Synthesis and structure of sodium 1-alkoxy-1,4-dioxo-2-alkenolates and bis-(4-alkylaryl)-1-oxo-1-alkoxyalkane-2,4-dionato) metals (II) based on them

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Abstract: A priority task in contemporary organic chemistry consists in the synthesis of practically useful metal complexes having carbonyl-containing ligands. The present article details the isolation of several new bis-(4-alkylaryl)-1-oxo-1-alkoxyalkane-2,4-dionato) metals (II) via complex formation of metal salts of (zinc (II), copper (II) and nickel (II)) with sodium 1-alkoxy-1,4-dioxo-2-alkenolates obtained by condensation of alkyl (aryl) methyl ketones with dialkyl oxalates in the presence of sodium or sodium hydride as a condensing reagent. The structure of the synthesised sodium oxoenolates and metal complexes was confirmed by spectral analysis methods (IR, NMR 1H-, 13C-spectroscopy and mass spectrometry). In the IR spectra of the solid samples of the isolated compounds, stretching vibrations bands of ester carbonyl groups were identified, as well as high-intensity ether bands due to the vibrations of C-O-C bonds. For compounds containing aromatic fragments, bands corresponding to vibrations of monosubstituted benzene rings were found in the IR spectra. The NMR spectra of 1H of sodium oxoenolates and metal complexes recorded in DMSO-d6 demonstrated characteristic signals of ethoxy and n-butoxy fragments, methine protons, as well as protons of aromatic rings. Chemical shifts of carbon atoms in the NMR spectra 13C of sodium oxoenolates correspond well to the reference values. In the mass spectra of synthesised compounds recorded in electrospray mode, signals of protonated and cationised molecules were observed [M+H]+, [M+NH4]+, [M+Na]+, [M+K]+. Using quantum chemical methods, the models of the obtained compounds were constructed along with a calculation of the formation energies and dissociation constants. Optimisation of the geometric parameters of the equilibrium states of sodium oxoenolate and metal complexes was carried out using the following two methods: density functional theory (DFT) and self-consistent field (SCF). The relative formation energies indicate high stability of the synthesised substances, while, according to the data obtained, copper complexes are characterised by greater stability in the gas phase compared to zinc and nickel.

Keywords: sodium oxoenolates, metal complexes, synthesis, spectral analysis

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Синтез и строение 1-алкокси-1,4-диоксо-2-алкенолатов натрия и бис-(4-алкил(арил)-1-оксо-1-алкоксиалкан-2,4-дионато)металлов(II) на их основе

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INTRODUCTION

The chemistry of metal complexes is an extensive and rapidly developing field due to the multifunctionality and practical significance of these materials. Among the interesting properties of metal-complex compounds are included biological, pharmaceutical, photochemical and photophysical attributes [1–15]. Additional some metal complexes have been successfully used in the development of novel nanoscale structures [16]. Among metal complexes having organic ligands, the least studied are those based on polycarbonyl systems with conjugated α- and β-dioxo links. In order to expand the number of available metal complexes having carbonyl-containing ligands, the present study set out to synthesise new representative compounds and evaluate their stability using quantum chemical methods.

EXPERIMENTAL

Synthesis of 4-alkyl(aryl)-1-alkoxy-1,4-dioxo-2-sodium alkanoates (1). General procedure. 0.58 g (25 mmol) of sodium was gradually added with stirring to a mixture of 25 mmol of the corresponding methyl ketones (3-methylbutanone-2 or acetophenone), 25 mmol of dialkyl oxalates (di-n-butyloxalate or diethyl oxalate) and 50–100 ml of benzene or toluene. The reagent mixture was boiled for 1.5–2 h (TLC control) in a round bottom flask with reflux condenser. Following evaporation of solvent, the obtained oxoeno-lates were washed with ether.

