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New examples of chelating triketone-like ligands that promote formation of binuclear complexes<sup>\*</sup>

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#### Abstract

The present work is to investigate of binding properties of chelating triketone-like ligands, which are able to forming of binuclear complexes. The studied compounds are able to exist in substituted or cyclic or 'close form' (phenyl unsubstituted 2-hydroxy-2-(trifluoromethyl)chroman-4-ones) as well as in their associated 'open form' (phenyl substituted or unsubstituted 1,1,1-trifluoro-4-(2-hydroxyphenyl)butan-2,4-diones). In this paper there is good evidence for the compounds are being in solid in 'close form' (pre-ligands), whereas in basic solutions and when involved in metal ion coordination sphere they are being in 'open form' (ligands). Protolytic equilibria of the compounds in aqueous ethylene glycol solutions were studied. Schemes of acid-base equilibria of these compounds were proposed. Apparent ionization constants of compounds containing electron-donor and electron-acceptor substituents in the benzene ring were determined using spectrophotometric method. The binding properties of 1,1,1-trifluoro-4-(2-hydroxyphenyl)butan-2,4-dione towards Cu(II), Ni(II) and Co(II) were studied. The formation of 2:2 metal-ligand complexes was observed. X-ray analysis gives evidence the formation of complexes in which the ratio metal to ligand can be 1:2 and 2:2. Similar to  $\beta$ -triketones the studied ligands tends to formation of binuclear complexes with transition metal ions.

Keywords: chroman-4-ones, binuclear complexes, triketone-like ligands, transition metal complexes

<sup>&</sup>lt;sup>\*</sup> Dedicated to the memory of Dr. Yury G. Yatluk, a teacher and colleague

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#### 1. Introduction

Binuclear complexes with first transition metals have found applications in a great number of areas. The most important ones include biomimetic enzymatic systems [1,2] including nuclease mimetics [3], antibacterial activity [4,5], etc. The complexes of metal ions like cobalt(II) [6], copper(II) [6–8], nickel(II) [6,8,9], palladium(II) [4], as well heterometallic complexes such as Cr(III)–Mn(III) [10] are of particular interest for molecular magnets.

Enamino ketone derivatives [11,12], Schiff-bases [4,13], pyrazole based ligands [8,9], and N-derivatives of 3-aminopropan-1-ol or  $\beta$ -alanine [14] are used for binuclear complexes synthesis based on reasonable design of chelating organic ligands. Many works so far, however, have concentrated mainly on the 2,6-disubstituted phenol derivatives [15] and  $\beta$ .  $\delta$ -tricarbonyl compounds [16] as chelating ligands, which undoubtedly made a formation of binuclear complexes possible.  $\beta$ -Diketophenoles [17,18] – acyclic tautomers of 2-hydroxychroman-4-one derivatives [19] are structural analogues of  $\beta$ , $\delta$ -tricarbonyl compounds. They are able to exist in 'open' structure in solutions depending on chemical structure and solvent [20] and act as ligands forming binuclear complexes [17]. Consequently they can found numerous opportunities when being integrated with transition metal ions. Although much research concerns synthesis and chemical properties, little attention has so far been paid to study the binding properties of ligands that include chromone system [21-23]. Mentioned type of the ligands is valuable alternative for 2,6-disubstituted phenol derivatives [15] and  $\beta$ , $\delta$ -tricarbonyl compounds [16]. Introducing of varied substituents into template structures of such ligands comes to the end of tether. So that, radical modification of complexes electronic structure is impossible in this way. Therefore, it is very motivating to study the binding properties of the 2-hydroxychroman-4-one derivatives in solutions as well as to investigate the synthesis and crystal structures of metal complexes of the ligands with transition metal ions.

In this work we focused on the properties of 2-hydroxy-2-(trifluoromethyl)chroman-4-one (1), 2-hydroxy-6-methyl-2-(trifluoromethyl)chroman-4-one (2) and 2-hydroxy-2,6-bis(trifluoromethyl)chroman-4-one (3). These compounds were used as pre-ligands for preparation of binuclear complexes with Co(II), Ni(II) and Cu(II). The structural characterization of the metal complexes using such methods as UV-Vis spectrophotometry, FT-IR, X-ray single crystallography, was performed.

#### 2. Experimental

#### 2.1. Chemicals

Reagent grade ethylene glycol was used without further purification. Distilled water was used for preparation of all solutions.

2-Hydroxy-2-(trifluoromethyl)chroman-4-one (1), 2-hydroxy-6-methyl-2-(trifluoromethyl)chroman-4-one (2) and 2-hydroxy-2,6-bis(trifluoromethyl)chroman-4-one (3) are the chromanone derivatives, which were prepared previously [19,24,25]. Other chemicals were commercially available and of pure grade. The metal salts were prepared and analyzed following the standard procedures.

NMR <sup>1</sup>H of **1** (HOCD<sub>2</sub>CD<sub>2</sub>OH,  $\delta$ , ppm, *J*/Hz): 2.96 (d, 1H, C<u>H</u>H, *J*<sub>AB</sub> = 16.4); 3.31 (d, 1H, CH<u>H</u>, *J*<sub>AB</sub> = 16.5); 7.14 (d, 1H, H(8), *J*<sub>o</sub> = 8.3); 7.21 (dd, 1H, H(6), *J*<sub>o</sub> = 7.6, 7.4); 7.67 (ddd, 1H, H(7), *J*<sub>o</sub> = 8.6, 7.0, *J*<sub>m</sub> = 1.6); 7.86 (dd, 1H, H(5), *J*<sub>o</sub> = 7.8, *J*<sub>m</sub> = 1.4).

<sup>1</sup>H NMR of **1** (CDCl<sub>3</sub>,  $\delta$ , ppm, *J*/Hz): 3.04 (d, 1H, C<u>H</u>H, *J*<sub>AB</sub> = 16.7); 3.10 (d, 1H, CH<u>H</u>, *J*<sub>AB</sub> = 16.7); 3.61 (s, 1H, OH); 7.07 (dd, 1H, H(8), *J*<sub>o</sub> = 8.3, *J*<sub>m</sub> = 1.0); 7.15 (ddd, 1H, H(6), *J*<sub>o</sub> = 7.8, 7.3, *J*<sub>m</sub> = 1.0); 7.58 (ddd, 1H, H(7), *J*<sub>o</sub> = 8.3, 7.3, *J*<sub>m</sub> = 1.7); 7.93 (dd, 1H, H(5), *J*<sub>o</sub> = 7.8, *J*<sub>m</sub> = 1.7).

<sup>1</sup>H NMR of **2** (CDCl<sub>3</sub>,  $\delta$ , ppm, *J*/Hz): 2.33 (s, 3H, Me); 3.00 (d, 1H, CHH, *J*<sub>AB</sub> = 16.7); 3.07 (d, 1H, CHH, *J*<sub>AB</sub> = 16.7); 3.60 (s, 1H, OH); 6.96 (d, 1H, H(8), *J*<sub>o</sub> = 8.4); 7.38 (dd, 1H, H(7), *J*<sub>o</sub> = 8.4, *J*<sub>m</sub> = 2.2); 7.71 (d, 1 H, H(5), *J*<sub>m</sub> = 2.2).

