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Synthesis and Spectral Studies of Pyranone Derivative and Its Cu(II), Co(II), Ni(II) and Zn(II) Complexes[1]

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Abstract—Under the thermolysis condition, 5-phenyl-2,3-dihydro-2,3-furandione (**IV**) in inert aprotic solvents as *p*-xylene at 130–140°C yields 3-benzoyl-4-hydroxy-6-phenyl-2*H*-pyran-2-one (**VI**) *via* phenyl ketene (**V**). The compound (**VI**) was converted into the corresponding 3-benzoyl-4-hydroxy-6-phenylpyridin-2(1*H*)-one (**VII**), and 3-benzoyl-2-oxo-6-phenyl-2*H*-pyran-4-yl acetate (**VIII**), by its reactions with ammonium hydroxyde, and acetic anhydride, respectively. On the other hand, a series of new various metal complexes (**IX-XIa, XIb**) of **VI** was synthesized. The results suggest that the compound **VI** as bidentate ligand indicate a binuclear structure for the Cu(II) complex with square-planar geometry. The Ni(II) and Zn(II) complexes are of tetrahedral and the Co(II) complex is also octahedral geometry with water molecules at the axial positions. The structures of compounds and complexes were characterized on the basis of elemental analysis, Mass, IR, ^{1}H, and ^{13}C NMR spectra.

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α-Oxoketenes are often used as structure particles in chemical design. Usually they can not be stabilized under reaction conditions. The most common method for the synthesis of these highly reactive molecules is the thermolysis of 2,3-dihydrofuran-2,3-diones and 1,3-dioxan-4-ones [1–7].

The ketenes usually were added to multiple bond systems *via* a [2+2] process across their C=C as well as C=O double bonds, while α-oxoketenes show a pronounced behavior to form [4π+2π] hetero-Diels Alder adducts when trapped with dienophiles. When the reaction is carried out in an inert medium, the –COC=C part of ketene molecule acts as heterodiene while the C=C bond of ketene acts as heterodienophile [7–11].

The nucleophilic addition is one of the most characteristic reactions of the ketenes [10–13, 15]. *N*-acrylamides of aroylacetic acids were obtained by the reaction of the arylketenes with aromatic and heterocyclic amines [16]. The reactions of ketene with 1,1-diamines form the substituted 6-aryl-2-methylene-4*H*-pyrimidin-4-ones [12]. The ketenes towards carbon-nucleophiles converted into 4-pyrone derivative [10].

Besides, the compounds containing pyranone ring are known as good complexing agents and therefore are of interest in coordination and bioinorganic chemistry [17–18]. The interests in these complex derivatives are due to the possibility of their enzyme inhibitory properties [19].

Herein we have reported synthesis of 3-benzoyl-4-hydroxy-6-phenyl-2*H*-pyran-2-one [11] in inert aprotic solvent. Thereafter, 3-benzoyl-4-hydroxy-6-phenyl-2*H*-pyran-2-one was converted into the corresponding 3-benzoyl-4-hydroxy-6-phenylpyridin-2(1*H*)-one, and 3-benzoyl-2-oxo-6-phenyl-2*H*-pyran-4-yl acetate, by its reactions with ammonium hydroxyde, and acetic anhydride, respectively. In addition the new Cu(II), Co(II), Ni(II) and Zn(II) metal complexes of the 3-benzoyl-4-hydroxy-6-phenyl-2*H*-pyran-2-one (**VI**) were synthesized and characterized.

The reactions of oxalyl chloride with a solution of alkenyloxysilanes in dry ether at room temperature gives 2,3-furandiones (**I**). They undergo decomposition, by heating to a temperature near the melting