1-Butoxy-5-methyl-1,4-dioxo-2-hexene-2-sodium-olate (1a). Yield 84 %, melting point (m melting 118–112 °C. IR spectrum, ν, cm⁻¹: 2959 νas (CH₃), 2931 νas (CH₂), 1698 (C=O), 1625 (C=C), 1379 δ (CH₃), 1267 ν (C-O-C) 951, 770 δ (CH) NMR spectrum ¹H, δ, ppm (DMSO-d₆): 0.91 t (3H, O(CH₃)₂CH₃, Jₚ=ₗ 7.7 Hz), 0.98 d (6H, (CH₂)₃CH), 1.35 m (2H, OCH₃CH₂CH₂CH₃), 1.60 m (2H, OCH₂CH₂CH₂CH₃), 2.40 m (1H, (CH₂)₂CH), 4.05 t (4H, OCH₂CH₂CH₂CH₃), 7.72 Hz), 5.65 s (1H, CH) NMR spectrum ¹C, δ, ppm (DMSO-d₆): 13.5 (OCH₃CH₂CH₂CH₃), 18.6 (OCH₃CH₂CH₂CH₃), 19.8 (CH₃)₂CH), 20.0 (OCH₃CH₂CH₂CH₃), 30.1 (CH₃)₂CH), 63.7 (OCH₂CH₂CH₂CH₃), 93.6 (CH), 167.0 (CONa), 168.7 (COOC₂H₅), 199.4 (CH₃)₂CHCO), Mass spectrum (ESI-TOF), m/z (%): 237.1099 (62) [M+Na]⁺ 259.0914 (47) [M+Na]⁺. Calculated: for C₁₅H₂₃O₅Na – 237.1097; for C₁₅H₂₃O₅Na₂, 259.0917.

Sodium 1,4-dioxo-4-phenyl-1-ethoxy-2-buten-2-olate (1b). Yield – 85 %, t melting 156–160 °C. IR spectrum, ν, cm⁻¹: 3060 ν (C-H, Ar), 2979 νas.
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tected in the electrospray ionisation (ESI) mode. Samples dissolved in DMSO diluted with acetonitrile or methanol were injected with a syringe pump at a flow rate of 240 μl/h.

The individuality of the obtained substances was confirmed by TLC on Silufol UV-254 plates in the benzene–ether–acetone (10:9:1) system or acetone–hexane (2:3) system; the chromatograms were stained using iodine vapour. The initial reagents were purified by distillation before use.

The optimisation of the geometric parameters of the equilibrium states of sodium oxoenate and metal complexes was carried out using the following two methods: density functional theory (DFT) and self-consistent field (SCF). When calculating using the SCF method, the aug-cc-pVDZ basis was used, while the DFT method used the PBE/DZP approximation. Accounting for solvents was carried out according to the PCM model, in the case of compounds 1a, 1b – benzene and water, for compounds 2a–2f – water. The relative formation energies of the structures 2a–2f were calculated using the following equations

\[ \Delta G^\circ(E) = G^\circ(E)(\text{MeX}) - G^\circ(E)(\text{Me}^2) + G^\circ(E)(2X); \]

\[ \Delta G^\circ(E) = G^\circ(E)\Sigma_{pr} - G^\circ(E)\Sigma_{res}^{[17]}. \]

The calculations were performed in the FireFly 8.1 software package.

RESULTS AND DISCUSSION

The condensation of alkylaryl)methyl-ketones (3-methylbutanone-2 and acetophenone) with dialkyl oxalates (diethyl oxalate and di-n-butyl-oxalate) in the presence of sodium or sodium hydride in benzene or toluene at a ratio of the starting reagents 1:1:1 yielded sodium 1-alkoxy-1,4-dioxo-2-alkenolates (1) (Fig. 1).

New bis-(4-alkyl(aryl)-1-oxo-1-alkoxyalkane-2,4-dionato)-metals (II) (2) were synthesised by complex formation of sodium oxoenate (1) with salts of zinc (II), copper (II) and nickel (II) in an aqueous medium with the initial ratio of reagents of 2:1 (Fig. 2).

The structure of the obtained sodium oxoenate (1) and metal (II) complexes (2) based on them was confirmed by means of IR, NMR\(^{1}\)\(^{1}\)-, NMR\(^{13}\)H- spectroscopy, as well as mass spectrometry\(^{1}\)\(^{2}\).

\[ R = i-Pr (1a), Ph (1b); Alk = n-Bu (1a), Et (1b) \]

**Fig. 1. Scheme of the synthesis of 1-alkoxy-1,4-dioxo-2-sodium alkenolates (1)**

\[ R = i-Pr (2a, 2b, 2c), Ph (2d, 2e, 2f); Alk = n-Bu (2a, 2b, 2c), Et (2d, 2e, 2f) \]

**Fig. 2. Scheme of synthesis of bis-[4-alkyl(aryl)-1-oxo-1-alkoxyalkane-2,4-dionato] metals (II) (2)**

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IR spectra of solid samples of sodium 1-alkoxy-1,4-dioxo-2-alkenolates (1) and bis-(4-alkyl(aryl)-1-oxo-1-alkoxyalkane-2,4-dionato) metals (II) (2) are characterised by the presence of a bright stretching band of the ester carbonyl group in the region of 1698–1687 cm\(^{-1}\) (for compounds 1a and 1b) and 172–1722 cm\(^{-1}\) (for compounds 2a–2f). The bands in the region of 1597–1456 cm\(^{-1}\) are due to vibrations of monosubstituted aromatic rings (for compounds 1b and 2d–2f). The high-frequency ether band arising due to vibrations of the C-O-C fragment appears in the region of 1267–1231 cm\(^{-1}\) (for compounds 1a and 1b) and 1317–1267 cm\(^{-1}\) (for compounds 2a–2f).

