



Synthesis and studies of complex compounds of carboxyl-derivatives of methylphloroglucinol with metals

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ABSTRACT

Ten new complexes of 2,4,6-trihydroxy-3-methyl benzoic acid (methylphloroglucinol, L^1) and 2,4,6-trihydroxy benzoic acid (phloroglucinol, L^2) are isolated in the solid state, and their formulae were detected.

The spectroscopic methods indicate that the coordination of L^1 and L^2 to the metallic ions occurs through one of the O-atom of the deprotonated carboxylic group and an O atom of the non-deprotonated neighboring hydroxy-group (bidentate chelating coordination). The schemes of the structure of complexes are proposed.

The complex formation in solution is studied, and formation constants are calculated. It is shown that for the metal complexes of the 1st transitional series, the formation constants for the complexes are arranged as $Mn(II) < Co(II) < Ni(II) < Cu(II) > Zn(II)$. The obtained results correlate with the Irving-Williams Series.

Indexing terms/Keywords

Methylphloroglucinol; phloroglucinol; complex compounds; synthesis; IR & UV spectroscopy; spectrophotometric titration.

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INTRODUCTION

2,4,6-Trihydroxytoluene (methylphloroglucinol, MPG) represents the technogenic waste. From the chemical point of view, it is one of the most interesting from the scientific and practical positions. The above substance can be obtained from the aromatic nitro-derivatives by a technological and economically acceptable way [1]. It should be noted that MPG chemistry is not practically developed owing to its former small availability. At the same time, such multifunctional compounds as MPG, are of a great interest as the composition and mutual disposition of its functional groups allows to perform various and usually multistep reactions of different types which aim to isolate carbo- or heterocyclic compounds which are perspective from both the theoretical and practical points of view [2-4].

The introduction of a carboxylic group into the methylphloroglucinol or phloroglucinol rings [5] leads to formation of structural analogues of the salicylic acid which is well known as a biologically active substance and good complexing agent. The two additional hydroxy-groups will bring some additional complexing ability which needs to be studied.

The goals of the presented investigations were to study the reactions of complex formation of carboxy-derivatives of methylphloroglucinol and phloroglucinol in solutions, to isolate and characterize some metal complexes in the solid state.

EXPERIMENTAL PART

Reagents and solutions

The polyfunctional carboxy--derivatives of methylphloroglucinol and phloroglucinol (Figure 1) were prepared according to the procedures described previously [5]. The other chemicals were used as received.

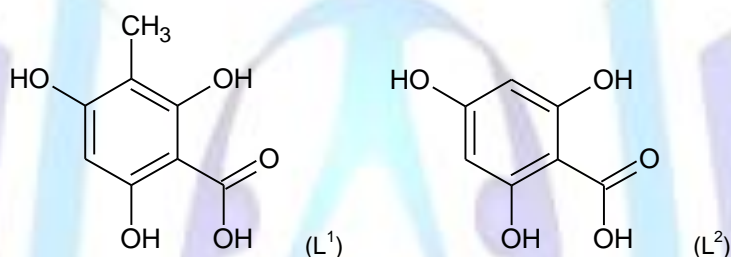


Fig. 1: The MPG and PG carboxy-derivatives used in the present work.

Apparatus and equipment

Electronic spectra of aqueous solutions of organic ligands and mixtures thereof with metal salts are recorded in a spectrophotometer Varian Cary 50 Spectrophotometer in the wavelengths interval 200 – 700 nm in a cuvette with a 1cm wide pH range from 2 to 12. Concentrations were selected individually for each compound. To determine the composition of the complexes and their formation constants in the solutions, the saturation method was used [6].

The IR absorption spectra were recorded in the Bruker Optics FT-IR spectrophotometer in the KBr pellets in the wavenumber interval 4000-400 cm⁻¹.

Synthesis and analysis

The synthesis of the complex compounds was performed according to the following procedure. The sample of L¹ or L² equivalent to 0.001 mole were dissolved in the minimal amount of ethanol (approx. 5 ml), and then a corresponding amount of a solid metal chloride was added (the molar ratio M:L=1:1) under reflux. The mixture was heated on the water bath until all the metal salt was dissolved. The change in color of the solutions indicated the process of complex formation. The precipitation of complexes started within 3 hours. The formed precipitates were separated from the solutions by centrifugation and dried until the constant mass. Yields 30-50%.