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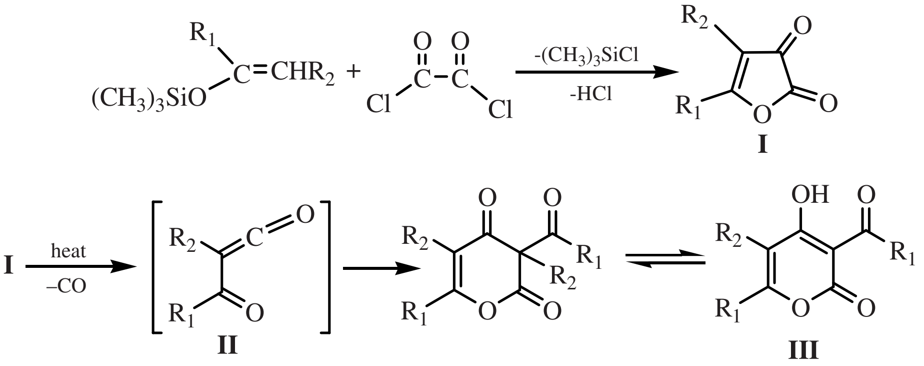
[1] The text was submitted by the authors in English.

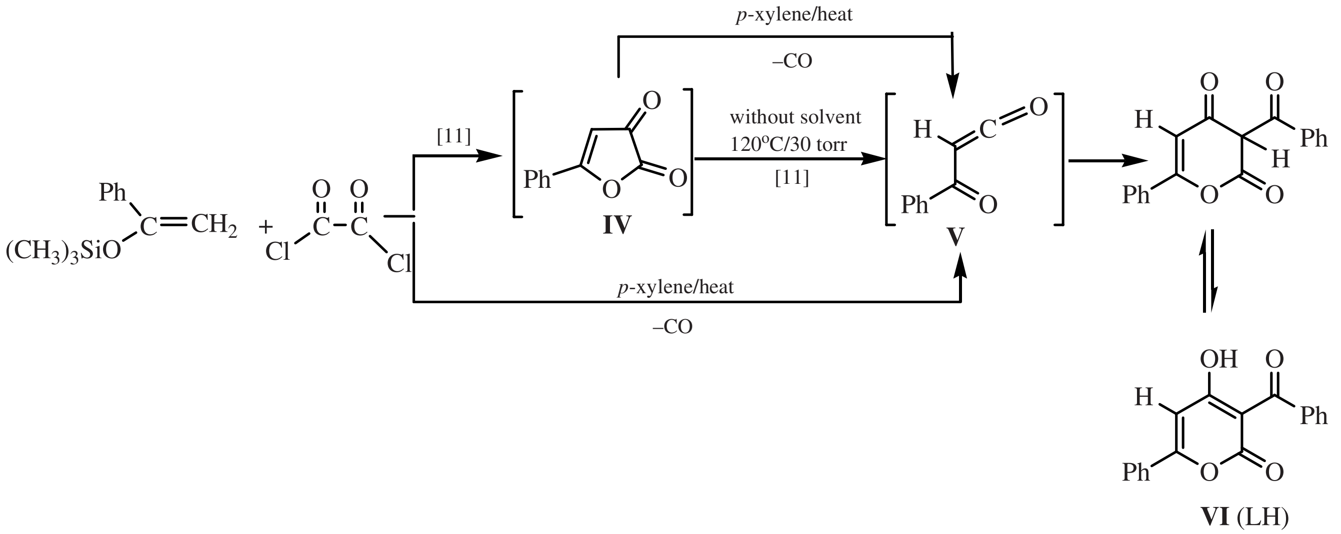
point (120–140°C), without solvents and give aroylketenes (**II**). They were converted into 3*H*-pyran-2,4-diones (**III**) [11] as a result of [4+2] cyclodimerization (Scheme 1).

Scheme 1.



We have synthesized the same pyranone (**VI**) (LH) compound in a good yield in refluxing *p*-xylene at 130–140°C (Scheme 2), instead of that described above.

Scheme 2.