<sup>1</sup>H NMR of **3** (C<sub>2</sub>D<sub>6</sub>SO,  $\delta$ , ppm, *J*/Hz): 2.98 (d, 1H, CHH, *J*<sub>AB</sub> = 16.7); 3.07 (d, 1H, CHH, *J*<sub>AB</sub> = 16.7); 3.58 (s, 1H, OH); 7.42 (d, 1H, H(8), *J*<sub>o</sub> = 8.4); 8.02 (dd, 1H, H(7), *J*<sub>o</sub> = 8.4, *J*<sub>m</sub> = 2.2); 8.06 (d, 1H, H(5), *J*<sub>m</sub> = 2.2).

<sup>19</sup>F NMR of **1** (HOCD<sub>2</sub>CD<sub>2</sub>OH, δ, ppm, C<sub>6</sub>F<sub>6</sub>): 77.71 (s, CF<sub>3</sub>(2)).

<sup>19</sup>F NMR of **3** (HOCD<sub>2</sub>CD<sub>2</sub>OH, δ, ppm, C<sub>6</sub>F<sub>6</sub>): 77.86 (s, CF<sub>3</sub>(2)); 101.18 (s, CF<sub>3</sub>(6)).

#### 2.2. Solutions

Spectrophotometric experiments were carried out at 25  $^{\circ}$ C in the aqueous ethylene glycol containing 70 % ethylene glycol by volume. The ionic strength was maintained at 0.1 with the KCl stock solutions.

#### 2.3. Apparatus

Microanalyses (C, H, N) were performed using a Perkin–Elmer PE 2400 elemental analyzer. The UV–VIS spectra were recorded over the range 200–800 nm on a Shimadzu UV-2401 PC spectrophotometer. <sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded on a Bruker 400 MHz FT NMR (model Avance DRX-400). The FTIR spectra of compounds were recorded over the range 4000–400 cm<sup>-1</sup> using Spectrum One spectrophotometer (Perkin Elmer, USA). Single-crystal X-ray diffraction performed on an Oxford Diffraction Xcalibur-3 diffractometer. TGA-DTA measurements were performed at heating rate of 5 °C min<sup>-1</sup> on instrument Mettler–Toledo TGA/DSC 1. Approximately 12-16 mg of sample were heated in ceramic crucible in air.

#### 2.4. Solution equilibria

All analyte concentrations were expressed in the molarity scale (mol/L, M). For potentiometric and UV measurements, working solutions of HCl (0.1 M), NaOH (0.1 M), chromanones (0.0025 M),  $CoCl_2 \cdot 5H_2O$ ,  $NiCl_2 \cdot 5H_2O$ ,  $CuCl_2 \cdot 5H_2O$  (0.05 M, containing HCl 0.1 M) were prepared and standardized. The starting solution for each titration and all working solutions contained known amounts of KCl to assure a constant 0.1 M ionic strength during the titrations.

UV measurements (Table 1) were carried out for solutions containing the chromanone alone, and for solutions containing the chromanone and the metal ion, at various pH values. The  $pK_a$  values for the chromanones were computed by the program FTMT [26].

#### 2.5. Synthesis of binuclear complexes

#### 2.5.1. Synthesis of complexes $Cu_2(L1)_2$

 $[Cu_2(L1)_2(H_2O)_2]$  (4-1). To a solution of  $Cu(AcO)_2 \cdot H_2O$  (0.86 g, 4.3 mmol) and urea (0.52 g, 8.6 mmol) in 20 mL of water the solution of 1 (0.5 g, 2.15 mmol) in 46 mL methanol. The mixture was kept in water bath for 1 h, then at room temperature for 24 h, after that the product was filtered off, washed with water and dried in vacuum. Yield: 0.6 g (92%). *Anal.* Calc. for  $C_{20}H_{10}F_6O_6Cu_2 \cdot 2H_2O$  (623.41): C, 38.53; H, 2.26; F, 18.29; Cu, 20.38%. Found: C, 38.91; H, 1.90; F, 18.09; Cu, 20.32.

 $[Cu_2(L1)_2(DMF)_2]$  (4-2). After the recrystallization of 4-1 from DMF the solvate complex was obtained. *Anal.* Calc. for C<sub>20</sub>H<sub>10</sub>F<sub>6</sub>O<sub>6</sub>Cu<sub>2</sub>·2C<sub>3</sub>H<sub>7</sub>NO (733.57): C, 42.57; H, 3.30; N, 3.82; F, 15.54; Cu, 17.33%. Found: C, 42.23; H, 2.91; N, 3.45; F, 15.26; Cu, 17.89%.

#### 2.5.2. Synthesis of complex $[Cu_2(L2)_2(DMF)_2]$ (5)

To a solution of  $Cu(AcO)_2 \cdot H_2O$  (0.42 g, 2 mmol) in 20 mL of water the solution of **2** (0.50 g, 2 mmol) and NaOH (0.16 g, 4 mmol) in 20 mL of methanol was added. The mixture was stirred at room temperature for 1 h and then the product was filtered off, washed with water and dried in vacuum. Yield: 0.62 g (98%). *Anal.* Calc. for  $C_{22}H_{14}F_6O_6Cu_2 \cdot H_2O$  (633.45): C, 41.71; H, 2.55; F, 17.99; Cu, 20.06%. Found: C, 41.88; H, 2.62; F, 17.75; Cu, 20.46%.

After the recrystallization of product from DMF the solvate complex was obtained. *Anal.* Calc. for  $C_{22}H_{14}F_6O_6Cu_2 \cdot 2C_3H_7NO$  (761.62): C, 44.16; H, 3.71; N, 3.68; F, 14.97; Cu, 16.69%. Found: C, 43.95; H, 3.41; N, 3.44; F, 14.27; Cu, 17.26%.

#### 2.5.3. Synthesis of complex $[Cu_2(L3)_2(H_2O)_4]$ (6)

To a solution of  $Cu(AcO)_2 \cdot H_2O$  (0.42 g, 2 mmol) in 20 mL of water the solution of **3** (0.60 g, 2 mmol) and NaOH (0.16 g, 4 mmol) in 20 mL of methanol was added. The mixture was

stirred at room temperature for 1 h and then the product was filtered off, washed with water and dried in vacuum. Yield: 0.70 g (88%). *Anal.* Calc. for  $C_{22}H_8F_{12}O_6Cu_2 \cdot 4H_2O$  (795.44): C, 33.22; H, 2.03; F, 28.66; Cu, 15.98%. Found: C, 33.26; H, 1.95; F, 28.28; Cu, 16.36%.

#### 2.5.4. Synthesis of complex $[Ni_2(L1)_2(H_2O)_3]$ (7)

To a solution of Ni(AcO)<sub>2</sub>·4H<sub>2</sub>O (0.50 g, 2 mmol) in 10 mL of water the solution of **1** (0.46 g, 2 mmol) and NaOH (0.16 g, 4 mmol) in 20 mL of methanol was added. The mixture was stirred at room temperature for 1 h and then the product was filtered off, washed with water and dried in vacuum. Yield: 0.60 g (95%). *Anal.* Calc. for  $C_{20}H_{10}F_6O_6Ni_2\cdot 3H_2O$  (631.72): C, 38.02; H, 2.55; F, 18.04; Ni, 18.58%. Found: C, 37.72; H, 2.90; F, 16.98; Ni, 19.08%.

