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# Synthesis, characterization, thermal and theoretical studies of cobalt(II) addition compounds with 2-hydroxy-phenones and $\alpha$ -diimines. Crystal and molecular structures of [Co(2-hydroxy-benzophenone)<sub>2</sub>(bipy)]·2-hydroxy-benzophenoneH (**3**) and [Co(2-hydroxy-benzophenone)<sub>2</sub>(phen)] (**8**)

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#### ABSTRACT

Ten Co(II) addition compounds [Co(ketone)<sub>2</sub>Y], where ketone is the anion of 2-hydroxy-phenones and Y = the neutral  $\alpha$ -diimines(bipy or phen), were synthesized and characterized by physicochemical and spectral (IR, UV–Vis) data. The molecular structures, vibrational and electronic spectra, and the energetics of the metal–ligand interactions for compounds [Co(2-hydroxy-benzophenone)<sub>2</sub>(bipy)]-2-hydroxy-benzophenoneH (**3**) and [Co(2-hydroxy-benzophenone)<sub>2</sub>(phen)] (**8**) were studied by means of density functional calculations (DFT). Good correlation was found between the theoretical calculations and the experimental values. The cyclic voltammetry study in CH<sub>3</sub>CN gave all the expected waves for the redox processes of the metal Co(II) and the studied ligands. The X-ray diffraction study of the two compounds (**3**) and (**8**) verified their analogous proposed octahedral arrangement of the ligands around the cobalt(II) atom. The thermal behaviour was investigated by means of simultaneous TG/DTG-DTA technique in nitrogen atmosphere up to 1000 °C, where metallic cobalt was found as the solid residue.

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#### 1. Introduction

Cobalt chelates with  $\alpha$ -diimines such as 2,2' bipyridine (bipy) or 1,10'-phenanthroline (phen) form cationic octahedral complexes, e.g.  $[Co(bipy)_3]^{2+}$  [1], which are known to have important biological properties [2]. Besides, the strong coordinating properties of 2-hydroxy-phenones or 2-hydroxy-benzaldehydes (salicylaldehyde, saloH) and their derivatives with 3d transition metals have stimulated research in these compounds, which find applications in both pure [3] and applied chemistry fields, especially in extractive metallurgy as analytical reagents [4,5] and specifically for cobalt compounds in tire industry as adhesion promoters [6]. These ligands are known to coordinate in a bidentate manner with transition metals in the mono-anionic form, adopting square-planar geometry, [Zn(salo)<sub>2</sub>], [Zn-5-Br-salo] [7], [Cu(5-Br-salo)<sub>2</sub>] [8], [Fe<sup>II</sup>(salo)<sub>2</sub>] [9] or octahedral arrangement [VO(3-OCH<sub>3</sub>-salo)<sub>2</sub>(H<sub>2</sub>O)] [10], [Fe<sup>III</sup>(2-hydroxy-propiophenone)<sub>3</sub>] [11].

For a better understanding of the bonds and properties in these compounds we have recently initiated a research project with the

\* Corresponding author. Tel./fax: +30 2310 997844. E-mail address: lalia@chem.auth.gr (M. Lalia-Kantouri). metal ions cobalt(II, III) or iron(III) and ligands with N and/or O donor atoms [12]. It has been found that the Lewis acidity of [Co<sup>II</sup>(salo)<sub>2</sub>] chelates, renders them susceptible to nucleoplilic attack and addition compounds can be obtained, such as  $[Co(salo)_2(\alpha-dii$ mines)] [13,14]. In this paper, our approach to the field concerns the synthesis of a series of 10 new cobalt(II) addition compounds under the formula [Co(2-OH-phenone)<sub>2</sub>( $\alpha$ -diimine)]. The resultant octahedral compounds were characterized by physico-chemical methods and spectroscopic (IR, UV-Vis) studies. A cyclic voltammetry (CV) study was employed to investigate their electrochemical behavior. The structures of two representative compounds were verified by X-ray diffraction analysis. The thermal stability and decomposition mode for four of the new compounds were studied in nitrogen atmosphere by using the simultaneous thermogravimetric and differential thermal analysis technique (TG/DTG-DTA).

Results of density functional calculations (DFT) for compounds  $[Co(2-hydroxy-benzophenone)_2(bipy)]$ ·2-hydroxy-benzophenoneH (**3**) and  $[Co(2-hydroxy-benzophenone)_2(phen)]$  (**8**) were used to interpret the vibrational and electronic spectra, as well as to explore the energetics of the metal-ligand interactions and the possibility for the compound to adopt different conformations.

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The 2-OH-phenones presented in this work have the molecular formula 2-OH-C<sub>6</sub>H<sub>4</sub>C(R)O, where R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub> or C<sub>6</sub>H<sub>5</sub>, commonly known and abbreviated as 2-OH-acetophenone(Hapo) (**1**'), 2-OH-propiophenone(Hppo) (**2**'), 2-OH-benzophenone(Hbpo) (**3**'), respectively, as well as their derivatives 2-OH, 5-CH<sub>3</sub>-acetophenone(Hmpo) (**4**') and 2-OH, 4-OCH<sub>3</sub>-benzophenone(Hopo) (**5**'), (Scheme 1).

#### 2. Experimental

#### 2.1. Materials

The ligands, 2-hydroxy-phenones (**1**'–**5**'), the  $\alpha$ -diimines (2,2'bipyridine, bipy and 1,10'-phenanthroline, phen), and the metal salt CoBr<sub>2</sub>·6H<sub>2</sub>O were obtained as reagent grade from Aldrich and used as received. The precursor compounds [Co( $\alpha$ -diimine)<sub>2</sub>Br<sub>2</sub>] were prepared according to the literature[15]. Solvents for preparation and physical measurements of "extra pure" grade were obtained from Fluka without further purification.

#### 2.2. Instrumentation/analytical procedures

Microanalyses were carried out using a Perkin–Elmer 240 B CHN microanalyzer and Perkin–Elmer 5100 PC Atomic Absorption Spectrophotometer for the metal content. Infrared spectra were recorded on a Perkin–Elmer 1600 FT-IR spectrometer in KBr discs at room temperature and are reported in cm<sup>-1</sup>. Electronic absorption spectra in CH<sub>3</sub>CN solutions were obtained on a Shimatzu 160 A spectrometer. Molar conductivities were measured in CH<sub>3</sub>CN solutions, employing a WTW conductivity bridge and a calibrated dip type cell. Magnetic susceptibility measurements on powdered samples were performed at 25 °C employing the Faraday method on a home-build balance calibrated against Hg[Co(SCN)<sub>4</sub>].