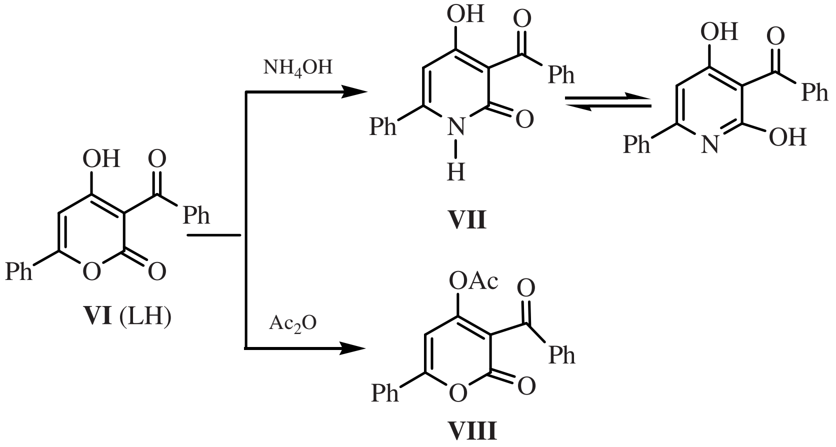


We also prepared the same pyranone (**VI**) (LH) compound in one step reaction between 1-phenyl–1-trimethylsiloxyethylene and oxalylchloride in refluxing *p*-xylene (Scheme 2). However, this reaction resulted in a very low yield.

The IR spectroscopic data of **VI** are in agreement with published data [11]. In the ^{1}H NMR spectra of **VI**, the 1-H (C^5) signal appeared as a singlet at δ 6.7 ppm. A singlet signal at δ 15.9 ppm was also exhibited due to OH proton. The behavior of a phenolic protons are generally downfield (7.5–4). If a carbonyl group in the ortho position to the phenolic protons is available, the absorption is downfield in the range of about (12–10) because of intramolecular hydrogen bonding [20]. Also, the signals from aromatic protons were presented. The ^{13}C NMR spectrum of **VI** revealed the signals at δ 202.2, 182.9 (C=O). The mass spectrum of **VI** showed the following ion peaks, *m/e*: 293.0, 292.0 (for further details of spectroscopic investigations see Experimental).

When the compound **VI** was allowed to react in 1-butanol with ammonium hydroxyde, the corresponding pyridine derivative **VII** was produced (Scheme 3). The IR spectrum of compound **VII** showed the bands at 3287 cm^{-1} (NH $\rightleftarrows$ OH), 1691, 1642 cm^{-1} (C=O). The ^{1}H NMR spectrum of compound **VII** (in DMSO-d_6) revealed the signals at 9.9 (1H, br. s, NH), 12.2 (1H, br. s, OH).

Scheme 3.



Treatment of the compound **VI** with acetic anhydride afforded a single product that was identified as 3-benzoyl-2-oxo-6-phenyl-2*H*-pyran-4-yl acetate (**VIII**), the chemical transformation of which was outlined in Scheme 3. The signals of hydroxyl function group disappeared in the IR and ^{1}H NMR spectra of compound **VIII**. The ^{1}H NMR spectrum of compound **VIII** revealed a singlet signal at δ 2.1 due to methyl protons. Its IR spectrum showed absorption bands at 1782, 1731, 1658 cm^{-1} due to three carbonyl functions, respectively (for details see Experimental).

