



## First cobalt complexes with methyl pyruvate semi/thiosemicarbazone – Synthesis, physicochemical and structural characterization

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**Abstract:** In the reaction of acetone solutions of  $\text{CoX}_2 \cdot n\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) with methyl pyruvate semi/thiosemicarbazone (Hmps, Hmpt) the first Co(II) complexes with these ligands, *i.e.*,  $[\text{Co}(\text{Hmps})(\text{H}_2\text{O})\text{X}_2]$  ( $\text{X} = \text{Cl}$  (**1**),  $\text{Br}$  (**2**)),  $[\text{Co}(\text{Hmpt})_2][\text{CoCl}_4] \cdot 2\text{H}_2\text{O}$  (**3**) and  $[\text{Co}(\text{Hmpt})_2]\text{Br}_2 \cdot \text{Me}_2\text{CO}$  (**4**) were obtained. Complexes **1** and **2** represent the first examples of metal complexes of Hmps. All the obtained compounds were characterized by elemental analysis, conductometry, magnetic measurements, and IR spectra, and for complexes **2–4**, single crystal X-ray diffraction analysis was also performed. The effective magnetic moments were close to the upper limit ( $5 \mu_{\text{B}}$ ) for complexes **1** and **2**, and close to the lower limit ( $4.4 \mu_{\text{B}}$ ) for complexes **3** and **4**, and as such are characteristic for high-spin Co(II) complexes. Structural analysis showed that both ligands coordinate in a neutral form in a tridentate manner, *via* the ester oxygen, imine nitrogen and the oxygen atom of the ureido (Hmps), or the sulfur atom of the thioureido group (Hmpt). The central metal atoms are situated in a deformed octahedral coordination environment. Complex **2** has *cis*-Br configuration, while complexes **3** and **4** have *mer*-configuration.

**Keywords:** cobalt complexes; hydrazones; single crystal X-ray analysis.

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## INTRODUCTION

Semicarbazones (SCs) and thiosemicarbazones (TSCs),  $R_1R_2C=N-NH-C(=X)-NH_2$ ;  $X = O$  (SCs),  $X = S$  (TSCs)), represent a very versatile group of hydrazone-type organic compounds. Considering that these compounds are condensation derivatives of semi/thiosemicarbazide and carbonyl compounds, and the large number and diversity of the latter, the extensive number of their hydrazones is also not surprising.

Due to relatively easy complexation with both d- and p-metals,<sup>1–3</sup> and due to the wide spectrum of their biological activities,<sup>4–8</sup> these compounds and their metal complexes are in the focus of the research of not only coordination chemists and analytics,<sup>9</sup> but also of pharmacologists. Thus, not only original scientific papers but also reviews in this area are expectedly numerous, as cited above.

Regarding coordination mode, the mutual characteristic for these ligands is that, besides the azomethine nitrogen atom, the oxygen/sulfur atom of the semi/thiosemicarbazide residue is coordinated and five-membered a metallocycle is formed. The denticity of these ligands vary in the range from two to six, but complexes with tridentate derivatives are, obviously, the most numerous. Among the latter, semi/thiosemicarbazones of keto-acids stand out, with special emphasis on the pyruvic acid semi/thiosemicarbazone ( $H_2ps$  and  $H_2pt$ , respectively). The examination of their coordination chemistry was started back in 1970 by Ablov *et al.*,<sup>10–12</sup> but later this field became interesting for many other researchers.<sup>13–26</sup> The number of  $H_2pt$  complexes is far greater than the number of complexes with  $H_2ps$ , which is the consequence of the better coordination properties of the thiosemicarbazone ligand. For example, the survey of the Cambridge Structural Database (CSD)<sup>27</sup> showed that there are only 3 determined crystal structures of  $H_2ps$  metal complexes, while there are 14 structures of metal complexes with  $H_2pt$ . The results showed that in complexes both ligands coordinate to the metal ion through the carboxylate oxygen, azomethine nitrogen and oxygen/sulfur atom of the ureido/thioureido residue.

Unlike those with  $H_2pt$ , complexes with methyl pyruvate thiosemicarbazone ( $Hmpt$ ), one of the titled ligands, are not very numerous. This could be explained by: *i*) the not so good coordinating properties of  $Hmpt$  unlike  $H_2pt$  and *ii*) the ease of ester group hydrolysis in  $Hmpt$  and the formation of complexes with  $H_2pt$ . For these reasons, the syntheses should be performed using anhydrous salts and solvents.