The metal cation quantitative analysis was carried out by the method of atomic emission with inductively coupled plasma on the instrument firm Varian 735-OES. The amounts of nitrogen, carbon and hydrogen was carried out by micro-methods. The results of the chemical analysis as well as the derived formulae of the complexes is presented in the Table 1.

The visual optical microscopic analysis indicated the individuality of the obtained precipitates. The shape and the color of the crystals observed through the microscope differs from those of the taken reactants (inorganic metal salts and organic ligands).

In the case of trivalent metal complexes (Cr³⁺ and Fe³⁺) according to the chemical analysis, one chloride ion is also present. To determine its nature, the qualitative analysis was performed. For this purposes we suspended some amounts of complexes in the distilled water and added the solution of AgNO₃. Neither precipitate of AgCl nor opalescence of its colloid solution was observed. Then we added some drops of concentrated HNO₃ and heated the suspension. In this case we observed the dissolution of the complex compound which followed by the appearance of a white precipitate of AgCl. Thus, we can conclude that the AgCl precipitate is formed only after decomposition of the complex, i.e. the chloride ion is in the coordination sphere of the complexes.

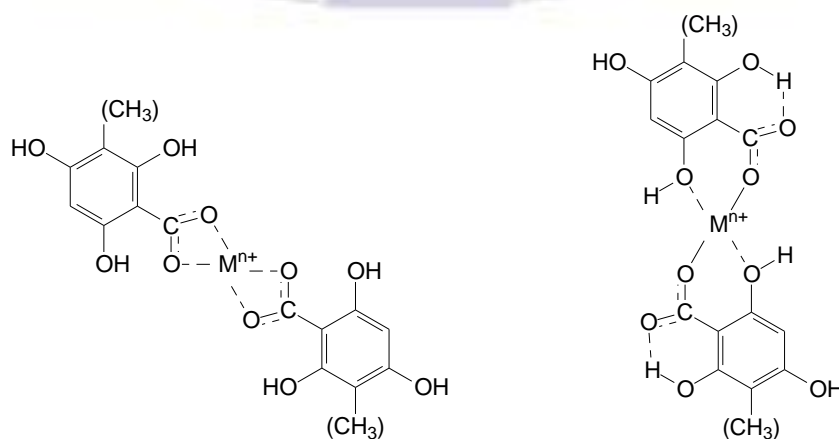
Table 1: The results of the chemical analysis and composition of the complexes

| No | Formula (color) | Composition | M, g/mol | Analysis calculations (calculated/found),% | | | |
|-----|--|---|----------|--|-------------|-----------|-----------|
| | | | | M | C | H | Cl |
| 1. | Co(L ¹) ₂ ·2H ₂ O (violet) | C ₁₆ H ₁₈ CoO ₁₂ | 461.24 | 12.78/12.48 | 41.66/40.81 | 3.93/3.79 | - |
| 2. | Ni(L ¹) ₂ ·2H ₂ O (light-green) | C ₁₆ H ₁₈ NiO ₁₂ | 461.00 | 12.73/13.01 | 41.69/41.17 | 3.94/4.02 | - |
| 3. | Zn(L ¹) ₂ ·4H ₂ O (colorless) | C ₁₆ H ₂₂ O ₁₄ Zn | 503.72 | 12.98/12.62 | 38.15/38.99 | 4.40/3.82 | - |
| 4. | Cr(L ¹) ₂ Cl·6H ₂ O (greyish-green) | C ₁₆ H ₂₆ ClCrO ₁₆ | 561.82 | 9.25/9.56 | 34.21/34.73 | 4.66/4.87 | 6.31/6.51 |
| 5. | Cd(L ¹) ₂ ·2H ₂ O (colorless) | C ₁₆ H ₁₈ CdO ₁₂ | 514.72 | 21.84/21.25 | 37.34/37.83 | 3.52/3.20 | - |
| 6. | Co(L ²) ₂ ·4H ₂ O (violet) | C ₁₄ H ₁₈ CoO ₁₄ | 469.22 | 12.56/13.02 | 35.84/36.21 | 3.87/4.68 | - |
| 7. | Ni(L ²) ₂ ·2H ₂ O (light-green) | C ₁₄ H ₁₄ NiO ₁₂ | 432.95 | 13.56/13.92 | 38.84/38.29 | 3.26/3.86 | - |
| 8. | Zn(L ²) ₂ ·2H ₂ O (colorless) | C ₁₄ H ₁₄ O ₁₂ Zn | 439.64 | 14.87/15.55 | 38.25/38.72 | 3.21/3.45 | - |
| 9. | Cu(L ²) ₂ (brown) | C ₁₄ H ₁₀ CuO ₁₀ | 401.77 | 15.82/16.44 | 41.85/42.00 | 2.51/3.37 | - |
| 10. | Fe(L ²) ₂ Cl·6H ₂ O (reddish-brown) | C ₁₄ H ₂₂ ClFeO ₁₆ | 537.62 | 10.39/10.08 | 31.28/30.92 | 4.12/4.56 | 6.59/6.54 |