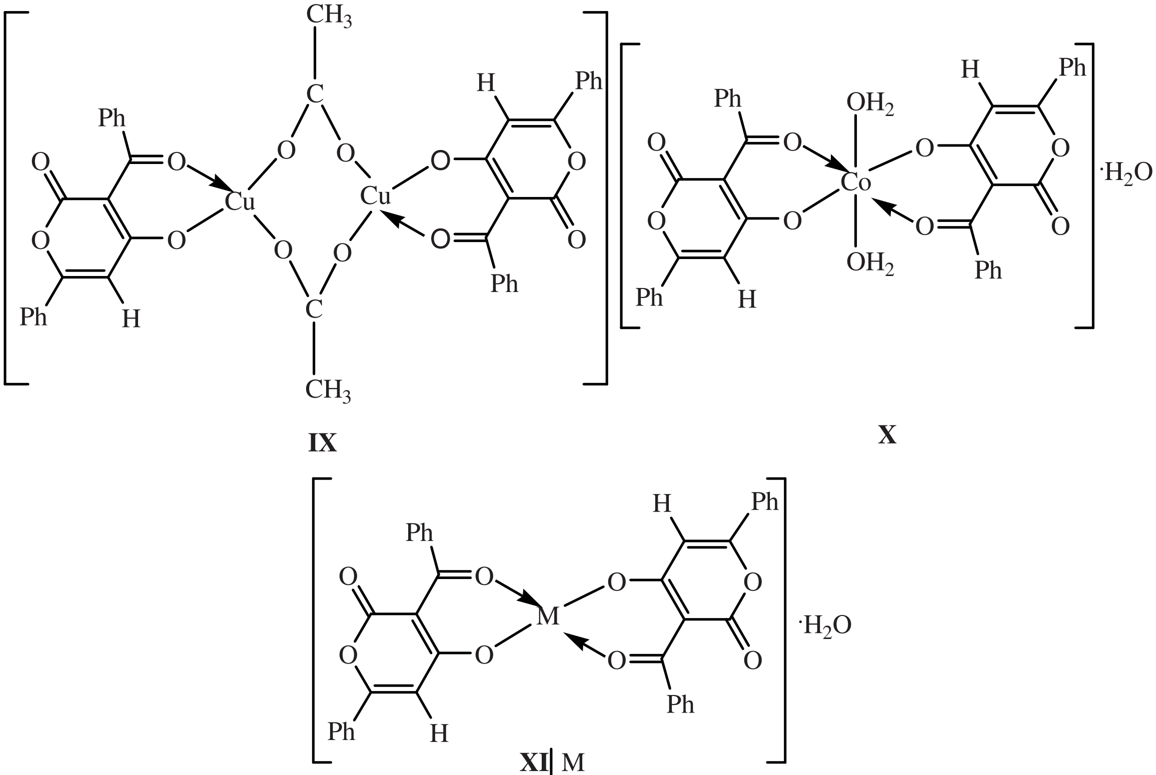
On the other hand, bidentate mononuclear complexes were obtained from 1/2 molar ratio reactions with metal ions and LH (**VI**) except for 1/1 molar ratio binuclear Cu(II) complex. The LH(**VI**), in reaction with $Co(CH_3COO)_2 \cdot 4H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$, $Zn(CH_3COO)_2 \cdot 2H_2O$, and $NiCl_2 \cdot 6H_2O$ salts yields complexes corresponding to the general formula $[Cu_2(L)_2(AcO)_2]$ (**IX**), $[Co(L)_2] \cdot 3H_2O$ (**X**), $[Ni(L)_2] \cdot H_2O$ (**XIa**) and $[Zn(L)_2] \cdot H_2O$ (**XIb**) (Scheme 4). The analytical data are in a good agreement with the proposed stoichiometry of the complexes. All the complexes were of nonelectrolyte type, as measured their conductivities in the range 2.8–9.5 Scm^2 mole^{-1}.

Strong bands observed at 3400, 1750, and 1626 cm^{-1} and 1544 cm^{-1} in the IR spectra of the free ligand assigned respectively to OH, C=O and C–O$_{\text{pyran}}$ was changed in the spectra of complexes, indicating coordination through phenolic oxygen and carbonyl oxygen of ligand LH. By comparing the spectra of the ligand and their complexes, the stretching vibrational band of OH disappeared in the complexes and the frequency shifts of some relevant bands of the ligand were observed, particularly for the stretching vibration of C=O [21] Co(II) and Ni(II) complexes showed a broad band around 3300 cm^{-1} indicating the presence of coordinated or lattice water in the complex. The *bis* (acetato) bridged Cu(II) complex shows strong bands at 1632 and 1468 cm^{-1}. New bands in all the complexes at 442–523 cm^{-1} are attributed to the M–O.

The ^{1}H-NMR spectra of diamagnetic Zn(II) complex showed approximately the same peaks identical to those of the free ligand with exception of the absent peak of OH group. This is considered as an additional evidence for the deprotonation of OH.

The electronic spectra values and the magnetic moment data of the complexes were given in the experimental section. The spectrum of the Cu(II) complex showed an absorption band at 724 nm attributed to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition, which is compatible with this complex having a square-planar structure [22]. The Co(II) complex showed two bands at 698 and 510 nm attributed to $^4T_{1g} \rightarrow {}^4A_{2g}$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively, in an octahedral

Scheme 4.



IX

X

XI	M
a	Ni
b	Zn

geometry around the Co(II) ion [21]. The spectrum of the Ni(II) complex is consistent with tetrahedral geometry showing to *d–d* transition band at 670 nm assignable to transition $^3T_1 \rightarrow {}^3T_1(\mathrm{P})$, which suggests tetrahedral geometry [22]. On the other hand, the spectra of the Zn(II) complex has bands in the 276–386 nm and these bands may be due to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition of the benzene and heterocyclic rings.