Cyclic voltammetry technique (CV) was used for the electrochemical measurements on a  $\mu$ -AUTOLAB Potentio-Galvanostat (ECO CHEMIE, Netherlands). A saturated calomel electrode was used as a reference electrode and a platinum plate one as an auxiliary electrode for all measurements. As a working electrode a platinum wire was used. The tests in CH<sub>3</sub>CN solution were carried out in the potential region -1900 to +2200 mV at ambient temperature. Recrystallized TEA perchlorate 0.1 M was used as the electrolyte at a scan rate 100 mV/s. All scans were recorded in degassed solvent and under current of moisture free argon over the solution surface. The thermal behavior of the title compounds was studied in nitrogen using the simultaneous TG/DTG-DTA technique, over the temperature range ambient-to-1000 °C, using a Setaram Model Setsys-1200 thermogravimetric analyzer. The samples, with a mass of about 12 mg were heated in platinum crucibles, at a heating rate 10 °C/min.

Computational details: the electronic structure and geometries of the complexes studied were computed within the density functional theory (DFT) using gradient corrected functionals, at the Becke3LYP computational level [16,17]. The effective core potential (ECP) approximation of Hav and Wadt was used [18–20]. For Co atom, the electrons described by the ECP were those of 1s, 2s and 2p shells. The basis set used was of valence double- $\zeta$  quality [21]. Full geometry optimizations were carried out without symmetry constraints. A frequency calculation after each geometry optimization ensured that the calculated structures are real minima or transition states in the potential energy surface of the molecules and allowed the calculation of the zero point energy. In calculating the interaction energies between molecular fragments in the complexes, we accounted for the basis set superposition error (BSSE) by recalculating the monomer energies using the full dimer basis at the optimized geometry of the dimer using the counterpoise method [22,23]. Time-dependent density functional theory (TD-DFT) calculations were performed employing the same functional and basis set for the analysis of the excitation energies for both compounds. Solvent (methanol) effects were computed by using the integral equation formulation-polarized continuum model IEF-PCM [24,25]. All the calculations were performed using the GAUSSIAN-03W ver. 6.0 package [26].

## 2.3. Preparation of the addition compounds $[Co(2-OH-phenone)_2(\alpha-diimine)]$ (1–10)

All complexes have been prepared by the following general procedure: a solution of 1 mmol 2-hydroxy-phenone and CH<sub>3</sub>ONa (1 mmol) in MeOH (25 mL), was added drop-wise to a solution of



Scheme 1. Structural formulae of the 2-hydroxy-phenone ligands.

 $[Co(bipy)_2Br_2]$  or  $[Co(phen)_2Br_2]$  (0.5 mmol) in H<sub>2</sub>O (15 mL) at room temperature. The solution was stirred for 2 h and then turned darker and an orange-brownish solid was formed. The solid was filtered, washed with water and dried in vacuo (mean yield 60%). All compounds were prepared in inert, under argon, conditions and well degassed solutions have been used.

#### 2.3.1. Preparation of [Co(apo)<sub>2</sub>(bipy)]·Hapo (1)

A solution of 2-OH–acetophenone(Hapo) (136 mg, 1 mmol) and CH<sub>3</sub>ONa (54 mg, 1 mmol) in MeOH (25 mL), was added drop-wise to a solution of [Co(bipy)<sub>2</sub>Br<sub>2</sub>] (0.266 g, 0.5 mmol) in H<sub>2</sub>O (15 mL) at room temperature, under argon atmosphere. The solution was stirred for 2 h and then turned darker and an orange-brownish solid was formed. The solid was filtered, washed with water and dried under vacuo (0.20 g, 64% yield). The crystalline compound analyzed as *Anal.* Calc. for C<sub>34</sub>H<sub>30</sub>N<sub>2</sub>O<sub>6</sub>Co<sub>1</sub> (MW 621): C, 65.70; H, 4.83; N, 4.51; Co, 9.49. Found: C, 65.57; H, 4.80; N, 4.49; Co, 9.45%. The magnetic value ( $\mu_{eff}$  = 4.24  $\mu_B$ ) gives the bivalent character of the cobalt ion in octahedral environment. The conductivity in freshly prepared CH<sub>3</sub>CN solutions was found equal to 2.0 µS/cm, denoting the neutral character of the compound. IR spectrum (KBr): selected peaks in cm<sup>-1</sup>: 1666 s, 1604 vs 1574 vs 1360 s, 828 m, 729 s, 585 m, 514, 420, 260 m.

#### 2.3.2. Preparation of [Co(ppo)<sub>2</sub>(bipy)]·Hppo (2)

A solution of 2-OH–propiophenone(Hppo) (150 mg, 1 mmol) and CH<sub>3</sub>ONa (54 mg, 1 mmol) in MeOH (25 mL), was added dropwise to a solution of [Co(bipy)<sub>2</sub>Br<sub>2</sub>] (0.266 g, 0.5 mmol) in H<sub>2</sub>O (15 mL) at room temperature, under argon atmosphere. The solution was stirred for 2 h and then turned darker and an orangebrownish solid was formed. The solid was filtered, washed with water and dried under vacuo (0.19 g, 57% yield). The crystalline compound analyzed as *Anal.* Calc. for C<sub>37</sub>H<sub>36</sub>N<sub>2</sub>O<sub>6</sub>Co<sub>1</sub> (MW 663): C, 66.97; H, 5.43; N, 4.22; Co, 8.88. Found: C, 66.57; H, 5.41; N, 4.20; Co, 8.84%. Magnetic value ( $\mu_{eff}$  = 4.23  $\mu_{B}$ ), conductivity in CH<sub>3</sub>CN 5.2  $\mu$ S/cm. IR spectrum (KBr): selected peaks in cm<sup>-1</sup>: 1662 s, 1603 vs 1584 vs 1363 s, 855 m, 728 s, 562 m, 512, 418, 248 m.