RESULTS AND DISCUSSION

Coordination modes of the ligands

The L¹ and L² ligands are polydentate as they contain 3 hydroxy-groups and 1 carboxy-group. Both these fragments can donate lone electron pairs for coordination with metals. As chelating effect increases the stability of complexes, we can propose two possible coordination modes of the ligands:


Coordination mode 1
Coordination mode 2



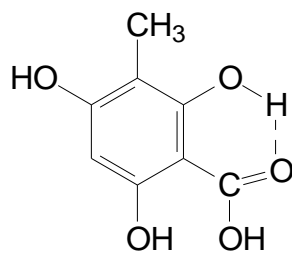
In the 1st case, the carboxylic groups of the organic anions act as bidentate chelating ligands, and the 4-membered metal-chelate rings are formed. The non-deprotonated hydroxyl groups may be involved in the axial interactions with the metal cations or in the formation of the lattice (intermolecular) hydrogen bonds. The coordination mode 2 proposes the formation of a 6-membered metal-chelate rings with the coordination through one O atom of a carboxy- group (monodentate coordination) and an O atom of a neighboring hydroxy group which is in its neutral form. The formation of an intramolecular hydrogen bond stabilizes the molecule of the complex compound.

To choose between the coordination modes, the IR spectra of the non-coordinated organic molecules and their metal complexes were recorded (see the **Table 2**).

Table 2: Some absorption bands (cm⁻¹) in the IR spectra of L¹, L² and their complex compounds and their assignments

| Compound | Assignment | $\nu(\text{OH})$ | $\nu(\text{C}=\text{O})$ | $\nu(\text{CC})_{\text{ar}}$ | $\nu^{\text{as}}(\text{COO}^-)$ | $\nu^{\text{s}}(\text{COO}^-)$ | Δ |
|---|------------|------------------------------|--------------------------|------------------------------|---------------------------------|--------------------------------|----------|
| L ¹ | | 3424 3367 | 1640 | 1620 | - | - | - |
| Co(L ¹) ₂ ·2H ₂ O | | 3600- 3400 | 1620 | 1624 | 1548 | 1436 | 122 |
| Ni(L ¹) ₂ ·2H ₂ O | | 3462 3422 3360 | 1620 | 1625 | 1541 | 1437 | 104 |
| Zn(L ¹) ₂ ·4H ₂ O | | 3587 3424 3342 3300 | 1620 | 1624 | 1541 | 1436 | 105 |
| Cr(L ¹) ₂ Cl·6H ₂ O | | 3600- 3400 | 1620 | 1624 | 1541 | 1437 | 104 |
| Cd(L ¹) ₂ ·2H ₂ O | | 3425 3336 3309 | 1620 | 1624 | 1548 | 1420 | 128 |
| L ² | | 3476 3380 | 1640 | 1620 | - | - | - |
| Co(L ²) ₂ ·4H ₂ O | | 3500- 3200 | 1620 | 1616 | 1539 | 1419 | 120 |
| Ni(L ²) ₂ ·2H ₂ O | | 3510- 3200 | 1620 | 1612 | 1535 | 1415 | 120 |
| Zn(L ²) ₂ ·2H ₂ O | | 3577 3472 3325 | 1620 | 1617 | 1539 | 1420 | 119 |
| Cu(L ²) ₂ | | 3580 3350 3346 | 1620 | 1618 | 1540 | 1445 | 95 |
| Fe(L ²) ₂ Cl·6H ₂ O | | 3482 3387 3318 3302 | 1620 | 1617 | 1540 | 1419 | 121 |