#### 2.5.5. Synthesis of complex $[Co_2(L1)_2(H_2O)]$ (8)

To a solution of  $Co(AcO)_2 \cdot 4H_2O$  (0.50 g, 2 mmol) in 20 mL of water the solution of **1** (0.46 g, 2 mmol) and NaOH (0.16 g, 4 mmol) in 20 mL of methanol was added. The mixture was stirred at room temperature for 1 h and then the product was filtered off, washed with water and dried in vacuum. Yield: 0.56 g (98%). *Anal.* Calc. for  $C_{20}H_{10}F_6O_6Co_2 \cdot H_2O$  (596.17): C, 39.10; H, 2.27; F, 18.56; Co, 19.21%. Found: C, 39.80; H, 2.17; F, 18.27; Co, 19.38%.

#### 2.6. Synthesis of mononuclear complexes

 $[Cu(HL1)_2(H_2O)_2]$  (9-1). To a solution of  $Cu(AcO)_2 \cdot H_2O$  (1.19 g, 6 mmol) in 120 mL of water the solution of 1 (1.39 g, 6 mmol) in 60 mL of methanol was added. The mixture was stirred at room temperature for 1 h and then the product was filtered off, washed with water and dried in vacuum. Yield: 1.7 g (9562%). *Anal.* Calc. for  $C_{20}H_8F_6O_6Cu \cdot 2H_2O$  (539.83): C, 44.50; H, 1.87; F, 21.12; Cu, 11.77%. Found: C, 45.62; H, 2.20; F, 21.54%; Cu 12.09.

 $[Cu(HL1)_2(DMSO)_2(H_2O)_2]$  (9-2) and  $[Cu(HL1)_2(TMU)_2]$  (9-3). After the recrystallization of complex 4-2 from DMSO and TMU the complexes 9-2 and 9-3 were obtained. *Anal.* Calc. for C<sub>20</sub>H<sub>8</sub>F<sub>6</sub>O<sub>6</sub>Cu·2C<sub>2</sub>H<sub>6</sub>SO·2H<sub>2</sub>O (714.12): C 40.22; H 3.35; F 15.92; S 8.93; Cu 8.93%. Found: C, 39.82; H, 2.62; F, 16.35; S, 9.21; Cu, 9.15%. *Anal.* Calc. for C<sub>20</sub>H<sub>8</sub>F<sub>6</sub>O<sub>6</sub>Cu·2C<sub>5</sub>H<sub>12</sub>N<sub>2</sub>O (754.14): C, 47.74; H, 4.24; N, 7.43; F, 15.12; Cu, 8.49%. Found: C, 47.49; H, 4.08; N, 7.13; F, 15.34; Cu, 8.56%.

#### 2.7. Synthesis of 1,3-dimethyl-2-imidazolidinimine hydrochloride

A mixture of 1,3-dimethyl-2-imidazolidinone (20.7 g, 0.18 mol), triphosgene (15.14 g, 0.051 mol) in 50 mL CCl<sub>4</sub> was stirred at room temperature for 5 h. The precipitate was filtered off, washed with hexane and dried in vacuum. To the product at the temperature  $-50^{\circ}$ C the NH<sub>3</sub> (5 ml) was added twice until complete evaporating of ammonia. Yield: 4.4 g (12%). *Anal.* Calc.

for C<sub>5</sub>H<sub>13</sub>N<sub>3</sub>Cl·NH<sub>4</sub>Cl (204.12): C, 29.42; H, 8.39; N, 27.45; Cl, 34.74%. Found: C, 28.98; H, 9.28; N, 27.74; Cl, 35.40%.

#### 2.8. Single crystal X-ray diffraction analysis and structure determination

Suitable single crystals of 1, 5, 9-3, and 10 were selected and XRD analyses were carried out on an automated four-circle  $\kappa$ -geometry diffractometer with CCD detector by standard procedure (graphite monochromated Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation,  $\omega$ -scanning with step 1° at r.t. T=295(2) K) by applying the CrysAlis CCD Software system, Version 1.171.29.9. Data reduction has been done by the same programs.

The structures were solved by direct methods, and refined in SHELXL-97 [27], including anisotropic displacement parameters for all non-H atoms. H-atoms at C-H bonds were included in calculated positions and refined isotropically in 'riding' model, H-atoms of the OH-groups refined independently in isotropic approximation.

The crystal parameters, data collection and refinement results for 1, 5, 9-3, and 10 are summarized in Table 5.

#### 3. Results and discussions

Studied in this paper substituted chroman-4-ones (2-hydroxy-2-(trifluoromethyl)chroman-4one (1), 2-hydroxy-6-methyl-2-(trifluoromethyl)chroman-4-one (2) and 2-hydroxy-2,6bis(trifluoromethyl)chroman-4-one (3)) served as pre-ligands. Possibility of existence of their associated 'open' form (1,1,1-trifluoro-4-(2-hydroxyphenyl)butan-2,4-dione ( $H_2L1$ ), 1,1,1trifluoro-4-(2-hydroxyphenyl-5-methyl)butan-2,4-dione ( $H_2L2$ ), 1,1,1-trifluoro-4-(2hydroxyphenyl-5-trifluoromethyl)butan-2,4-dione ( $H_2L3$ )) is caused by ring-chain tautomerism (Scheme 1). The results of FT-IR study add considerable support for the existence of 'close' form of the compounds in solid state.



 $R = H(1, H_2L1), CH_3(2, H_2L2), CF_3(3, H_2L3)$ 



#### 3.1. FT-IR spectroscopy of chroman-4-ones (pre-ligands)

The FT-IR spectra of **1-3** was registered (Fig. 1S, Supporting materials). The characteristic IR bands and corresponding assignment are presented in Table 1. The assignments have been made on the basis of the literature data of similar compounds [28–30]. The broad bands in the regions of 3470-3090, 3470-3060, 3470-3000 cm<sup>-1</sup> for **1**, **2** and **3**, respectively, are appeared for v(O-H) that is characteristic band of hydroxyl group. The characteristic stretching vibrations of chromone carbonyl are usually located in the region of 1690-1640 cm<sup>-1</sup>, whereas the bands of enol form of  $\beta$ -diketones appeared at 1620-1600 cm<sup>-1</sup>. IR spectra showed characteristic stretching vibrations in the region of 1680 (**1**), 1682 (**2**), and 1693 (**3**) cm<sup>-1</sup> due to v(C=O) vibrations of chromone carbonyl. Additionally, v(C=O) vibration of **1** is observed at 1643 cm<sup>-1</sup>. That confirms the existence of the studied compounds in 'close' form in solid. In the spectra three bands in the range of 1615-1467 (**1**), 1619-1492 (**2**), 1625-1500 (**3**) cm<sup>-1</sup> are assigned to the skeletal C=C stretching modes in benzene ring. This is in a good agreement with the literature values [28–30].

Mostly v(C–C) as well as the bands of CF<sub>3</sub> at chromone ring exist in similar wavenumber, but it ought to be noted that new strong bands at 1335 and 1235 cm<sup>-1</sup>, which can be assigned to  $v_{as}$ (C–F) and  $v_s$ (C–F) of CF<sub>3</sub> group of benzene ring, were registered only for compound **3**.

#### 3.2. Protolytic properties

As we said above, the complexes of di- and triketonate ligands with metal ions are very perspective for catalytic application. Thus, important task is studying binding properties of studied compounds. For this reason it is necessary to evaluate their protolytic properties. Because of the low solubility of chromanones in water, their properties can be evaluated in such solvents like water/methanol, water/ethanol, water/DMA, water/EG [22,31]. However methanol and ethanol are high volatile, N,N-DMA has high absorbance in the range 200-260 nm, we decided to use water/EG 30/70 vol. as solvent for studying properties of chromanones. Ionic strength was adjusted by KCl (0.1 mol/L). The determination of ionization constants as well as binding properties were performed using spectrophotometry because this method is an ideal method when a substance is insoluble for potentiometry [22].