The first  $Hmpt$  complexes were synthesized by Belicchi-Ferrari *et al.*<sup>28</sup> Namely, in the reaction of tetrameric  $[Cu(PPh_3)Cl]_4$  and  $Hmpt$  in warm toluene, these authors isolated two Cu(I) complexes, *i.e.*, trigonal  $[Cu(Hmpt)_2Cl]$  (CSD refcode: SOJVES) and tetrahedral  $[Cu(PPh_3)_2(Hmpt)Cl]$  (CSD refcode: SOJVIW) in which this, potentially tridentate ONS ligand coordinates as monodentate, *via* the sulfur atom. They also described the reaction of anhydrous  $ZnCl_2$  with  $Hmpt$

in MeOH, in which microcrystalline  $[\text{Zn}(\text{mpt})\text{Cl}]$  was formed. In this complex, the monoanionic ligand (with the deprotonated thioureido fragment) is coordinated in a tridentate mode (ONS).<sup>23</sup> In addition to the afore mentioned, tetrahedral complexes of Cu(I) with methyl pyruvate  $\text{N}^1$ -ethyl/phenylthiosemicarbazone of the formula  $[\text{Cu}(\text{PPh}_3)_2(\text{Et}/\text{Ph}\text{-Hmpt})]\text{NO}_3$  are reported in the literature (CSD refcodes: FOSTAJ, FOSTEN and FOSTOX).<sup>29</sup> In these complexes, both ligands are bidentate (NS).

There are many examples of reactions in which Hmpt hydrolyzes, but one of the representatives is the reaction of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and the ligand in absolute EtOH, in which, besides hydrolysis, transesterification of the ligand occurs, resulting in  $\text{H}_2\text{pt}$  and Hept complexes (Hept = ethyl pyruvate thiosemicarbazone) of the formulas  $[\text{Cu}(\text{Hpt})\text{Cl}]$  (KAGFED) and  $[\text{Cu}(\text{ept})\text{Cl}]$  (CSD refcode: KAGFAZ).<sup>18</sup> In these complexes, the tridentate (ONS) coordination mode of both ligands was found.

Recently, another interesting transformation of this ligand was reported.<sup>30</sup> Namely, in the reaction of  $[\text{Cu}(\text{PPh}_3)_2\text{CH}_3\text{COO}]$  and Hmpt in warm MeOH from the acyclic Hmpt, six-membered heterocycle 2-thio-6-azathymine[6-methyl-3-thioxo-1,2,4-triazin-5-(2H, 4H)-one] (HL) was formed. In the obtained Cu(I) complex of the formula  $[\text{Cu}(\text{PPh}_3)_2(\text{HL})\text{L}] \cdot \text{H}_2\text{O}$  (CSD refcode: BUYBON), one molecule of the ligand is coordinated in monoanionic form, while the other one is neutral, but both of them are coordinated through the sulfur atom. It should be mentioned that isolation of free HL upon heating an aqueous solution of Hmpt has already been reported.<sup>31</sup>

Except for the mentioned Cu(I) and Zn(II) complexes, to the best of the authors' knowledge, there are no other metal complexes with Hmpt, nor reactions of methyl pyruvate semicarbazone (Hmps) with metal ions in general. Therefore, the herein described syntheses of Co(II) complexes with these ligands (Fig. 1) resulted in the first metal complexes with Hmps, as well as the first complexes of Co(II) with Hmpt.

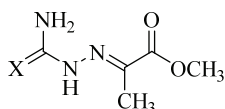


Fig. 1. Structural formula of Hmps (X = O) and Hmpt (X = S).

## EXPERIMENTAL

### Reagents

All chemicals used were commercially available products of analytical reagent grade, with the exception of  $\text{CoBr}_2 \cdot 2\text{H}_2\text{O}$  and the ligands.  $\text{CoBr}_2 \cdot 2\text{H}_2\text{O}$  was obtained by heating of commercially available  $\text{CoBr}_2 \cdot n\text{H}_2\text{O}$  at 100 °C, while Hmps and Hmpt ligands are synthesized according to the procedures described in the literature.<sup>32,18</sup>

### Synthesis of the complexes

$[Co(Hmps)(H_2O)Cl_2]^*$  (**1**).  $Me_2CO$  (5 mL) was poured over a mixture of  $CoCl_2 \cdot 6H_2O$  (95 mg, 0.40 mmol) and Hmps (32 mg, 0.20 mmol), and slightly heated. The resulting dark blue solution was left at room temperature to evaporate to a small volume. The obtained blue–purple microcrystals were filtered and washed with  $Me_2CO$ . Yield: 52 mg (85 %).