#### 2.3.3. Preparation of [Co(bpo)<sub>2</sub>(bipy)].Hbpo (3)

A solution of 2-OH-benzophenone(Hbpo) (198 mg, 1 mmol) and CH<sub>3</sub>ONa (54 mg, 1 mmol) in MeOH (25 mL), was added drop-wise to a solution of [Co(bipy)<sub>2</sub>Br<sub>2</sub>] (0.266 g, 0.5 mmol) in H<sub>2</sub>O (15 mL) at room temperature, under argon atmosphere. The solution was stirred for 2 h and then turned darker and an orange-brownish solid was formed. The solid was filtered, washed with water and dried under vacuo (0.17 g, 42% yield). The crystalline compound analyzed as *Anal.* Calc. for C<sub>49</sub>H<sub>36</sub>N<sub>2</sub>O<sub>6</sub>Co<sub>1</sub> (MW 807): C, 72.80; H, 4.40; N, 3.40; Co, 7.30. Found: C, 72.50; H, 4.35; N, 3.38; Co, 7.28%. Magnetic value ( $\mu_{eff}$  = 4.16  $\mu_{B}$ ), conductivity in CH<sub>3</sub>CN 2.7  $\mu$ S/cm. IR spectrum (KBr): selected peaks in cm<sup>-1</sup>: 1662 s, 1602 vs 1585 vs 1360 s, 862 m, 737 s, 591 m, 516, 419, 250 m.

#### 2.3.4. Preparation of [Co(mpo)<sub>2</sub>(bipy)]·Hmpo (4)

A solution of 2-OH, 5-CH<sub>3</sub>-acetophenone(Hmpo) (150 mg, 1 mmol) and CH<sub>3</sub>ONa (54 mg, 1 mmol) in MeOH (25 mL), was added drop-wise to a solution of [Co(bipy)<sub>2</sub>Br<sub>2</sub>] (0.266 g, 0.5 mmol) in H<sub>2</sub>O (15 mL) at room temperature, under argon atmosphere. The solution was stirred for 2 h and then turned darker and an orange-brownish solid was formed. The solid was filtered, washed with water and dried under vacuo (0.22 g, 66% yield). The crystalline compound analyzed as *Anal.* Calc. for C<sub>37</sub>H<sub>36</sub>N<sub>2</sub>O<sub>6</sub>Co<sub>1</sub> (MW 663): C, 66.97; H, 5.43; N, 4.22; Co, 8.88. Found: C, 66.87; H, 5.42; N, 4.20; Co, 8.85%. Magnetic value ( $\mu_{eff}$  = 4.20  $\mu_B$ ), conductivity in CH<sub>3</sub>CN 3.7  $\mu$ S/cm. IR spectrum (KBr): selected peaks in cm<sup>-1</sup>:

1665 s, 1618 vs 1580 vs 1369 s, 856 m, 729 s, 570 m, 514, 437, 249 m.

#### 2.3.5. Preparation of [Co(opo)<sub>2</sub>(bipy)] Hopo (5)

A solution of 2-OH, 4-OCH<sub>3</sub>-benzophenone(Hopo) (228 mg, 1 mmol) and CH<sub>3</sub>ONa (54 mg, 1 mmol) in MeOH (25 mL), was added drop-wise to a solution of [Co(bipy)<sub>2</sub>Br<sub>2</sub>] (0.266 g, 0.5 mmol) in H<sub>2</sub>O (15 mL) at room temperature, under argon atmosphere. The solution was stirred for 2 h and then turned darker and an orange-brownish solid was formed. The solid was filtered, washed with water and dried under vacuo (0.20 g, 44% yield). The crystalline compound analyzed as *Anal.* Calc. for C<sub>52</sub>H<sub>42</sub>N<sub>2</sub>O<sub>9</sub>Co<sub>1</sub> (MW 897): C, 69.56; H, 4.68; N, 3.12; Co, 6.57. Found: C, 69.46; H, 4.62; N, 3.12; Co, 6.55%. Magnetic value ( $\mu_{eff}$  = 4.26  $\mu_B$ ), conductivity in CH<sub>3</sub>CN 2.2  $\mu$ S/cm. IR spectrum (KBr): selected peaks in cm<sup>-1</sup>: 1665 s, 1605 vs 1575 vs 1381 s, 832 m, 733 s, 572 m, 514, 413, 249 m.

#### 2.3.6. Preparation of $[Co(apo)_2(phen)]$ (6)

A solution of 2-OH–acetophenone(Hapo) (136 mg, 1 mmol) and CH<sub>3</sub>ONa (54 mg, 1 mmol) in MeOH (25 mL), was added drop-wise to a solution of [Co(phen)<sub>2</sub>Br<sub>2</sub>] (0.290 g, 0.5 mmol) in H<sub>2</sub>O (15 mL) at room temperature, under argon atmosphere. The solution was stirred for 2 h and then turned darker and an orange-brown solid was formed. The solid was filtered, washed with water and dried under vacuo (0.17 g, 66% yield). The crystalline compound analyzed as *Anal.* Calc. for C<sub>28</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>Co<sub>1</sub> (MW 509): C, 66.01; H, 4.32; N, 5.50; Co, 11.58. Found: C, 65.88; H, 4.30; N, 5.42; Co, 11.55%. Magnetic value ( $\mu_{eff}$  = 4.24  $\mu_B$ ), conductivity in CH<sub>3</sub>CN 2.0  $\mu$ S/cm. IR spectrum (KBr): selected peaks in cm<sup>-1</sup>: 1601 vs 1588 s, 1362 s, 848 m, 725 s, 575 m, 515, 430, 250 m.

#### 2.3.7. Preparation of [Co(ppo)<sub>2</sub>(phen)] (7)

A solution of 2-OH–propiophenone(Hppo) (150 mg, 1 mmol) and CH<sub>3</sub>ONa (54 mg, 1 mmol) in MeOH (25 mL), was added dropwise to a solution of [Co(phen)<sub>2</sub>Br<sub>2</sub>] (0.290 g, 0.5 mmol) in H<sub>2</sub>O (15 mL) at room temperature, under argon atmosphere. The solution was stirred for 2 h and then turned darker and an orangebrown solid was formed. The solid was filtered, washed with water and dried under vacuo (0.13 g, 48% yield). The crystalline compound analyzed as *Anal.* Calc. for C<sub>30</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>Co<sub>1</sub> (MW 537): C, 67.04; H, 4.84; N, 5.21; Co, 10.97. Found: C, 66.87; H, 4.80; N, 5.17; Co, 10.77%. Magnetic value ( $\mu_{eff}$  = 4.16  $\mu_B$ ), conductivity in CH<sub>3</sub>CN 3.2  $\mu$ S/cm. IR spectrum (KBr): selected peaks in cm<sup>-1</sup>: 1608 vs 1590 s, 1372 s, 852 m, 729 s, 567 m, 512, 420, 248 m.