As it is evident from the Table 2, a strong absorption band of C=O stretching is observed at 1640 cm⁻¹ in the IR spectra of L¹ and L² and no more absorption bands are present between 2000 and 1640 cm⁻¹. The position of the C=O absorption band indicates a strong intramolecular H bond as presented below:



The low frequency shoulder at 1624 cm^{-1} is due to the overlap of $\nu(\text{C}=\text{O})$ vibrations with the $\text{C}=\text{C}$ aromatic stretchings.

The $\nu(\text{O}-\text{H})$ bands lie in a wide interval of $3424\text{--}3367\text{ cm}^{-1}$ and are represented by several absorption bands. The high frequency modes belong to the “free” hydroxy-groups which are not involved in the H-bonding, and the low-frequency components indicate the existence of strong H-bonds.

In the IR spectra of complex compounds of L^1 and L^2 the $\nu(\text{C}=\text{O})$ bands shift to 1620 cm^{-1} , and two new bands in the intervals $1560\text{--}1540$ and $1445\text{--}1419\text{ cm}^{-1}$ are observed (Table 2). They correspond to anti-symmetrical and symmetrical stretchings of the carboxylate anion COO^- . The Δ value ($\Delta = \nu^{\text{as}} - \nu^{\text{s}}$) lies in the interval $95\text{--}128\text{ cm}^{-1}$ which indicates the monodentate coordination of a carboxylic group (in the case of the bidentate coordination the Δ value is close to 200 cm^{-1}).

High frequencies of $\nu(\text{OH})$ vibrations (Table 2) indicate that not all the hydroxy-groups of L^1 and L^2 are involved in coordination and formation of H bonds.

Thus, from the point of view of IR spectroscopy and elemental analysis, the organic ligands coordinate the metals in the form of monoanions through one of the O-atom of the deprotonated carboxylic group and an O atom of the non-deprotonated neighboring hydroxy-group (coordination mode 2). This is in accordance of the coordination mode of salicylic acid with metals [7].

Complex formation in solutions

The electronic absorption spectra of L^1 and L^2 are characterized by 3 absorption bands in the UV part of the spectrum. The most intense one ($\lambda = 210\text{--}220\text{ nm}$) is related to $\pi\text{--}\pi^*$ transitions in the benzene ring, and two others at $255\text{--}260$ and $300\text{--}310\text{ nm}$ – to $n\text{--}\pi^*$ transitions of the carboxy- and hydroxy-groups. The addition of ethanol solutions of metal salts to the ethanol solutions of the organic ligands provokes the change in intensities of $\pi\text{--}\pi^*$ transitions and shifting of the absorption bands of $n\text{--}\pi^*$ transitions to the lower wavelengths. This indicates the involvement of hydroxy- and carboxy-groups in coordination which correlates with the conclusions obtained from IR spectral data. The examples of the changes in the spectra are presented in the Figure 2 a, b.