The spectral changes of water/EG (30/70 v./v.) solutions of chroman-4-ones depending on pH are presented in Fig. 2S–4S (Supporting materials). The pH change of solutions of **1** induces absorption changes at several distinct bands. Two bands in Fig. 2aS, i.e. band-3 and band-4 are associated with the concentration of the monobasic form (HL<sup>-</sup>), while band-1 band-2 and is a part of the characteristic spectra of the acid form (H<sub>2</sub>L). The presence of isosbestic points confirms that spectral transitions occur between different species. Rationally suppose that band-5

with maximum at 360 nm as well as a band at a longer wavelength range (band-6) can be assumed to sequential ionization of ligands (Scheme 2). However, the compounds are unstable in strongly alkaline media and decompose. It can be observed from dramatic change of spectra (Fig. 2bS) above pH > 10.5. The solutions of the compound having pH > 9 were investigated using GC-MS. The results proved the decomposition of the ligand at pH > 10.5. In the solutions the starting materials – 2-hydroxyacetophenone and 1,1,1-trifluoroacetate were identified. For this reason the second ionization constant could not be determined.



Scheme 2. Protonation/destruction patterns for 1–3 (H<sub>2</sub>L1–H<sub>2</sub>L3)

The graphical analysis of band-4 with  $\lambda_{max} = 340$  nm can be used to estimate the p $K_{a1}$  value of 1,1,1-trifluoro-4-(2-hydroxyphenyl)butan-2,4-dione. The spectral data were processed mathematically using FTMT program [26]. Equilibrium constant is shown in Table 2.

Spectra of **2** and **3** generally have similar characteristic bands (Fig. 3S and 4S, Supporting materials) with absorbance maxima differ from ones of **1**. Destruction of third ligand is accompanied by rising novel band-7 (Fig. 4bS). For calculation the  $pK_{a1}$  value of **H**<sub>2</sub>**L2** and **H**<sub>2</sub>**L3** wavelength 345 nm ( $\lambda_{max}$  of band-4) was chosen.

The first protolytic constant of  $H_2L1$ , which does not have substituents in the benzene ring, is  $pK_{a1}=8.21\pm0.09$ . The  $H_2L2$ , where the methyl group is in 6 position, shows a higher acidity respect to  $H_2L1$ , that is a decrease in  $pK_{a1}$  (8.12±0.06). The value of protonation constant for the **3**, which has a trifluoromethyl group in the 6 position, also increases ( $pK_{a1}=7.20\pm0.07$ ). Introducing the CH<sub>3</sub> group into the benzene ring has led to slight increase in acidity of OH-group ( $\delta \log K_a = \log K_{a1}(H_2L2) - \log K_{a1}(H_2L1) = 0.09$ ). At the same time presence of the CF<sub>3</sub> group in

the 6 position significantly affect the ligand protonation constant ( $\delta \log K_a = \log K_a(3) - \log K_a(1) = 1.08$ ).

3.3. Binding properties of 1,1,1-trifluoro-4-(2-hydroxyphenyl)butan-2,4-dione (H<sub>2</sub>L1) in solution

Upon addition of **1** to the aqueous ethylene glycol solutions of  $CoCl_2$ ,  $NiCl_2$ , and  $CuCl_2$  their initial color (pink, green and blue, respectively) changed to yellow indicating an octahedral–tetrahedral geometry change, giving evidence to formation of complex compounds.

Inasmuch as in the course of ionization chromanones 1-3 undergo ring-chain rearrangement, it is evident that it is precisely 'open' form of the compounds that is the ligand which involved in complexation with metal ions.

For the determination of optimum pH complexation of  $H_2L1$  with Co(II), Ni(II), Cu(II) the dependencies of absorbance of metal ions/ligand solutions on pH were studied (Fig. 5S, Supporting materials). The new bands at approximate 400 nm originate from the formation of metal ion – ligand charge-transfer complexes arise. As shown in the inset plots, which traced at 400 nm, optimum pH of complexation of the ligand with Co(II) – 10-11, with Ni(II) – 10-11, with Cu in pH range 7.5-8.5.

To elucidate the stoichiometric composition of the complexes in the solution we originally used the molar ratio method [32] and Job's method [33]. In the molar ratio method, various amounts of metal ions were added to the constant amount of the ligand (0.1 mM). The absorbance of each solution was measured and plotted against the metal-to-ligand mole ratio at pH 10 for cobalt and nickel, pH 7.5 for copper.

As it is shown in Fig. 6aS (Supporting materials), the increase of cobalt to ligand molar ratio at pH 10 gives rise to new shoulder at 400 nm which is absent in chromanone solutions. The new shoulder for nickel–chroman-4-one solutions spectra (Fig. 6bS) becomes a maximum ( $\lambda_{max} = 400$  nm) in a gradual manner. In case of copper (Fig. 6cS) distinct maximum with  $\lambda_{max} = 415$  nm is observed. In subsequent studies the mentioned wavelengths were maintained throughout the experiment. The intercepts, arising from extrapolated tangent lines of the curves in the inset plots, suggested the formation of complexes with the mole ratio M(II):**H**<sub>2</sub>L1 = 1:1.

Job's method (Fig. 1) clearly display ratios in the complexes are 1:1 for all studied metals indeed. The absorbance of isomolar solutions containing Co(II), Ni(II) or Cu(II) and  $H_2L1$  was measured at the total concentrations  $C_R/(C_{Me}+C_R)$  were 0.1 mM.

However, molar ratio method and Job's method can only show the ratio of components in the complexes. Meanwhile, theoretically the composition of the complexes can be 1:1, 2:2, etc. We used Starik-Barbanel relative yield method [34] for determination molar ratios between the components of the complexes and found that for all studied metal ions  $M(II) : H_2L1=2 : 2$ .

Whereas studied ligand forms complexes with the composition M(II) :  $H_2L1= 2$  : 2, the formation of bond between chroman-4-one ligands and metals in solid proceeds both 2:2 and 1:2.

#### 3.4. Preparation of complexes

Complexes 2 : 2 can be prepared in an (aqueous) methanol solutions in the presence of base (Scheme 3). Synthesis of the complexes without the addition of base leads to the formation of complexes  $ML_2$ . The same composition can be obtained by recrystallization of  $M_2L_2$  complexes using DMSO or tetramethylurea (TMU).



Scheme 3. Synthesis of complexes

Complex  $[Cu_2(L1)_2(H_2O)_2]$  (4-1) was prepared by the reaction of copper(II) acetate hydrate and 1 in an aqueous methanol solution in the presence of urea. Recrystallization 4-1 from DMF resulted to complex  $[Cu_2(L1)_2(DMF)_2]$  (4-2). Complexes 4-1 and 4-2 were characterized by elemental analyses, complex 4-1 was characterized by FT-IR. However, single crystal none of them, suitable for X-ray crystal structure analysis, was obtained.

Complex  $[Cu_2(L2)_2(DMF)_2]$  (5) was prepared by the reaction of copper(II) acetate hydrate and 2 in an aqueous methanol solution in the presence of sodium hydroxide and recrystallization from DMF. The X-ray crystal structure analysis is reported here (See Section 3.5).