#### 2.3.8. Preparation of [Co(bpo)<sub>2</sub>(phen)] (8)

A solution of 2-OH-benzophenone(Hbpo) (198 mg, 1 mmol) and CH<sub>3</sub>ONa (54 mg, 1 mmol) in MeOH (25 mL), was added drop-wise to a solution of [Co(phen)<sub>2</sub>Br<sub>2</sub>] (0.290 g, 0.5 mmol) in H<sub>2</sub>O (15 mL) at room temperature, under argon atmosphere. The solution was stirred for 2 h and then turned darker and an orange-brown solid was formed. The solid was filtered, washed with water and dried under vacuo (0.15 g, 47% yield). The crystalline compound analyzed as *Anal*. Calc. for C<sub>38</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub> Co<sub>1</sub> (633): C, 71.49; H, 4.00; N, 4.59; Co, 9.31. Found: C, 71.39; H, 4.00; N, 4.52; Co, 9.29%. Magnetic value ( $\mu_{eff}$  = 4.29  $\mu_{B}$ ), conductivity in CH<sub>3</sub>CN 3.0  $\mu$ S/cm. IR spectrum (KBr): selected peaks in cm<sup>-1</sup>: 1608 s, 1585 vs 1351 s, 843 m, 727 s, 591 m, 513, 421, 275 m.

#### 2.3.9. Preparation of $[Co(mpo)_2(phen)]$ (9)

A solution of 2-OH, 5-CH<sub>3</sub>-acetophenone(Hmpo) (150 mg, 1 mmol) and CH<sub>3</sub>ONa (54 mg, 1 mmol) in MeOH (25 mL), was added drop-wise to a solution of  $[Co(phen)_2Br_2]$  (0.290 g, 0.5 mmol) in H<sub>2</sub>O (15 mL) at room temperature, under argon atmosphere. The solution was stirred for 2 h and then turned darker and

an orange-brown solid was formed. The solid was filtered, washed with water and dried under vacuo (0.11 g, 41% yield). The crystalline compound analyzed as *Anal*. Calc. for C<sub>30</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>Co<sub>1</sub> (MW 537): C, 67.04; H, 4.84; N, 5.21; Co, 10.97. Found: C, 66.97; H, 4.78; N, 5.20; Co, 10.78%. Magnetic value ( $\mu_{eff}$  = 4.28  $\mu_B$ ), conductivity in CH<sub>3</sub>CN 3.6  $\mu$ S/cm. IR spectrum (KBr): selected peaks in cm<sup>-1</sup>: 1603 s, 1595 vs 1365 s, 848 m, 725 s, 570 m, 514, 420, 260 m.

#### 2.3.10. Preparation of [Co(opo)<sub>2</sub>(phen)] (10)

A solution of 2-OH, 4-OCH<sub>3</sub>-benzophenone(Hopo) (228 mg, 1 mmol) and CH<sub>3</sub>ONa (54 mg, 1 mmol) in MeOH (25 mL), was added drop-wise to a solution of  $[Co(phen)_2Br_2]$  (0.290 g, 0.5 mmol) in H<sub>2</sub>O (15 mL) at room temperature, under argon atmosphere. The solution was stirred for 2 h and then turned darker and an orange-brown solid was formed. The solid was filtered, washed with water and dried under vacuo (0.18 g, 52% yield). The crystal-line compound analyzed as *Anal*. Calc. for C<sub>40</sub>H<sub>30</sub>N<sub>2</sub>O<sub>6</sub>Co<sub>1</sub> (MW 693): C, 69.26; H, 4.33; N, 4.04; Co, 8.50 Found: C, 69.20; H, 4.00; N, 4.03; Co, 8.40%. Magnetic value ( $\mu_{eff}$  = 4.25  $\mu_{B}$ ), conductivity in CH<sub>3</sub>CN 2.0  $\mu$ S/cm. IR spectrum (KBr): selected peaks in cm<sup>-1</sup>: 1606vs, 1584 vs 1365 s, 847 m, 727 s, 570 m, 514, 417, 260 m.

#### 2.4. X-ray crystallography

All crystals were obtained from the reaction mixture after slow evaporation. They were air and beam stable during the data collection. Data for single crystals of both compounds  $[Co(bpo)_2(bi$ py)].Hbpo (**3**) and  $[Co(bpo)_2(phen)]$  (**8**) (Table 1) were collected with a Bruker SMART APEX CCD system with Mo K $\alpha$  radiation (*K* = 0.71073 Å) and corrected for absorption by semi-empirical methods (multiscan).

All data for both crystals were collected at ambient temperature. Both structures were solved using direct methods. Data refinement of (**3**) was finalized using SHELXS [27] while for (**8**) CRYS-TALS version 12.86 was used [28]. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were revealed to be at their expected positions and refined using riding constraints to their parent atoms. Final unit cells parameters were determined by least-squares method using all unique reflections. Further details concerning data collection, crystals analysis and structures refinement are summarized in Table 1.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

The reaction of the precursor compounds  $[Co(\alpha-diimine)_2Br_2]$ ( $\alpha$ -diimine = bipy or phen) with the anion of a 2-OH–phenone ligand (keto), under proper inert conditions, led to the formation of ten microcrystalline orange-brown products. They are stable in air, soluble in almost all the organic solvents, but insoluble in diethylether and water. Their elemental analyses and the absence of electrical conductivity in CH<sub>3</sub>CN solutions indicated neutral compounds, with the general formulae  $[Co^{II}(keto)_2(bipy)]$ ·Hketo or  $[Co^{II}(keto)_2(phen)]$ , while their magnetic moments at room temperature (mean  $\mu_{eff} = \sim 4.2 \ \mu_B)$  corroborate with high-spin octahedral coordination of the cobalt(II) ion, in accordance with other analogous complexes [29,30].

The coordination mode of the ligands in the new cobalt compounds was examined using spectroscopic methods (IR and electronic excitation spectra). The X-ray diffraction study of two of them provided evidence regarding the geometry around cobalt(II) ion and the configuration of the ligands.

#### 3.2. Description of the structures

In the unit cell of  $[Co(bpo)_2(bipy)]$ -Hbpo (**3**) four independent mononuclear neutral Co(II) complexes together with four protonated 2-OH-benzophenones (bpo) free ligands can be found. The unit cell of  $[Co(bpo)_2(phen)]$  (**8**) contains just four independent mononuclear neutral Co(II) complexes. In both cases the complexes are formatted as the metal ion is coordinated to two deprotonated 2-OH-benzophenones ligands and one nitrogenous base molecule. Figs. 1 and 2 present the clinographic projections of the complexes **3** and **8**, while selected distances and bond angles are given as supplementary material in Tables 1s and 2s, respectively.