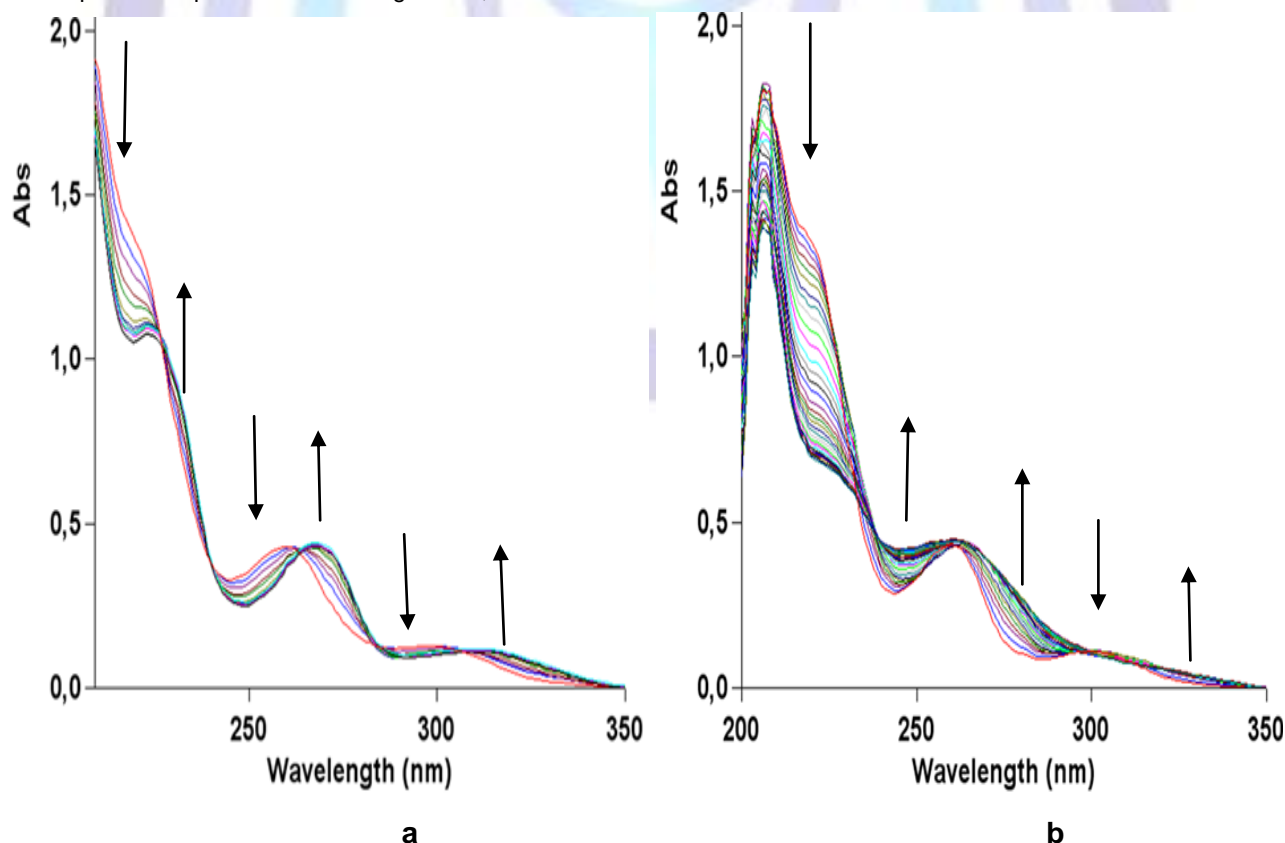


Fig. 2: Changes in the UV-VIS spectra of ethanol solutions of L^1 after stepwise addition of the ethanol solution of AlCl_3 (a) and CuCl_2 (b).



The comparison of the spectra presented on the **Figure 2 a,b** indicates that the changes in the spectra are more significant for trivalent metals comparing with the di-charged metallic ions. This fact may indicate a more covalent character of the M-L bonds in the case of trivalent metals.

In all the cases the isobestic points appear in the spectra which indicate the equilibrium of a reversible process between the non-coordinated ligand and its complex.

Basing on the results of the titration, the saturation curves were obtained, and the ligand-to-metal ratio (n) and the formation constants of the complexes were calculated. The results are presented in the **Table 3**.

Table 3: The composition of some metal complexes of L^1 and L^2 in ethanol solutions and their formation constants