$[Co(Hmps)(H_2O)Br_2]$  (**2**).  $Me_2CO$  (10 mL) was poured over a mixture of  $CoBr_2 \cdot 2H_2O$  (100 mg, 0.400 mmol) and Hmps (64 mg, 0.40 mmol) and dissolved at room temperature. The resulting dark blue solution was slowly evaporated to a small volume. The obtained blue–purple single crystals were filtered and washed with  $Me_2CO$ . Yield: 90 mg (57 %).

$[Co(Hmpt)_2][CoCl_4] \cdot 2H_2O$  (**3**). A solution of Hmpt (40 mg, 0.20 mmol) in  $Me_2CO$  (5 mL) was added to the solution of  $CoCl_2 \cdot 6H_2O$  (50 mg, 0.20 mmol) in  $Me_2CO$  (5 mL), at room temperature. The obtained long hexagonal plate-like green single crystals were filtered and washed with  $Me_2CO$ . Yield: 50 mg (83 %).

$[Co(Hmpt)_2]Br_2 \cdot Me_2CO$  (**4**). A mixture of  $CoBr_2 \cdot nH_2O$  (50 mg) and Hmpt (80 mg, 0.40 mmol) was dissolved in  $Me_2CO$  (10 mL). The resulting green solution was left at room temperature to evaporate to a small volume. The obtained red single crystals were filtered and washed with  $Me_2CO$ . Yield: 68 mg (55 %).

### Analytical methods

Air-dried compounds were used for all analytical procedures. Elemental analyses (C, H, N and S) of the compounds were realized by standard micro-methods. Molar conductivity measurements of freshly prepared MeOH solutions ( $c = 1.0 \text{ mmol dm}^{-3}$ ) were performed on a Jenway 4010 conductivity meter. IR spectra were recorded on a Nicolet Nexus 670 (Thermo Scientific) FTIR spectrophotometer, in the range of  $400\text{--}4000 \text{ cm}^{-1}$ , using the KBr pellet technique. Magnetic susceptibility measurements were conducted at room temperature on an MSB-MKI (Sherwood Scientific Ltd.) magnetic susceptibility balance.

### Crystal structure determination

Diffraction experiments were performed on a Gemini S diffractometer (Oxford Diffraction) equipped with a sealed X-ray tube ( $MoK\alpha$ ,  $\lambda = 0.71073 \text{ \AA}$ ) and a Sapphire CCD detector. CrysAlisPRO<sup>33</sup> was used for instrument control and data processing (reflections integration and data reduction). Structures were solved by SHELXT<sup>34</sup> and refined by using the full-matrix least-squares method implemented in SHELXL.<sup>35</sup> SHELXLE<sup>36</sup> was used as a graphical user interface for the refinement procedures. Crystallographic and refinement details are listed in Table S-I of the Supplementary material to this paper.

The crystal structure of **3** contains voids occupied by disordered water molecules. Introduction of the solvent disorder model was attempted, but such an approach did not lead to a satisfactory result. Thus, the solvent contribution to the calculated structure factors was calculated by the Platon Squeeze tool,<sup>37</sup> and the structure was subsequently refined incorporating this contribution by using the ABIN instruction in SHELXL. The amount of unresolved water molecules was assessed by the number of electrons found in the solvent accessible voids. The four voids detected in the unit cell (expanded to  $P1$  space group) contain eight water molecules in total, corresponding to two water molecules per one formula unit of complex **3**. This result is in accordance with the results of elemental analysis.

\* Coordination formulas of **2–4** are determined by single crystal XRD (*vide infra*), while the formula of **1** was assumed based on similarities (color, IR spectra,  $\mu_{\text{eff}}$ ) with **2**.

The structures were validated internally using Platon<sup>38</sup> and externally with the help of the CSD.<sup>27,39,40</sup> Calculation of polyhedral deformation indices was performed by Vesta.<sup>41</sup> Hirshfeld surface analysis<sup>42</sup> was performed with CrystalExplorer.<sup>43</sup>