In the NMR spectra of \(^1\)H sodium oxoenoates (1a and 1b) and zinc complexes (2a and 2d) recorded in DMSO-d_6, the characteristic ethoxy fragments signals are observed for 1b and 2d and n-butoxy fragments signals (for compounds 1a and 2a). Methine protons are identified by singlet signals in the region of 5.65–6.42 ppm. Proton signals of the monosubstituted aromatic rings for compounds 1b and 2d with phenyl fragments were recorded in the range 7.24–7.82 ppm.

The NMR spectra of \(^1\)C sodium oxoenoates (1a and 1b) recorded in DMSO-d_6, contain signals of alkyl carbon atoms in the range 13.5–30.1 ppm. The signals of aromatic carbon atoms (for compound 1b) were recorded in the region of 126.4–142.2 ppm. Carbon atoms of carbonyl groups of ester fragments were detected at 168.7 (for n-butoxycarbonyl group of compound 1a) and 170.6 (for ethoxycarbonyl group of compound 1b).

In the mass spectra of synthesised compounds recorded in the electrospray mode, signals of protonated and cationised molecules are observed [M+H]^+, [M+NH4]^+, [M+Na]^+ [M+K]^+.

In order to study the stability of the synthesised compounds, quantum-chemical calculations of their formation energies were carried out (Table 1). The calculations demonstrate the best convergence under the HF / aug-cc-pVDZ approximation. The solvation effects were considered only in the PBE / DZP approximation; in view of the complexity of the calculation, the solvation correction for the aug-cc-pVDZ basis was not considered in the SCF method. According to the obtained data, copper complexes have the greatest stability in the gas phase out of all the complexes tested. In general, according to the relative values of the formation energies, all compounds are stable, and metal complexes (2) are characterised by greater stability compared to sodium oxoenoates (1).

The values of the theoretically calculated dissociation constants of the obtained compounds are provided in Table 2. The obtained values indicate that zinc complexes (2a, 2d) possess the highest electrolytic dissociation capacity of all obtained metal complexes, while the compounds 1a, 1b are relatively similar in terms of electrolyte strength.

### Table 1

| Compound | HF / aug-cc-pVDZ | PBE / DZP | PBE / DZP + PCM |
|----------|------------------|----------|----------------|
|          | E\(^0\), Hartree | G\(^0\), Hartree | G\(^0\), Hartree | E\(^0\), Hartree | G\(^0\), Hartree |
| 1a       | -887.923689      | -143.3  | -891.566532    | -161.5         | -891.584457    |
| 1b       | -922.301360      | -145.2  | -926.104389    | -157.3         | -926.125552    |
| 2a       | -3229.962850     | -1315.8 | -3237.721356   | -1435.8        | -3237.765320   |
| 2b       | -3091.107386     | -1354.0 | -3098.915975   | -1556.8        | -3098.947774   |
| 2c       | -2959.021762     | -1270.8 | -2966.768176   | -1509.1        | -2966.787241   |
| 2d       | -3298.717676     | -1311.7 | -3306.801958   | -1448.6        | -3306.847853   |
| 2e       | -3159.861688     | -1348.6 | -3167.994962   | -1565.4        | -3168.030201   |
| 2f       | -3027.776747     | -1267.1 | -3035.849309   | -1523.3        | -3035.872814   |

### Table 2

| Compound | PBE / DZP + PCM |
|----------|----------------|
| 1a       | 9.5 \times 10^{-38} |
| 1b       | 4.5 \times 10^{-38} |
| 2a       | 1.7 \times 10^{-42} |
| 2c       | 7.3 \times 10^{-96} |
| 2d       | 8.0 \times 10^{-41} |
| 2f       | 1.4 \times 10^{-95} |
CONCLUSIONS
During the study, potentially valuable sodium 1-alkoxy-1,4-dioxo-2-alkenolates and complexes of zinc (II), copper (II) and nickel (II) with carbonyl-containing ligands were successfully synthesized.

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