| Ligand | Metal ion | n | A | A_{max} | C_M | C_L | $\log \beta$ | $\log \beta/n$ |
|--------|-----------|-----|--------|-----------|-------|--------|--------------|----------------|
| L^1 | Al^{3+} | 2 | 0.416 | 0.436 | 0.005 | 0.0001 | 11.72 | 5.86 |
| | Cu^{2+} | 1 | 0.444 | 0.448 | 0.005 | 0.0001 | 8.54 | 8.54 |
| | Cd^{2+} | 1 | 0.3265 | 0.3275 | 0.005 | 0.0001 | 8.09 | 8.09 |
| | La^{3+} | 2 | 0.4142 | 0.4214 | 0.005 | 0.0001 | 7.72 | 3.86 |
| | Ba^{2+} | 2 | 0.3875 | 0.3885 | 0.005 | 0.0001 | 8.68 | 4.34 |
| | Co^{2+} | 2 | 0.444 | 0.449 | 0.005 | 0.0001 | 13.86 | 6.93 |
| | Mn^{2+} | 2 | 0.4225 | 0.4275 | 0.005 | 0.0001 | 9.10 | 4.55 |
| | Fe^{3+} | 1 | 0.4933 | 0.4966 | 0.005 | 0.0001 | 4.98 | 4.98 |
| | Ni^{2+} | 1 | 0.836 | 0.85 | 0.01 | 0.0001 | 7.00 | 7.00 |
| | Zn^{2+} | 1 | 0.731 | 0.764 | 0.01 | 0.0001 | 5.67 | 5.67 |
| L^2 | Al^{3+} | 3 | 0.32 | 0.324 | 0.005 | 0.0001 | 13.72 | 4.57 |
| | Cu^{2+} | 2 | 0.915 | 0.923 | 0.001 | 0.0001 | 18.18 | 9.09 |
| | La^{3+} | 2 | 0.221 | 0.226 | 0.005 | 0.0001 | 9.78 | 4.89 |
| | Ba^{2+} | 3 | 0.269 | 0.276 | 0.005 | 0.0001 | 12.78 | 4.26 |
| | Co^{2+} | 1 | 0.761 | 0.762 | 0.005 | 0.0001 | 8.73 | 8.03 |
| | Mn^{2+} | 2 | 0.106 | 0.107 | 0.005 | 0.0001 | 14.08 | 7.04 |
| | Ni^{2+} | 2 | 0.825 | 0.845 | 0.001 | 0.0001 | 16.04 | 8.02 |

From the data of the Table 3 it is evident that for the metal complexes of the 1st transitional series, the formation constants for the complexes are arranged as $Mn(II) < Co(II) < Ni(II) < Cu(II) > Zn(II)$ (**Figure 3**). This is known as the Irving-Williams Series [8].

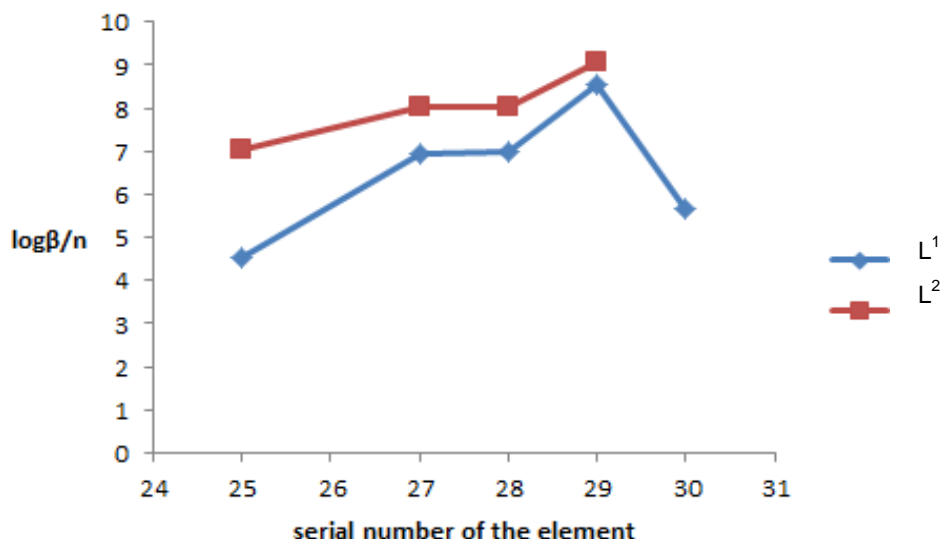


Fig. 5. Irving-Williams Series for L¹ and L²

The existence of such a dependence can be explained as following. The ionic radius decreases from Mn²⁺ to Zn²⁺. This accounts for the general increase in stability. The Crystal Field Stabilization Energy (CFSE) increases from zero for manganese(II) to a maximum at nickel(II). This also increases the stability of complexes. For zinc(II), the CFSE value comes again to zero, and the stability of the complexes decreases. Although the CFSE of copper(II) has a less value than that of nickel(II), the octahedral copper(II) complexes are subject to the Jahn-Teller effect, which affords extra stability to the complexes [9].

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