Complex  $[Cu_2(L3)_2(H_2O)_4]$  (6) was prepared by the reaction of copper(II) acetate hydrate and 3 in an aqueous methanol solution in the presence of sodium hydroxide.

Complexes  $[Ni_2(L1)_2(H_2O)_3]$  (7), and  $[Co_2(L1)_2(H_2O)]$  (8) were prepared by the reaction of metal(II) acetate hydrate and 1 in an aqueous methanol solution in the presence of sodium hydroxide. However, the efforts to grow the single crystals were also failed.

Complex  $[Cu(HL1)_2(H_2O)_2]$  (9-1) was prepared by the reaction of copper(II) acetate hydrate and 1 in an aqueous methanol solution without the addition of base for any initial ratio Cu(II): 1. Recrystallization of complex 4-2 from DMSO or TMU have changed the structure and

complexes  $[Cu(HL1)_2(DMSO)_2(H_2O)_2]$  (9-2) and  $[Cu(HL1)_2(TMU)_2]$  (9-3) have been obtained (Scheme 4).



Thus, the complexes of both compositions  $ML_2$  and  $M_2L_2$  are capable of amides coordinating. Increasing the donor properties of amide leads to the structural transformation  $(M_2L_2 \text{ into } ML_2)$ . It can be demonstrated in next example. After the recrystallization of **9-1** from methanol solution of urea, urea was not included in coordination sphere; the composition of complex did not change. At the same time, the crystallization of **6** from methanol solution of 1,3dimethyl-2-imidazolidinimine (DMI), which is more strong amide, resulted to displacement of ligand **3** from  $[Cu_2(HL3)_2(DMF)_2]$  (**6**) by DMI (Scheme 5). The complex of four coordinated copper  $[Cu(DMI)_4]Cl_2$  (**10**) was obtained, its molecular structure have been determined by X-ray crystallography (See Section 3.5).



#### 3.5. Crystal structures

The X-ray crystal structure of **1**, grown by slow evaporation of a methanol solution at room temperature is presented in Fig. 2. The heterocyclic ring in **1** has a half-boat conformation. The O2 – C7 and O3 – C9 bond distances are 1.2253 (18) and 1.4203 (17) Å, respectively. Intermolecular O–H...O hydrogen bonds link the molecules into linear supramolecular chains

along the *a*-axis. The observed bond distances and angles (Table 5) are in a good agreement with the previously reported data [35].

Molecular structure of  $[Cu_2(L2)_2(DMF)_2]$  **5** and  $[Cu(HL1)_2(TMU)_2]$  **9-3** are depicted in Fig. 3 and 4. The crystallographic data with selected bond lengths and bond angles are listed in Table 4 and 5. All the compounds crystallized in triclinic lattice with space group *P*-1.

The crystal substructure of 5 comprises centrosymmetric molecules  $Cu_2L_2$  and two DMF solvate molecules. Cu(II) centers exhibit a distorted square pyramid geometry comprising of two equivalent dianionic ligands coordinated in a meridional fashion, whilst solvent DMF ligands occupy axial coordination positions on Cu(II), thereby completing a square-pyramidal geometry at the two centers, very common with this metal [36]. The basal plane of the pyramid is defined by phenol deprotonated hydroxyl oxygen atom O1, oxygen O3, and two O2 atoms of both ligand molecules. The central of the three O atoms of the ligands, O2, has a fundamentally different coordination, as it interacts with both Cu atoms, similar to diacetylacetonate ligands [37]. Thus, O2 exhibits longer Cu – O distances [1.950(4) and 1.966(4) Å] than O1 and O3 [1.857(4) and 1.915(4) Å, respectively, for Cu1 – O1 and Cu1 – O3]. Two oxygen atoms O2 and O2<sup>i</sup> play a bidentate-bridging function forming bridges between the copper ions. There are also two cocrystallized DMF molecules (O4 axial oxygen atoms) in the structure of 5. The axial Cu1 – O4 bond distance [2.314(4) Å] is longer than the basal Cu – O bonds, which are almost equal [1.857(4), 1.966(4), 1.950(4), 1.915(4) Å, respectively, for Cu1 – O1, Cu1 – O2, Cu1 – O2<sup>i</sup>, Cu1 - O3]. The ligand 2 in the complex 5 is nominally dianion. One of the negative charges is localized on the phenol deprotonated hydroxyl oxygen atom O1, when another is delocalized between two oxygen atoms O2 and O3. The shorter the C - O bond, the more double-bond character it has; hence, the longer C7 – O2 [1.308(6) Å] bond possesses more single-bond character, *i.e.* is slightly more enolate-like than C9 – O3 [1.262(6) Å] bond. However, the C7 – C8 bond is slightly longer [1.393(8) Å] than the C8 – C9 bond [1.377(7) Å]. These observations are in accord with the data for bis(diacetylacetonato)bis[pyridinecopper(II)] [37]. The bond distance Cu – Cu is 3.013 Å. These values are in good agreement with those reported for other structures involving triketone-like ligands [36,37]. Weak C-H...O hydrogen bonds link the components of the structure into two-dimensional networks parallel to (011) and (101). The O1...H12A and O3...H14A intermolecular interactions along the *a*-axis and O4...H13C intermolecular interactions along the *b*-axis generate the 2D sheets along the *ab*-plane.

The crystal substructure of 9-3 comprises centrosymmetric molecules  $CuL_2$  and two tetramethylurea solvate molecules. Cu(II) centers exhibit a square bipyramid geometry (4+2) comprising of two equivalent monoanionic ligands coordinated in a meridional fashion. The ligand is coordinated in a bidentate chelating mode forming six-membered chelate rings. The

basal plane of the bipyramid is defined by two hydroxyl oxygen O2 of enol and two carbonyl O3 atoms of both ligand molecules. The axial oxygen atoms O1 belong to two co-crystallized TMU molecules. The phenol hydroxyl does not participate in the coordination to copper. In the same way as for **5** in the crystal **9-3** the axial Cu1 – O1 bonds [2.440(2) Å] are longer than the bonds in basal plane which are almost equal [1.928(17), 1.935(16) Å, respectively, for Cu1 – O2, Cu1 – O3. The O1 – Cu1 – O1(A) and O2 – Cu1 – O2(A) trans angles were found as 180.00(1)° and O2 – Cu1 – O3 angle was found as 92.71(7)°. These observations suggested that the coordination geometry around the copper ion had almost not undergone distortion from a perfect square bipyramid. The C12 – O3 [1.270(3) Å] bond is slightly longer, than C14 – O2 [1.258(3) Å] bond, and the C12 – C13 bond is longer [1.410(3) Å] than the C13 – C14 bond [1.348 (3) Å]. Weak C–H...O and C–H...F hydrogen bonds link the components of the structure into two-dimensional networks parallel to (110) and (011). The F3...H2C intermolecular interactions along the *a*-axis and O1...H9A intermolecular interactions along the *b*-axis generate the 2D sheets along the *ab*-plane.

Complex 10 crystallizes in centrosymmetric monoclinic space group P2(1). The ORTEP drawing is depicted in Fig. 5. The complex 10 exhibits a tetrahedral geometry in which the Cu(II) center is coordinated to four imino nitrogen atoms from four DMI ligands. The Cu(II) center has also two second-sphere chlorine atoms. The DMI functions as a monodentate ligand.