## RESULTS AND DISCUSSION

### *Syntheses and characterization*

All the complexes were obtained in the reactions of acetone solutions of cobalt(II)-halogenides and the ligands at room temperature, with the exception of the complex  $[\text{Co}(\text{Hmps})(\text{H}_2\text{O})\text{Cl}_2]$  (**1**), which was obtained upon mild heating. Regardless of the molar ratio of the reactants ( $\text{CoX}_2$  and ligands), the mono(ligand) complexes of the general formula  $[\text{Co}(\text{Hmps})(\text{H}_2\text{O})\text{X}_2]$  ( $\text{X} = \text{Cl}$  (**1**),  $\text{Br}$ (**2**)) were obtained with Hmps, while bis(ligand) complexes of the formula  $[\text{Co}(\text{Hmpt})_2][\text{CoCl}_4] \cdot 2\text{H}_2\text{O}$  (**3**) and  $[\text{Co}(\text{Hmpt})_2]\text{Br}_2 \cdot \text{Me}_2\text{CO}$  (**4**) were formed in the reactions with Hmpt. In the reaction of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and Hmpt the tendency to form complexes with  $[\text{CoCl}_4]^{2-}$  as counter ion was so pronounced that this complex was obtained not only when the molar ratio was 1:1, but also 2:1 and 1:2, which is the possible consequence of better complexing properties of Hmpt in comparison with Hmps, as well as stabilization of crystal lattice made of voluminous  $[\text{Co}(\text{Hmpt})_2]^{2+}$  and large (and  $\text{Me}_2\text{CO}$  stable)  $[\text{CoCl}_4]^{2-}$ . On the other hand, in the reaction of  $\text{CoX}_2$  with Hmps, the attempts to obtain the bis(ligand) complexes were unsuccessful (molar ratio  $\text{Co}:\text{Hmps}$  1:2), as the crystals of mono(ligand) complex formed and the excess of the ligand precipitated.

It is worth noting that the investigation of the reaction of  $\text{CoX}_2 \cdot n\text{H}_2\text{O}$  with Hmpt gave results that are in contradiction to the results obtained by Belicchi-Ferrari *et al.*<sup>31</sup> Namely, in the reaction of a MeOH solution of Hmpt and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , at room temperature, the ligand undergoes hydrolysis, thus the Co(III) complex with  $\text{H}_2\text{pt}$ , *i.e.*,  $[\text{Co}(\text{Hpt})(\text{pt})]$  was formed. These differences are undoubtedly the consequence of the nature of the solvent.

Complexes **1–4** are air-stable at room temperature, well soluble in MeOH, poorly soluble in EtOH, almost insoluble in  $\text{Me}_2\text{CO}$ , and degradable in water. The values of molar conductivities of MeOH solutions of the Hmps complexes **1** ( $140 \text{ S cm}^2 \text{ mol}^{-1}$ ) and **2** ( $170 \text{ S cm}^2 \text{ mol}^{-1}$ ), which are neutral in the solid state, were between the upper limit for 1:1 ( $80\text{--}115 \text{ S cm}^2 \text{ mol}^{-1}$ ) and lower limit for 1:2 ( $160\text{--}220 \text{ S cm}^2 \text{ mol}^{-1}$ ) types of electrolytes.<sup>44</sup> This implicates the high degree of substitution of the coordinated  $\text{Cl}^-$  and  $\text{Br}^-$  ions with the solvent molecules. Molar conductivities of MeOH solutions of Hmpt complexes **3** and **4** have values characteristic for 1:2 type of electrolyte, with the value for **4** ( $180 \text{ S cm}^2 \text{ mol}^{-1}$ ) near the lower, and for **3** ( $222 \text{ S cm}^2 \text{ mol}^{-1}$ ), which contains two ions, near the upper limit of the range characteristic for this type of electrolyte. The high value of the molar conductivity for **3** is the result of  $[\text{CoCl}_4]^{2-}$  instability in MeOH solution, with a dark-red color of the solution (the solution of **4** has the

same color), obtained from the green crystals, being an indicator for its decomposition in MeOH solution.