All ligands act as chelates donors. 2-OH-benzophenones are coordinated through the phenolic deprotonated oxygen atoms, as well as through the carbonyl oxygen atoms, while the nitrogenous bases are coordinated through both pyridyl nitrogen atoms. These six coordinated atoms form a distorted octahedron around the metal ion. Nitrogen atoms from the nitrogenous base coordinated always have on their diagonal carbonyl oxygen atoms from the 2-OH-benzophenones ligands while the deprotonated phenolic oxygens lie on the remaining axis of the octahedron.

In both complex structures the most axial vector is the one passing through one nitrogen and its diagonal carbonyl oxygen atom but the vector passing through the deprotonated phenolic oxygen atoms is only about 1° up to 1.5° less axial than the previous described. We prefer to consider the deprotonated phenolic oxygens as lying on the axial positions of the coordination octahedron and the nitrogen atoms as well as the carbonyl oxygens on their diagonals forming the equatorial plane. These atoms forming the equatorial plane are in both cases placed at considerably longer distances from the metal ion than those lying on the axial positions and thus the coordination octahedron can be better described as tetragonally distorted. In the case of complex 8, the cobalt ion lies 0.146 Å lower the mean equatorial plane passing through N(1), N(2), O(2) and O(4) directed towards O(1), which is the closest from the two axially placed oxygen atoms. The mean amine plane is not coplanar with the mean equatorial plane forming with it an angle of 8.33°. On the contrary in the case of complex 8, the cobalt atom lies practically on the equatorial coordination plane formed from N(1P), N(10P), O(7A) and O(7B) with a deviation smaller than the error. The equatorial plane forms an angle of 7.22° with the mean bipy plane.

#### 3.3. Theoretical calculations

The molecular structure of complexes  $[Co(bpo)_2(bipy)]$  (3) and [Co(bpo)<sub>2</sub>(phen)] (8) in their quadruple ground state was optimized under no symmetry constrains at the density functional level of theory using the B3LYP. Fig. 3 shows the optimized structures, whereas selected calculated bond lengths and angles concerning the coordination sphere are given in Table 2. Mean experimental bond lengths, determined by X-ray structure analysis, are also given for comparison. In both cases the final optimized structure has essentially C2 symmetry with the two fold rotational axis passing through the Co atom and bisecting the N…N line. An overall agreement has been found between the calculated and experimental structure in each case with the largest deviation of bond distances being about 0.04 Å, while this of bond angles being about 6°. The two rings of benzophenone deviate from planarity by  $40^{\circ}$  in both **3** and **8**, with the experimental values being  $5^{\circ}$  and  $45^{\circ}$ , respectively. This discrepancy is possibly due to crystal packing effects.

The adiabatic interaction energy between molecular fragments within each complex was also calculated including the BSSE error. Thus, the interaction energy of the  $\alpha$ -diimine chelate ligands bipy

	3	8
Empirical formula	C49H36Co1N2O6	C <sub>38</sub> H <sub>26</sub> Co <sub>1</sub> N <sub>2</sub> O <sub>4</sub>
Formula weight	807.73	633.57
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	P 21/c	P 21/c
Unit cell dimensions		
a (Å)	9.5296(15)	11.6020(10)
b (Å)	22.753(4)	17.185(2)
c (Å)	20.084(3)	16.951(2)
β (°)	111.229(4)	92.180(10)°
Volume (Å <sup>3</sup> )	4059.3(11)	3377.3(6)
Ζ	4	4
Calculated density (Mg m <sup>-3</sup> )	1.322	1.25
Absorption coefficient (mm <sup>-1</sup> )	0.476	0.549
F(000)	1676	1308
Crystal size (mm)	0.64  imes 0.21  imes 0.14	0.21  imes 0.23  imes 0.23
θ Range for data collection (°)	1.41-28.16	1.77-25.27
Limiting indices	$-12 \leqslant h \leqslant 12, -25 \leqslant k \leqslant 29,$ $-22 \leqslant l \leqslant 26$	$-13 \leqslant h \leqslant 13, 0 \leqslant k \leqslant 20, 0 \leqslant l \leqslant 20$
Reflections (observed/ unique)	24627/9080	14178/6124
Completeness to $\theta$ max (%)	99.1	99.9
Refinement	full-matrix least-squares on $F^2$	full-matrix least-squares on $F^2$
Weighting scheme	w = 1/	$w = [w]^* [1 - (\Delta F/6^* \Delta F)^2]^2$
	$[\Sigma^2(F_o^2) + (0.055P)^2 + 1.5P]$ where $P = (F_o^2 + 2F_c^2)/3$	where $w^* = [P_0T'_0(x) + P_1T'_1(x) + \dots P_{n-1}T'_{n-1}(x)]^{-1}$ , and $P_i$ are the coefficients of a Chebychev series in $t_i(x)$ , and $x = F_{calc}^2/F_{calc}^2_{max}$
Data/restraints/ parameters	9080/1/526	4309/0/406
Goodness-of-fit on $F^2$	1.061	1.041
Final R indices	$R_1 = 0.0632, wR_2 = 0.1297$ [ $I > 2\sigma(I)$ ]	$R_1 = 0.0549, wR_2 = 0.0602$ [ $I > 1 \sigma(I)$ ]
Largest diff. peak and hole ( $e^{A^{-3}}$ )	0.46 and -0.26	-0.35 and -0.38

 Table 1

 Crystal data for compounds [Co(bpo)<sub>2</sub>(bipy)]-Hbpo (3) and [Co(bpo)<sub>2</sub>(phen)] (8).



**Fig. 1.** Clinographic projection of  $[Co(bpo)_2(bipy)]$ ·Hbpo (**3**) with 30% present probability of the ellipsoids. The free protonated ligand (Hbpo) present in the unit cell and the hydrogen atoms are omitted for clarity.



Fig. 2. Clinographic projection of  $[Co(bpo)_2(phen)]$  (8) with 30% present probability of the ellipsoids. Hydrogen atoms are omitted for clarity.



**Fig. 3.** Optimized geometries of complexes [Co(bpo)<sub>2</sub>(bipy)] (**3**) and [Co(bpo)<sub>2</sub> (phen)] (**8**). Hydrogens not shown for clarity.

#### Table 2

Selected bond distances (Å) and angles (deg) calculated for complexes  $[Co(bpo)_2(-bipy)]$  (3) and  $[Co(bpo)_2(phen)]$  (8)<sup>a</sup>.

