N ₂ O ₁₃ Ni (760.71 g/mole)	Light Green	220 Dec	82	2.77	56.3 (56.8)	4.5 (4.5)	3.4 (3.7)	7.8 (7.7)	21.4
(3b) [Ni(HNE) ₂ (H ₂ O) ₂].H ₂ O C ₃₂ H ₂₈ N ₄ O ₁₃ Ni (734.71 g/mole)	Pale Green	310<	70	3.35	52.6 (52.3)	3.6 (3.8)	7.4 (7.6)	7.9 (8.0)	25.1
(3c) [Ni(EEB) ₂ (H ₂ O) ₂].2H ₂ O C ₃₈ H ₄₀ N ₂ O ₁₄ Ni (806.71 g/mole)	Olive Green	190 Dec	63	2.76	56.7 (56.5)	4.75 (5.0)	3.2 (3.5)	7.3 (7.4)	14.4
(3d) [Co(MEB) ₂ (H ₂ O) ₂].0.5H ₂ O C ₃₆ H ₃₃ N ₂ O _{12.5} Co (751.93 g/mole)	Light Orange	186 Dec	85	4.27	57.6 (57.45)	4.3 (4.4)	3.4 (3.7)	7.8 (7.8)	20.7
(3e) [Co(HNE) ₂ (H ₂ O) ₂].H ₂ O C ₃₂ H ₂₆ N ₄ O ₁₃ Co (732.93 g/mole)	Crimson	310<	69	5.06	52.8 (52.4)	4.4 (4.3)	7.4 (7.6)	8.2 (8.0)	26.8
(3f) [Co(EEB) ₂ (H ₂ O) ₂] C ₃₈ H ₃₆ N ₂ O ₁₂ Co (770.93 g/mole)	Orange	197 Dec	78	4.70	59.4 (59.15)	4.7 (4.7)	3.3 (3.6)	7.1 (7.6)	11.5

Table 3 Characteristic IR and Uv-vis spectra data of all the metal

Compd	OH/H ₂ O	CH _{aliph} .	C=OM	NH	MO	Ar-NO ₂	λ _{max} (nm)
3a	3421–3595 m,br	2946–3057 w	1693–1598 m	3250 s	480–506 w	–	666, 404, 346, 308, 278
3b	3473 w,br	2926–3073 w	1658–1600 m	3285 s	436–492 w	1479–1548 m	642, 428, 350, 308
3c	3435 m,br	2978–3061 m	1685–1598 m	3246 s	456–492 w	–	644, 410, 309, 276
3d	3498 m,br	2951–3063 w	1679–1595 m	3298 w	480–509 w	–	670, 474, 308, 274
3e	3373–3487 m,br	2964–3061 w	1660–1600 m	3288w	430–490 w	1481–1546 m	650, 510, 382, 318, 268
3f	3481 m,br	2986–3061 w	1679–1595 m	3273 w	448–492 w	–	640, 482, 332, 270

Complexes: s = strong, m = medium, w = weak, br = broad.

analysis: Calc. for C₁₉H₁₇NO₅: C, 67.25; H, 5.05; N, 4.1%. Found: C, 67.3; H, 5.1; N, 4.1%. The characteristic FTIR, ¹H NMR and ¹³C NMR spectral data are presented in Table 1.

N-(4-nitrophenyl)-2,4-dioxo-4-phenylbutanamide¹¹ (**2c**): The compound **2c** was obtained according to general procedure (b) in yield 0.194 g (62.2%).

Synthesis of the metal complexes (**3a–f**)

General procedure for the preparation of compounds 3a–f: The appropriate quantity of the ligands **2a–c** (1 mmol) was dissolved in methanol (35 ml), and a solution of Co(AcO)₂·H₂O or Ni(AcO)₂·4H₂O (0.5 mmol) in methanol (15 ml) was added dropwise with continuous stirring. The mixture was stirred further for 1.5–2.5 h. at 60°C. The precipitated solid was then filtered off, washed with cold methanol, followed by diethyl ether and dried in a vacuum desiccator.

The characteristic FTIR, UV-vis, analytical and physical data of all the metal complexes are presented in Tables 2 and 3.

The authors would like to thank Dr Musa Turker from the Department of Biology, Faculty of Art and Science, Yuzuncu Yil University, for his linguistic support.

Received 20 February 2008; accepted 15 April 2008

Paper 08/5109 doi: 10.3184/030823408X318307

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