EXPERIMENTAL

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 Analyzer. The IR spectra were obtained in potassium bromide pellets using a Mattson 1000 FTIR spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance DPX-400 spectrometers, using TMS as an internal standard. The mass spectra (100 eV) were run 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 conductance of the ligand and their metal complexes were determined in DMSO at room temperature by using a Jenway model 4070 conductivitymeter.

3-Benzoyl-4-hydroxy-6-phenyl-2*H*-pyran-2-one (VI). The compound **IV** (1.74 g, 10 mmol) in 20 ml of anhydrous *p*-xylene was refluxed 3 h at 130–140°C. After the solvent was evaporated, then the oily residue was treated with ether and the formed crude product was crystallized from 2-propyl alcohol to give **VI**. Yield 2 g (70%); mp 169–170°C; or to a stirred solution of 1-phenyl–1-trimethylsiloxyethylene (4.8 g, 25 mmol) in 20 ml of anhydrous *p*-xylene was added oxalylchloride (1.6 g, 12.5 mmol) over a period of one hour at 25°C. After 2 h the mixture was heated for 3 h. The solvent was evaporated, then the oily residue was treated with ether and the formed crude product was crystallized from 2-propyl alcohol to give **VI**. Yield 0.8 g (10.9%); mp 169–170°C; IR spectrum (KBr): 1750, 1626, 1544 cm^{-1}. ^{1}H NMR ($CDCl_3$): 6.68 s (1H, C^5), 7.5–7.9 m (10H, Ar), 15.9 s (1H, OH). ^{13}C NMR ($CDCl_3$) δ, ppm: 200.3 (C=O, benzoyl), 180.9 (C=O, C^4), 166.1, 160.2, 138.0, 132.7, 132.3, 130.1, 129.2, 128.3, 127.9, 126.6, 99.5, 98.1. The mass spectrum (100 eV), *m/e*: 294.1, 293.0, 292.0, 291.0, 288.6, 264.0, 262.9, 236.0, 214.9, 188.0, 186.9, 148.0, 146.9, 145.9, 131.0, 105.9, 104.8, 101.9, 79.8, 76.9, 68.9, and 63.9.

3-Benzoyl-4-hydroxy-6-phenylpyridin-2(1*H*)-one (VII). To the solution of **VI** (0.292 g, 1 mmol) in 20 ml 1-butanol was added excess of saturated aqueous solution of ammoniumhydroxyde with stirring. Then the reaction mixture was refluxed for 5 h. The resulting mixture was kept at room temperature for 24 h. The precipitate was filtered off and recrystallized from 1-butanol to give **VII**. Yield 0.160 g (55%); mp. 284–285°C; IR spectrum, (KBr), ν, cm^{-1}: 3287 (NH $\rightleftarrows$ OH), 1691, 1642 (C=O). ^{1}H NMR ($CDCl_3$): 6.6 s (1H, C^5), 7.5–7.9 m (10H, Ar), 9.9 br.s (1H, NH), 12.2 br.s (1H, OH). Found, %: C 74.14; H 4.45; N 4.80. $C_{18}H_{13}NO_3$. Calculated, %: C 74.22; H 4.50; N 4.81.

3-Benzoyl-2-oxo-6-phenyl-2*H*-pyran-4-yl acetate (VIII). Compound **VI** (0.292 g, 1 mmol) was treated with 5 ml of acetic anhydride and H_2SO_4 (2 drops), and then mixture was stirred at cautious heating (no gas evolution) for 30 more min. The reaction mixture was cooled, and then the solution was treated with 100 ml water. The precipitate was filtered off and recrystallized from ethyl alcohol. The compound **VIII** was obtained in yield 0.20 g (60%). mp 144–145ºC. IR: 1782, 1731, 1658 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): 6.8 s (1H, C^5), 7.2–7.9 m (10H, Ar), 2.1 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$), δ, ppm: 191.4, 168.7, 164.5, 164.1, 162.2, 138.5, 135.7, 134.1, 132.3, 131.2, 131.1, 130.7, 128.2, 115.3, 101.5, 22.7. Found, %: C 71.82; H 4.20. $C_{20}H_{14}O_5$. Calculated, % : C 71.85; H 4.22.