The presence of electronegative chlorine atoms leads to the occurrence of intermolecular hydrogen bonds in the crystal structure. The neighboring molecules interact through C–H...Cl hydrogen bonds. In the crystal, the molecules are linked into chains parallel to (011) and (110). In one of the interactions, the H-donor atoms are from a methyl carbon (C14) and imidazolyl carbon (C17), with the bridging chlorine atom (Cl2) acting as the H-atoms acceptor. A two-dimensional network structure is generated, lying along the *a*-axis. The second one occurs between the imine groups, the methyl groups of the imidazolyl fragment and the free chlorine ions. These intermolecular interactions form a layered structure, lying along the *c*-axis. As a result the molecules are connected into a three-dimensional architecture by intermolecular interactions. These hydrogen-bonded networks help to stabilize the crystal structure.

#### 3.6. FT-IR spectra of complexes

In order to study IR spectra of 'open' structure, the potassium salt of 1,1,1-trifluoro-4-(2-hydroxyphenyl)butan-2,4-dione has been obtained by the reaction between chroman-4-one **1** and potassium hydroxide in methanol solution followed by evaporation of solvent in vacuum. FT-IR spectrum of **KHL1** were registered (Table 6); the assignments relied on the data of trifluorobenzoylacetone [38]. The band assigned to chromone carbonyl is absent in the spectrum.

In place of this band the very strong band at 1621 cm<sup>-1</sup> assigned to asymmetric C=C–C=O stretching of the enol moiety coupled strongly to the OH in-plane bending motion appeared. New very strong band at 1526 cm<sup>-1</sup> is assigned to symmetric C=C–C=O stretching. The strong band at 1467 cm<sup>-1</sup> of asymmetric O–C=C–C stretching shifts to 1478 cm<sup>-1</sup> upon opening of the chromone ring and ionization. Spectral changes due to ring–chain rearrangement (1–KHL1) can be followed as well in a wide range of frequencies.

The analysis of FT-IR spectra of copper  $[Cu_2(L1)_2(H_2O)_2]$  (4-1),  $[Cu_2(L2)_2(DMF)_2]$  (5),  $[Cu(HL1)_2(TMU)_2]$  (9-3), nickel  $[Ni_2(L1)_2(H_2O)_3]$  (7), and cobalt  $[Co_2(L1)_2(H_2O)]$  (8) complexes compared to potassium salts of 1,1,1-trifluoro-4-(2-hydroxyphenyl)butan-2,4-dione (Table 6) gives evidence of significant  $\pi$ -electronic distribution due to tautomeric transformations and coordinate bonds formation (taking into consideration that difference between (1,1,1-trifluoro-4-(2-hydroxyphenyl)butan-2,4-dione (H<sub>2</sub>L1) and 1,1,1-trifluoro-4-(2hydroxyphenyl-5-methyl)butan-2,4-dione ( $H_2L2$ ) is insignificant). In spectra the bands of ligand arised from C=C stretching mode shift in complexes. It is more significant that a shift of the asymmetric C=C-C=O stretching at 1621 cm<sup>-1</sup> towards lower frequencies after  $\beta$ -diketone coordination to the metallic center occurs as a result of the participation of carbonyl oxygen in the coordination of metal ions. The frequency shifts for 4-1, 5, 7, 8 and 9-3 are 13, 15, 20, 17 and 17 cm<sup>-1</sup>, respectively. The C=O stretching vibrations of coordinated DMF (5) and TMU (9-3) in comparison with the corresponding values for free DMF (1676 cm<sup>-1</sup>) and TMU (1650 cm<sup>-1</sup>) are shifted to lower frequencies (1620 cm<sup>-1</sup> and 1640 cm<sup>-1</sup>, respectively), attesting that the metal bound to this group. In support of the conjecture of ring-chain rearrangement during complexation it should be noted that the band assigned to chromone carbonyl is absent in all spectra of complexes.

#### 4. Conclusions

In conclusion, substituted chroman-4-ones which are capable to undergo ring-chain tautomerism have been used for the first time as pre-ligand and single crystals of metal complexes were obtained. Protolytic properties of chroman-4-ones in aqueous ethylene glycol solutions have been studied using UV-Vis spectrophotometry. It has been demonstrated that in the process of ionization and complexation with metal ions the compounds go through opening the chromone ring and act as mono- and dibasic di- and tridentate ligand. The mechanism of ionization of studied compounds were suggested and the first ionization constants were determined. The second ionization constant could not be determined because of the easy decomposability of the compounds in strongly alkaline media. The complex formation between Co(II), Ni(II), and Cu(II) and H<sub>2</sub>L1 in aqueous ethylene glycol solutions was investigated

through spectroscopic method. It was shown that the composition of complexes for all studied metals is 2:2. The complexes of 'open form' of studied compounds (1,1,1-trifluoro-4-(2-hydroxyphenyl)butan-2,4-diones) with Co(II), Ni(II) and Cu(II) were synthesized and studied by FT-IR spectroscopy, elemental analysis. It was shown that the complexes are capable of amides coordinating. The structures of binuclear and mononuclear chroman-4-one complexes  $[Cu_2(L2)_2(DMF)_2]$  **5** and  $[Cu(HL1)_2(TMU)_2]$  **9-3** were confirmed by single crystal X-ray crystallography. It was shown that the crystallization of copper complex in the presence of strong amide leads to the displacement of the ligand by amide, that also was confirmed by X-ray crystallography.

#### Appendix A. Supplementary data

CCDC 1064086, 1064087, 1064088, and 1404509 contain the supplementary crystallographic data for ligand **1** and complexes **5**, **9-3**, and **10**. These data can be obtained free of charge via <u>http://www.ccdc.cam.ac.uk/conts/retrieving.html</u>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or e-mail: <u>deposit@ccdc.cam.ac.uk</u>.

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### Table 1

UV-Vis measurements.

Solution	$C_{\text{metal}} (10^{-4} \text{ M})$	$C_{chromanone} (10^{-4} M)$	pН	$\lambda$ (nm)	
1		1.0	6.5-10.5	340	
2		1.0	6.5-10.5	345	
3		1.0	6.5-10.5	345	
Co(II)/1	1.0	1.0	10.5	400	
Ni(II)/2	1.0	1.0	10.5	400	
Cu(II)/ <b>3</b>	1.0	1.0	7.5	415	
Table 2   Frequence	ies of the absorp	tion bands for chroma	an-4-ones 1	1-3.	
F	requency (cm <sup>-1</sup> )		Assign	iment	
1	2	2			