	3	8
Co-N	2.129 (2.112) <sup>b</sup>	2.149 (2.143)
Co-O(1)	2.031 (2.025)	2.027 (2.058)
Co-O(2)	2.108 (2.100)	2.106 (2.071)
O(1)-Co-O(1)'	174.4 (173.4)	175.3 (171.9)
O(2)-Co-O(2)'	92.0 (85.9)	91.9 (86.8)
O(1)-Co-O(2)	92.6 (84.7)	93.2 (84.6)
N-Co-N'	77.0 (77.1)	78.0 (79.7)
N-Co-O(1)	96.0 (93.2)	94.8 (94.1)
N-Co-O(2)	168.9 (173.6)	169.6 (171.3)

<sup>a</sup> Numbering scheme as in Fig. 3.

<sup>b</sup> Mean experimental values in parentheses.

and phen with the metal fragment  $[Co(bpo)_2]$  is equal to 52.2 kcal/ mol and 49.7 kcal/mol, respectively. These values are in accordance with the shorter calculated and experimental Co-N bond distances found in complex **3** than in **8**. Moreover, the almost equal interaction energy of the metal fragments  $[Co(bipy)]^{2+}$  and  $[Co(phen)]^{2+}$ with the two 2-hydroxy-benzophenone,  $[(bpo)_2]^{2-}$ , calculated equal to 494.1 kcal/mol and 491.7 kcal/mol, respectively, account well for the almost identical calculated and experimental values for the Co–O bond distances. The BSSE error in all cases is about 2–3%.

In both complexes **3** and **8**, as well as in all the closely related substituted bis salicylaldehydo Co(II) complexes we have recently studied [13,14], the two salicylaldehydo ligands adopt a mutual orientation where the two carbonyl oxygen atoms adopt a cis orientation and are coplanar with the two nitrogen atoms of the  $\alpha$ diimine chelate ligand, consisting thus the [NNOO] basal plane of the octahedron, while the two phenolic oxygen atoms occupy the axial trans positions. To explore any other possible mutual orientation of the two salicylaldehydo ligands a series of calculations were carried out on a model representative complex namely [Co(salo)<sub>2</sub>(bipy)], **11** (salo = salicylaldehyde anion). Starting from appropriate initial structures full optimizations at the same level of theory gave three isomeric conformations as shown in Fig. 4. All isomers are minima in the potential energy hyper-surface of the molecule according to the hessian calculations. The conformation of the first isomer, 11a, is identical to that found in the experimental complexes with the calculated bond distances and angles being very close to the experimental ones. In the second, 11b, the [NNOO] basal plane of the octahedron includes one carbonyl and one phenolic oxygen atom, while in the third, **11c**, the basal plane includes the two phenolic oxygen atoms and the two carbonyl oxygen atoms occupy the axial trans positions. The calculated relative total energies of the isomers are 1.7, 0.0 and 0.8 kcal/mol, whereas those including the zero point energy are 1.8, 0.0 and 0.9 kcal/mol for **11a**, **11b** and **11c**, respectively. These energy differences are quite low, but the apparent conclusion is that isomer 11a, although corresponds to the experimentally found conformation, has the higher energy.

Taking into account that the preceding density functional calculations were done in gas phase, we performed a single point calculation for the optimized structures **11a**, **11b** and **11c** in the presence of the methanol solvent, used in the preparation of all the experimental complexes. Indeed, according to these calculations the isomer **11a** is greatly stabilized in the presence of solvent and seems to be the more stable structure, as the calculated relative total energies of the isomers are now 0.0, 0.9 and 1.2 kcal/ mol for **11a**, **11b** and **11c**, respectively.

#### 3.4. Electronic excitation (UV-Vis) study

The experimental UV–Vis spectra of the title compounds in acetonitrile solutions presented five dominant bands in the region 250–1100 nm, a representative one given for compound **8** in Fig. 5.

The assignment of the bands observed in the experimental UV-Vis spectra of the studied compounds and the evaluation of the properties of their excited states were done by means of TD-DFT calculations on the optimized structures of complexes 3 and 8. The calculated excitation energies are shown in Fig. 6, where representative density diagrams of the MOs participating in each electron transition with the higher CI coefficient are also depicted, in order to intuitively understand the absorption process. The computed electronic transitions are in good agreement with the experimental ones. The three calculated low energy excitations at 980-995 nm. 650-670 nm and 500-515 nm are of d-d character. The first two bands are clearly located in the experimental spectra of the complexes [3: 1010 ( $\varepsilon$  = 20), 640 ( $\varepsilon$  = 80); 8: 1020 ( $\varepsilon$  = 25), 660 ( $\varepsilon = 100$ )], while the third one is not shown, possibly masked due to the neighbouring position and the higher  $\varepsilon$  of the intra-ligand bands.

The two calculated excitations at 410–440 nm are of MLCT character as they arise from electronic transitions between low energy MOs, located at the d-orbitals of the metal and the highly delocalized unoccupied  $\pi$ -MOs of the bipy or phen ligand. These



**Fig. 4.** Optimized geometries of the three isomers, **11a**, **11b** and **11c**, of the complex [Co(salo)<sub>2</sub>(bipy)]. Hydrogens not shown for clarity.

bands are seen in the experimental spectra as a shoulder *at about* 420 nm.



Fig. 5. Electronic excitation (UV–Vis) spectrum of the complex  $[Co(bpo)_2(phen)]$  (8) in  $10^{-4}$  M CH<sub>3</sub>CN.

Finally, the calculated excitations at 310–320 nm and 280–290 nm arise from intra-ligand  $\pi$ – $\pi$  transitions within the bpo and bipy or phen ligands, respectively and are clearly seen in the spectra of the complexes [**3**: 283 ( $\varepsilon$  = 13000), 317 ( $\varepsilon$  = 11000); **8**: 284 ( $\varepsilon$  = 13000), 318 ( $\varepsilon$  = 10500)].

#### 3.5. Infrared spectra (IR)

In the spectra of the free 2-hydroxy-phenone ligands the intense bands stemming from the stretching and bending vibrational modes of the phenolic OH around 3200 cm<sup>-1</sup> and 1410 cm<sup>-1</sup>, respectively, disappear from the spectra of all complexes indicating the ligand deprotonation [31]. Also, the bands originating from the C-O stretching vibrations at 1245-1285 cm<sup>-1</sup> in the complexes exhibit positive shifts at 1342-1385 cm<sup>-1</sup> while their intensity is enhanced appreciably denoting coordination through the carbonyl oxygen of the phenone ligand. The band at  $\sim 1660 \text{ cm}^{-1}$  attributable to the carbonyl bond  $\ell$ (C=O) of the free ligand, upon coordination, in the complexes is shifted to lower frequencies at  $\sim 1605 \text{ cm}^{-1}$  thus denoting the bidentate mono- anionic character of the studied hydroxyl-phenone ligands (Table 3). In the case of the studied cobalt compounds with bipy, however, the presence of an extra intense band at  $\sim$ 1660 cm<sup>-1</sup> suggests the existence of a neutral non-coordinated ketone ligand.