Synthesis of the complexes. 0.292 g (1 mmol) of the ligand (**VI**) was dissolved in 30 ml of chloroform, and a solution of 0.5 mmol of the metal salt [$Cu(AcO)_2\cdot H_2O$ (0.099 g), $Co(AcO)_2\cdot 4H_2O$ (0.124 g), $NiCl_2\cdot 6H_2O$ (0.120 g) and $Zn(AcO)_2\cdot 2H_2O$ (0.109 g)] in 15 ml methanol was added dropwise with continuous stirring. The mixture was stirred further for 1.5–2.5 h at 80°C. The precipitated solid was then filtered off, washed with diethyl ether, followed by cold ethanol and dried in a vacuum dessicator.

μ-Diacetato-bis(3-benzoyl-6-phenyl-2*H*-pyran-2,4(3*H*)-dionato)dicopper(II) (IX). Yield 0.160 g (65%); mp < 320°C. Found, %: C 57.60; H 3.13. $C_{40}H_{28}O_{12}Cu_2$. Calculated, %: C 58.03; H 3.38. IR (KBr), ν, cm^{-1}: 1707, 1632 (C=O), 1293 (C–O$_{\text{phenolic}}$), 1581, 1422 ($OCOCH_3$), 463, 520(M–O). Λ_M (in DMSO 1×10^{-3} M) 4.1 Scm^2 mol^{-1}; μ_{eff}. 1.69μ_B; $\lambda_{\max}$ (DMSO-*d*$_6$), nm: 396, 520, 724.

Bis(3-benzoyl-6-phenyl-2*H*-pyran-2,4(3*H*)-dionato)diaquacobalt(II)monohidrate (X). Yield 0.160 g (62%); mp < 320 °C. Found, %: C 62.56; H 3.97. $C_{36}H_{28}O_{11}Co$. Calculated, %: C 62.16; H 4.02. IR (KBr), ν, cm^{-1}: 3300 (OH/H_2O), 1697, 1640 (C=O), 1285 (C–O$_{\text{phenolic}}$), 442, 520 (M–O). Λ_M (in DMSO-*d*$_6$ 1 × 10^{-3} M) 5.6 Scm^2 mol^{-1}; μ_{eff}. 3.10 μ_B; $\lambda_{\max}$ (DMSO), nm: 394, 510, 698.

Bis(3-benzoyl-6-phenyl-2*H*-pyran-2,4(3*H*)-dionato)nickel(II)monohidrate (XIa). Yield 0.160 g (54%); mp < 320°C. Found, %: C 66.03; H 3.98. $C_{36}H_{26}O_9Ni$. Calculated, %: C 65.58; H 3.64. IR (KBr), ν, cm^{-1}: 3216 (OH/H_2O), 1672, 1632 (C=O), 1280 (C–O$_{\text{phenolic}}$), 450, 517 (M–O). Λ_M (in DMSO-*d*$_6$ 1 × 10^{-3} M) 9.5 Scm^2 mol^{-1}; μ_{eff} 2.85μ_B; $\lambda_{\max}$ (DMSO), nm: 358, 392, 540, 670.

Bis(3-benzoyl-6-phenyl-2*H*-pyran-2,4(3*H*)-dionato)zinc(II)monohidrat (XIb). Yield 0.160 g (70%); mp < 320°C. Found. %: C 66.97; H 3.68. $C_{36}H_{22}O_8Zn$. Calculated, %: C 66.72; H 3.40. IR (KBr), ν, cm^{-1}: 1672, 1630 (C=O), 1283 (C–O$_{\text{phenolic}}$), 442, 522 (M–O). ^{1}H NMR (DMSO): 6.62 s (1H, C^5), 7.3–7.9 m (10H, Ar). Λ_M (in DMSO 1 × 10^{-3} M) 2.8 Scm^2 mol^{-1}; μ_{eff} Dia; $\lambda_{\max}$ (in DMSO-*d*$_6$ 1 × 10^{-3} M), nm: 276, 308, 356, 386.

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