#### Table 2

Frequencies of the absorp	ion bands for chroman-4-one	es 1-3.
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	Frequency (cm <sup>-1</sup> )			Assignment	
	1	2	3	$\sim$	
	2928w	2931w	2938w	v <sub>as</sub> (C–H)	
	2821vw	2856vw	2844vw	v <sub>s</sub> (C–H)	
	1680vs	1682vs	1693vs	v(C=O) chromone carbonyl	
	1643m			v(C=O)	
	1615s	1619s	1625s	v(C=C)	
	1583m	1586m	1590m	v(C=C)	
	1477m			v(C=C), v(C-O)	
	1467s	1492s	1500s	$v_{as}(O-C=C-C)$	
	1411m	1422m	1442m	$\nu$ (C–O), $\delta_s$ (C–H)	
	1365m	1359w	1355sh	ν(C–C), δ(C–H)	
			1335s	v <sub>as</sub> (C–F)	
	1316s	1318w	1318m	$\nu$ (C–C), $\delta$ (C–H), $\nu$ <sub>as</sub> (C–F)	
$\mathbf{O}$	1293s	1287s	1276vs	$v_{as}(C-O-C), v(C-C), \delta(C-H), v_{as}(C-F)$	
	1246m	1248m	1247m	v <sub>as</sub> (C–Ph), v(C–C), v <sub>s</sub> (C–F)	
			1235s	$v_s(C-F)$	
	1218s	1217s		δ <sub>as</sub> (C–H)	
	1196vs	1201vs		$\nu$ (C–H), $\delta$ (COC), $\delta$ (CF)	
		1183s	1187s	ν(C–H), δ(COC), δ(CF)	
	1156s		1151m	$\nu$ (C–H), $\delta$ (COC), $\delta$ (CF)	

<b>A</b>	CCEPT		NUSCRIPT
 1132vs	1131vs	1126vs	ν(C–H), δ(COC)
1117s			$\delta$ (CH), v(C–O), v <sub>s</sub> (CF <sub>3</sub> )
1078m	1070m	1083m	ν <sub>s</sub> (C–O–C), γ(CH)
1054m	1053m	1050m	ν <sub>s</sub> (C–O–C), γ(CH)
995s	990m	991s	v(C–C)
875w	894w	882vw	δ(CCC), γ(CH)
856w	953w	851m	δ(CCC), γ(CH)
839m	829m	836m	δ(CCC), γ(CH)
768s	790w	783vw	γ(CH)
713w	717w	723m	$\gamma$ (CH), $\delta_s$ (CF <sub>3</sub> )
652w	671m	642w	$\gamma$ (CH), $\delta_s$ (CF <sub>3</sub> )
543w	548w	541w	γ(COC)
493m	500m	503m	γ(COC)

### Table 3

Equilibrium constants in aqueous ethylene glycol solutions.

Ligand	pK <sub>a1</sub>
$H_2L1$	8.21±0.09
$H_2L2$	8.12±0.06
$H_2L3$	7.20±0.07
Table 4	

#### Table 4

Crystallographic and refinement data for 1,  $[Cu_2(L2)_2(DMF)_2]$  (5),  $[Cu(HL1)_2(TMU)_2]$  (9-3), and  $[Cu(DMI)_4]Cl_2$  (10).

Compound	1	5	9-3	10
Empirical formula	$C_{10}H_7F_3O_3$	$C_{28}H_{28}Cu_2F_6N_2O_8$	$C_{30}H_{36}CuF_6N_4O_8$	$C_{20}H_{44}Cl_2CuN_{12}$
Formula weight	232.16	761.60	758.16	587.11
Temperature (K)	295(2)	295(2)	295(2)	120(2)
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2(1)
<i>a</i> (Å)	6.0111(7)	5.927(2)	9.6801(12)	8.0304(4)
<i>b</i> (Å)	8.7212(9)	10.386(3)	10.3078(14)	15.7767(9)
<i>c</i> (Å)	10.2100(9)	12.390(3)	10.5037(14)	11.4534(7)
α (°)	67.127(9)	100.84(2)	62.089(13)	90.00

	ACCEPTE	ED MANUS	CRIPT	
β (°)	80.261(9)	97.28(2)	68.581(12)	106.535(5)
γ (°)	78.227(9)	91.43(3)	77.700(11)	90.00
$V(\text{\AA}^3)$	480.39(9)	742.1(4)	861.1(2)	1391.06(14)
Ζ	2	1	1	2
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.605	1.704	1.462	1.402
$\mu (\mathrm{mm}^{-1})$	0.155	1.524	0.719	1.011
<i>F</i> (000)	236	386	391	622
$\Theta$ range (°)	2.69-30.51	3.47-26.37	2.70-26.37	2.65-26.37
Index ranges	$-8 \le h \le 5$	$-7 \le h \le 7$	$-12 \le h \le 12$	$-5 \le h \le 10$
	$-12 \le k \le 10$	$-12 \le k \le 12$	$-12 \le k \le 12$	$-19 \le k \le 11$
	$-14 \le l \le 14$	$0 \le l \le 154$	$-13 \le l \le 13$	$-14 \le l \le 14$
Measured reflections	5797	2906	11413	4748
Independent reflections	2638	2906	3457	3920
Observed reflections [ $I \ge$	1421	1460	2053	2618
2σ( <i>I</i> )]				
Final <i>R</i> indices [ <i>I</i> >	$R_1 = 0.0438, wR_2$	$R_1 = 0.0569, wR_2$	$R_1 = 0.0426, wR_2$	$R_1 = 0.0358, wR_2$
$2\sigma(I)$ ]	= 0.1118	= 0.1211	= 0.0930	0.0580
R indices [all data]	$R_1 = 0.0869, wR_2$	$R_1 = 0.1303, wR_2$	$R_1 = 0.0837, wR_2$	$R_1 = 0.0544, wR_2$
	= 0.1245	= 0.1322	= 0.1004	0.0593
Goodness-on-fit	1.000	1.000	1.005	0.999
Maximum, minimum	0.233, -0.152	1.096, -0.546	0.403, -0.277	0.584,-0.460
electron density ( $e \text{ Å}^{-3}$ )				

### Table 5

Selected bond lengths (Å) and bond angles (°).

1			
Bond lengths		Bond angles	
C(7)–O(2)	1.226(2)	O(2)–C(7)–C(8)	121.4(1)
C(1)–O(3)	1.387(2)	O(2)-C (7)-C(6)	122.7(1)
C(9)–O(3)	1.420(2)	O(3)–C(1)–O(2)	170.46(17)
C(9)–O(1)	1.384(2)	C(1)-O(3)-C(9)	115.2(1)
C(7)–C(8)	1.505(2)	O(1)–C(9)–O(3)	111.5(1)
C(6)–C(7)	1.466(2)	O(1)–C(9)–C(8)	108.6(1)
C(9)–C(10)	1.535(2)	O(1)-C(9)-C(10)	109.4(1)

C(8) - C(9)1.511(2) C(7)-C(8)-C(9) 111.5(1)

$[Cu_2(\mathbf{L2})_2(\mathbf{DN}$	/IF) <sub>2</sub> ] ( <b>5</b> )		
Bond lengths		Bond angles	
Cu(1)–O(1)	1.857(4)	O(3)–Cu(1)–O(1)	94.36(16)
Cu(1)–O(2)	1.966(4)	O(2)–Cu(1)–O(1)	92.50(16)
$Cu(1) - O(2)^{i}$	1.950(4)	O(3)–Cu(1)–O(2)	170.46(17)
Cu(1)–O(3)	1.915(4)	O(1)–Cu(1)–O(4)	98.92(18)
Cu(1)–O(4)	2.314(4)	O(3)–Cu(1)–O(4)	85.19(17)
C(1)–O(1)	1.307(6)		
O(2)–C(7)	1.308(6)		
O(3)–C(9)	1.262(6)		
C(8)–C(7)	1.393(8)		
C(9)–C(8)	1.377(7)		
Symmetry coo	de: (i) –x, –	y, -z.	
[Cu( <b>HL1</b> ) <sub>2</sub> ( <b>T</b> ]	MU) <sub>2</sub> ] ( <b>9-3</b> )		
Bond lengths		Bond angles	<u>A</u>
Cu(1)–O(1)	2.440(2)	O(1)–Cu(1)–O(1A)	180.00(1)
$C_{11}(1) = O(2)$	1.028(2)	$O(2) = C_{11}(1) = O(2A)$	180.00(1)