The intense bands at  $1596 \text{ cm}^{-1}$ , attributable to the stretching vibration of C=N (aromatic bond) are present in all complexes. The band at  $750 \pm 20 \text{ cm}^{-1}$ , ascribed to the rocking vibrations of the pyridyl C-H bonds and the band at  $870 \pm 15 \text{ cm}^{-1}$ , attributable to the deformation vibrations of the pyridyl C-H bonds, disclosed the occurrence of the nitrogenous bases in the studied compounds. The medium to low intensity bands at about 590 and 512, 421,  $270 \text{ cm}^{-1}$  are attributed to the coordination bonds (Co-O and Co-N, respectively) according to the literature [32].

For better certainty the assignment of the Co–N and Co–O stretching frequencies was done with the aid of frequencies calculation on the optimized structures of complexes **3** and **8**, which gave the frequencies of the fundamental vibrations of the complexes. The calculated frequencies for the Co–N ( $281 \text{ cm}^{-1}$  for comp.3;  $290 \text{ cm}^{-1}$  for comp.8), and Co–O (579,603, aver.591.0 cm<sup>-1</sup>, for comp.3; 579,604, aver.591.5 cm<sup>-1</sup> for comp.8) stretching vibrations, as well as the corresponding normal modes for both complexes are those shown in Fig. 7. Thus the medium to low intensity experimental bands located at ~ $260 \text{ cm}^{-1}$  and ~ $590 \text{ cm}^{-1}$  for all complexes should be assigned to these Co–N and Co–O vibrations, respectively.



Fig. 6. Excitation energies, oscillator strengths and single-electron transition with the higher CI coefficient in the TD-DFT calculations for the MLCT band of [Co(bpo)<sub>2</sub>(bipy)] (3) and [Co(bpo)<sub>2</sub>(phen)] (8) complexes.

## Table 3 Characteristic frequencies in the IR spectra of the cobalt compounds [Co(keto)<sub>2</sub>(bipy)]-Hketo and [Co(keto)<sub>2</sub>(phen)].

α/α	Complex	v(C==0)	v(C=N)	v(C-O)	v(=C-H) (py)	v(Co-O)	v(Co-N)
1	[Co(apo) <sub>2</sub> (bipy)]·Hapo	1666s,1604vs	1574vs	1360s	828m,729s	585m	514,420m,260
2	[Co(ppo) <sub>2</sub> (bipy)]·Hppo	1662s,1603vs	1584vs	1363s	855m,728s	562m	512,418m,248
3	[Co(bpo) <sub>2</sub> (bipy)]·Hbpo	1662s,1602vs	1585vs	1360s	862m,737s	591m	516m,419m,250
4	[Co(mpo) <sub>2</sub> (bipy)]·Hmpo	1665s,1618vs	1580vs	1369s	856m,729s	570m	514,437m,249
5	[Co(opo) <sub>2</sub> (bipy)]·Hopo	1665s,1605vs	1574vs	1381s	832s,733s	572m	514,413m,249
6	[Co(apo) <sub>2</sub> (phen)]	1601vs	1588vs	1362s	848s,725s	575m	515,430m,250
7	[Co(ppo) <sub>2</sub> (phen)]	1608vs	1590s	1372s	852s,729s	567m	512,420m,248
8	[Co(bpo) <sub>2</sub> (phen)]	1608vs	1585vs	1351s	843s,727s	591m	513,421m, 275
9	[Co(mpo) <sub>2</sub> (phen)]	1603vs	1595vs	1365s	848s,725s	570m	514,420m,260
10	[Co(opo) <sub>2</sub> (phen)]	1606vs	1584vs	1365s	847s,727s	570m	514,417m,260

vs = Very strong, s = strong, m = medium, br = broad.



Fig. 7. Characteristic normal modes and calculated IR frequencies (cm<sup>-1</sup>) of the Co–N and Co–O stretching vibrations for [Co(bpo)<sub>2</sub>(bipy)] (3) and [Co(bpo)<sub>2</sub>(phen)] (8) complexes (experimental frequencies in italics).

#### 3.6. Cyclic voltametry (CV)

All the studied compounds exhibit similar behavior during the cyclic voltammetry experiments. The typical CV diagrams of compounds **3** and **8** are representatively depicted in Figs. 8 and 9, while the experimental data for the studied compounds are presented in Table 4. The CVs in the region –1950 mV to 2100 mV revealed five or six waves depending on the crystal ingredients of the studied compounds. The well separated reversible waves of the couples Co(I)–Co(II) around –830 mV (Wave I) and Co(II)–Co(III) around 550 mV (Wave II) were the first assigned. Both waves represent a one electron redox transformation as figured out by comparison with the wave observed from an equimolar amount of ferrocene under the same experimental conditions. These values were situated very close to them found from the CVs of similar compounds [13,14] and references therein].

The wave in the anodic region around 1510 mV (Wave III) and the cathodic wave around -1820 mV (Wave IV) are due to the oxidation and the reduction, respectively of the phenolic oxygen of



**Fig. 8.** Cyclic voltammetry diagram of  $[Co^{II}(2-hydroxy-benzophenone)_2(bipy)]$ 10<sup>-3</sup> M in CH<sub>3</sub>CN (0.1 M TEAP, C = 10<sup>-3</sup> M, scan rate 100 mV/s).



**Fig. 9.** Cyclic voltammetry diagram of  $[Co^{II}(2-hydroxy-benzophenone)_2(phen)]$  in CH<sub>3</sub>CN (0.1 M TEAP, C =  $10^{-3}$  M, scan rate 100 mV/s).

the ligand in the addition compounds. Both are two electron waves and this suggests that the ligands in the complex are equivalent as expected. These values are lower compared with the redox values of the same group in the free ligand. This fact could be expected upon coordination of the studied groups.

The peaks in the anodic region at around 1860 mV and at higher voltage values (Wave V) can be attributed to the oxidation of the nitrogen atoms of the nitrogenous base. The oxidation of the nitrogen atoms belonging to the bipyridine ligand seems to occur at higher voltage values compared with them of the phenanthroline ligand and appears around 1940 mV.

One more wave around 1730 mV (wave VI), present in the voltammograms of compounds (1) until (4), can be assigned to the oxidation of the phenolic oxygen of the free ligand, present in the unit cell of these compounds. It represents one electron oxidation, as expected and is found in the same region compared with the voltage values of the waves present in the cyclic voltamograms of the free ligands, when scanned alone under the same experimental conditions.

Table 4 Redox waves of the studied compounds in CH<sub>3</sub>CN. (0.1 M TEAP,  $C = 10^{-3}$  M, scan speed 100 mV/s).

Compounds	Wave I				Wave II		Wave III	Wave IV	Wave V	Wave VI
	Epa	$E_{\rm pc}$	$E_{1/2}$	$E_{\rm pa}$	Epc	E <sub>1/2</sub>	$E_{\rm pa}$	$E_{\rm pc}$	$E_{\rm pa}$	$E_{\rm pa}$
1	-0.86	-0.84	-0.83	0.57	0.55	0.53	1.52	-1.84	1.93	1.74
2	-0.85	-0.83	-0.81	0.56	0.54	0.52	1.54	-1.83	1.94	1.72
3	-0.87	-0.85	-0.83	0.55	0.53	0.51	1.50	-1.80	1.95	1.74
4	-0.85	-0.83	-0.81	0.56	0.55	0.54	1.51	-1.82	1.94	1.73
5	-0.86	-0.84	-0.82	0.56	0.54	0.52	1.52	-1.83	1.86	
6	-0.86	-0.85	-0.84	0.58	0.56	0.54	1.50	-1.81	1.87	
7	-0.85	-0.83	-0.82	0.57	0.56	0.54	1.52	-1.82	1.86	
8	-0.86	-0.84	-0.82	0.55	0.53	0.52	1.53	-1.83	1.85	

#### 3.7. Thermal studies

The thermal behavior for five of the title compounds (1, 3, 8, 9) and **10**) was studied in nitrogen atmosphere, over the temperature range ambient to 980 °C by using the simultaneous TG/DTG-DTA technique. The studied compounds can be separated in two groups, according to their thermal behavior. In the first group belong the compounds **1** [Co(apo)<sub>2</sub>(bipy)]·Hapo and **3** [Co(bpo)<sub>2</sub>(bipy)]·Hbpo and in the second one the compounds 8 [Co(bpo)<sub>2</sub>(phen)], 9 [Co(m $po_2(phen)$ ], and **10** [Co(opo)<sub>2</sub>(phen)]. The thermoanalytical curves (mass loss-TG, derivative mass loss-DTG, and heat flow-DTA) are given as supplementary material in Figs. 1s and 2s for the compounds 1 and 10 (one from each group), respectively. The studied compounds are unstable upon heating, decomposing in many successive endothermic stages. The decomposition for all the compounds is very complicated. It presents at least three different areas of mass loss and each area starts before the ending of the previous one. For this reason it is very difficult to correspond to different areas of mass loss in as specific way of decomposition of the compounds.

For both groups the main residue at 980 °C is metallic cobalt, proved by powder XRD measurements. In the first group the experimental mass loss at 980 °C is about 85–90%, while for the second one is only 60–63%. This means that the bulkier base phenanthroline, which is the component of the second group of the studied compounds, can not be pyrolized completely leaving an amount of un-combusted carbon in the solid residue, in comparison with the base bipyridine, which is the component of the first group of the studied compounds and is completely decomposed.

Using mass loss and derivative mass loss plots (TG/DTG) we can conclude that the first mass loss of the first group (Fig. 1s for compound 1) coincides with the mass loss of a phenol molecule (PhOH) derived from a ketone ligand (comp.1: DTG peak is ending at 200 °C, experimental mass loss 14.5% f. and theoretical 14.9% c.; comp.3: DTG peak is ending at 160 °C, experimental mass loss 11.0% f. and theoretical 11.5% c.). The second and sudden mass loss until 310 °C for compound 1 coincides with the mass loss of one acetaldehyde molecule (CH<sub>3</sub>CHO) plus two moieties (L–O), where L = the coordinated acetophenone ligand, apo (45% f. and 45.3% c.). For compound 3, the second mass loss at 310 °C coincides with the mass loss of a benzaldehyde molecule (PhCHO) plus one moiety (L–O), where L = the coordinated benzophenone ligand, bpo (35.0% f. and 35.5% c.).

Finally, the last stages happen in a wide temperature range (310–980 °C) with gradually mass loss, which coincides with the loss of the bipy molecule plus the remaining fragments of the ketone ligand, leading to the isolation of pure metallic cobalt at 980 °C for the compound 1(9.5% f. and 9.5% c.), while for the compound 3 to a mixture of metallic cobalt and a small amount of cobalt oxide (CoO) and carbon (15.0% f. and 9.3% c. for CoO or 7.3% c. for Co). The elimination of the bipy molecule happens up to 650 °C, evidence arised from the IR spectra of the intermediates at 310 and 650 °C.

The thermal decomposition of the second group is even more complicated. For the compounds **8**, 9 and 10 (Fig. 2s for compound **10**) the TG and DTG plots until 430 °C represent two multi-step decomposition stages with mass loss corresponding to the mass loss of one ketone ligand. This means that the cleavage of the coordination bonds Co–O happens together with the rupture of the bonds inside the ketone ligand. (mass loss for comp.8: 30.5% f. and 31.1% c.; for comp. 9: 27% f. and 27.7% c.; for comp. 10: 32.0% f. and 32.7% c.).

Taking into account the amount of the residue, as it was calculated by TG measurements, we can conclude that the decomposition was not completed until the temperature 980 °C leading to a solid mixture of CoO, Co and a large amount of carbon ( $\sim$ 30%).

#### 4. Conclusions

Ten novel octahedral compounds  $[Co(ketone)_2Y]$  where ketone is the anion of 2-hydroxy-phenones and Y = the neutral  $\alpha$ -diimines (bipy or phen), were synthesized and characterized.

The theoretical DFT investigation with GAUSSIAN-03 for the prediction of the electronic and vibrational spectra, gave good correlation with the experimental values.

X-ray study of the compounds **3** and **8** verified the existence of mononuclear octahedral Co(II) compounds with similar geometries around the metal ion. The cyclic voltammetry study in CH<sub>3</sub>CN gave all the expected waves for the redox processes of the metal Co(II) and the studied ligands.

The compounds are stable at ambient temperature, but unstable upon heating decomposing in several stages, giving at 980 °C in nitrogen atmosphere a solid product consisting of carbonaceous metallic cobalt.

#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2010.11.010.

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