Bond lengths		Bond angles	
Cu(1)–O(1)	2.440(2)	O(1)-Cu(1)-O(1A)	180.00(1)
Cu(1)–O(2)	1.928(2)	O(2)–Cu(1)–O(2A)	180.00(1)
Cu(1)–O(3)	1.935(2)	O(2)-Cu(1)-O(3)	92.71(7)
O(3)–C(12)	1.270 (3)		
O(2)–C(14)	1.258 (3)		
C(13)–C(12)	1.410 (3)		
C(13)-C(14)	1.348 (3)		

#### [Cu(DMI)<sub>4</sub>]Cl<sub>2</sub> (10)

Bond lengths		Bond angles	
Cu(1)–N(1)	1.966(3)	N(1)–Cu(1)–N(4)	99.9(1)
Cu(1)–N(4)	1.953(3)	N(1)-Cu(1)-N(7)	93.7(1)
Cu(1)–N(7)	1.958(4)	N(1)-Cu(1)-N(10)	138.3(1)
Cu(1)–N(10)	1.955(3)	N(4)-Cu(1)-N(7)	139.2(1)
		N(4)-Cu(1)-N(10)	94.6(1)
		N(7)-Cu(1)-N(10)	100.3(1)

### Table 6

Frequenc	$y (cm^{-1})$		Assignment			
KHL1	4-1	5	7	8	9-3	-
		1620s			1640vs	v(C=O)
1621vs	1608m	1606m	1601s	1604vs	1604m	$v_{as}(C=C-C=O)$
1582w	1583s		1587s	1590s		v(C=C)
					1567w	γ(N–H)
1526vs	1529vs	1527s	1530vs	1536vs	1525m	v <sub>s</sub> (C=C-C=O)
		1502m			1499vs	Amide II
1478s	1464vs			1469vs		$v_{as}(O-C=C-C)$
		1456m	1456vs	1454s	1452m	ν(C=C), δ <sub>as</sub> (C–O)
1434m			1427w		1429w	ν(C–O), δ <sub>s</sub> (C–H)
	1378w			1400w	1407w	$v_{as}(C-C=C-O)$
		1384m			1368vs	v(C-N)
1349w	1345s					ν(C–C), δ <sub>s</sub> (C–H)
1316m	1319s	1315w	1325s	1324s	1313w	ν(C–C), δ(C–H), ν <sub>as</sub> (C–F)
1292m			1297w			ν <sub>as</sub> (C–O–C), ν(C–C), δ(C–H),
						$v_{as}(C-F)$
	1286s		1284m	1279s		ν <sub>as</sub> (C–O–C), ν(C–C), δ(C–H),
						$v_{as}(C-F)$
1255vs	1250vs		1263m			v <sub>as</sub> (C–Ph), v(C–C), v <sub>s</sub> (C–F)
		1240m	1243vs	1246vs	1236m	v <sub>as</sub> (C–O–C), v(C–C), v <sub>s</sub> (C–F)
	1213m			1224m		$\delta_{as}(C-H)$
1187s	1192s	1195m	1188vs	1193vs	1197w	ν(C–H), δ(COC), δ(CF)
1169s	1175m		1171s	1172s		ν(C–H), δ(COC), δ(CF)
	1130vs	1130vs	1137sh	1136vs	1135vs	ν(C-H), δ(COC)
1112s			1119vs	1127vs		δ(CH), v(C–O), v <sub>s</sub> (CF <sub>3</sub> )
1045vw	1053vw	1080m	1053sh		1061m	ν <sub>s</sub> (C–O–C), γ(CH)
	952vw			960vw		γ(OH)
935w	943m	940w	942m	940w	914m	$\delta(CCC), \delta(CH)$
861 vw	869w		862w	859w		$\delta(CCC), \gamma(CH)$
842w		844w	849w		848vw	$\delta(CCC), \gamma(CH)$
802vw	810m	800m	806w	815w		γ(CH)
775vw	794m		785w	775m	783m	γ(CH)

750s	766m				761w	γ(CH)
	755m	752m	754s	750w	738w	γ(CH)
	713m	710w	708s	708m	708vw	$\gamma$ (CH), $\delta_s$ (CF <sub>3</sub> )
702m	690w		691w			$\gamma$ (CH), $\delta_s$ (CF <sub>3</sub> )
667vw	671w			693vw	682vw	$\gamma$ (CH), $\delta_s$ (CF <sub>3</sub> )
645m	627vw		657m	650w	651vw	$\gamma$ (CH), $\delta_s$ (CF <sub>3</sub> )
575m	574m	575w	566m	562w	578w	γ(COC), ν(M–O)
527w	528w		527w	517w	554m	γ(COC), ν(M–O)

#### **Figure captures**

**Fig. 1.** The determination of stoichiometry of M(II)- $H_2L1$  complexes by Job's method, absorbance measured at 400 nm for Co and Ni (pH 10), at 415 nm for Cu (pH 7.5).

**Fig. 2.** ORTEP drawings of **1**. Ellipsoids are plotted at 50% probability level, hydrogen atoms are omitted.

Fig. 3. ORTEP drawings of 5. Ellipsoids are plotted at 50% probability level, hydrogen atoms are omitted.

**Fig. 4.** ORTEP drawings of **9-3**. Ellipsoids are plotted at 50% probability level, hydrogen atoms are omitted.

Fig. 5. ORTEP drawings of 10. Ellipsoids are plotted at 50% probability level, hydrogen atoms are omitted.

#### **Figures in Supporting materials**

Fig. 1S. FTIR spectra of chroman-4-ones.

**Fig. 2S.** Absorption spectra of water/EG 1 solutions (0.1 mM, I = 0.1 M) depending on the pH (a) 1.00-9.79 and (b) 9.79-12.01.

Fig. 3S. Absorption spectra of water/EG 2 solutions (0.1 mM, I = 0.1 M) depending on the pH (a) 1.08-10.64 and (b) 10.64-11.83.

Fig. 4S. Absorption spectra of water/EG 3 solutions (0.1 mM, I = 0.1 M) depending on the pH (a) 1.33-9.48 and (b) 9.16-11.75.

**Fig. 5S.** Absorption spectra of water/EG M(II)/ $H_2L1$  (1:1) solutions (0.1 mM, I = 0.1 M) depending on the pH: M = Co, pH 1.33-11.70 (a), M = Ni, pH 1.30-11.57 (b), M = Cu, pH 2.40-11.48 (c).

Fig. 6S. The determination of stoichiometry of M(II)- $H_2L1$  complexes by molar ratio method, absorbance measured at pH 10 for Co and Ni, at pH 7.5 for Cu.











1. The protolytic properties of 2-hydroxy-2-(trifluoromethyl)chroman-4-one, 2-hydroxy-6methyl-2-(trifluoromethyl)chroman-4-one and 2-hydroxy-2,6-bis(trifluoromethyl)chroman-4-one have been studied.

2. The substituted chroman-4-ones were used as pre-ligands in study of binding properties of triketone-like ligands with Cu(II), Ni(II) and Co(II) in solution.

n ro, 3. Mononuclear and binuclear complexes of the studied compounds with copper(II) were