All the obtained complexes had values of effective magnetic moments ( $\mu_{\text{eff}}$ ) in the range 4.3–5.2  $\mu_{\text{B}}$ , which is typical for high spin Co(II) complexes ( $d^7$  system).<sup>45</sup> Thereby, the values of  $\mu_{\text{eff}}$  for Hmps complexes (**1** and **2**) were near the upper limit (5  $\mu_{\text{B}}$ ), while those for Hmpt complexes (**3** and **4**) were near the lower limit (4.4  $\mu_{\text{B}}$ ) of the mentioned range, thus these values are higher in comparison with the pure spin values for three unpaired electrons ( $\mu_{\text{s}} = 3.89 \mu_{\text{B}}$ ). Significantly higher values of  $\mu_{\text{eff}}$  of Hmps complexes **1** and **2** implicate the maximal contribution of orbital angular momentum to the resulting  $\mu_{\text{eff}}$ . This could be explained by the generally weak ligand field in these complexes, which consist of one  $\text{O}_2\text{N}$  ligand and three monodentate ligands (two halide and one aqua ligand), with the monodentate ligands having weak ligand field and being unable to extinguish the orbital component of the magnetic moment. Unlike these, the Hmpt complex cation  $[\text{Co}(\text{Hmpt})_2]^{2+}$  contains the two tridentate ONS molecules of Hmpt, which are clearly more effective in “quenching” the orbital component of the magnetic moment. The value of  $\mu_{\text{eff}}$  for **3** (4.41  $\mu_{\text{B}}$ ) is practically identical to the mean (4.47  $\mu_{\text{B}}$ ) of the values for octahedral complex **4** (4.36  $\mu_{\text{B}}$ ) and tetrahedral  $[\text{CoCl}_4]^{2-}$  (4.59  $\mu_{\text{B}}$ ).<sup>45</sup>

Single crystal X-ray analysis (*vide infra*) revealed that both ligands are coordinated in the expected tridentate manner, *via* the ester oxygen atom, imine nitrogen atom and oxygen/sulfur atom of the ureido/thioureido fragment. By comparative IR spectral analysis, the following could be concluded. In the IR spectrum of Hmps in the high-energy region (above 3100  $\text{cm}^{-1}$ ) two sharp bands of high intensity are present at 3502 and 3369  $\text{cm}^{-1}$ , as well as a weak band at 3195  $\text{cm}^{-1}$ , which originate from  $\nu_{\text{as}}/\nu_{\text{s}}(\text{NH}_2)$  and  $\nu(\text{NH})$  vibrations, respectively. Unlike this, in the spectra of the Hmps complexes **1** and **2**, which are almost identical, four bands (3410, 3306, 3230 and 3125  $\text{cm}^{-1}$ ) of different intensities are found in the mentioned area. These bands could be ascribed to both the  $\nu(\text{NH})$  vibrations of the ligand and the  $\nu(\text{OH})$  vibrations of the coordinated water molecules. A reliable assignation of these bands is difficult due to the presence of numerous intermolecular H-bonds, as was found for **2**:  $\text{NH}_2/\text{NH}\cdots\text{Br}$ ,  $\text{NH}_2\cdots\text{O}=\text{C}$ ,  $\text{H}_2\text{O}\cdots\text{Br}$ ,  $\text{H}_2\text{O}\cdots\text{OMe}$  (*vide infra*).

Unlike the spectrum of the anhydrous Hmps ligand, which in the region above 3100  $\text{cm}^{-1}$  contains only three bands, the spectrum of  $\text{Hmpt}\cdot 0.5\text{H}_2\text{O}$  contains an additional band, due to the  $\nu(\text{OH})$  vibrations of the water molecule. The presence of H-bonds between all H-donors and H-acceptors renders the assignment of this band difficult. In the spectrum of the Hmps ligand, two very strong bands at 1715 and 1700  $\text{cm}^{-1}$  are notable. These could be ascribed to  $\nu(\text{C}=\text{O})$  vibrations of COOMe- and CONH<sub>2</sub>-groups, respectively.<sup>46</sup> On the contrary, the spectrum of the Hmpt ligand in this region contains only one band of very high



intensity at  $1724\text{ cm}^{-1}$ , which corresponds to  $\nu(\text{C}=\text{O})$  vibration of the  $\text{COOMe}$ -group. In the spectra of the Hmps complexes, these bands are shifted towards lower wavenumbers by 30 and  $65\text{ cm}^{-1}$ , respectively, due to the coordination of the ester oxygen atom. Similarly, in the spectra of the Hmpt ligand and its complexes, a negative shift by  $50\text{ cm}^{-1}$  was found. As a consequence of the coordination of the azomethine nitrogen,  $\nu(\text{C}=\text{N})$  bands, which are found in the spectra of the ligands at 1608 (Hmps), and 1630 and  $1614\text{ cm}^{-1}$  (Hmpt),<sup>18</sup> are also shifted towards lower frequencies by  $25\text{ cm}^{-1}$  (Hmps complexes) and by  $8\text{ cm}^{-1}$  (Hmpt complex). Two  $\nu(\text{C}=\text{S})$  bands, located at 968 and  $863\text{ cm}^{-1}$  in the spectrum of free Hmpt,<sup>18</sup> are downshifted upon complexation by *ca.* 10 and  $7\text{ cm}^{-1}$ , respectively.

#### Crystal structure description

The crystal structure of **2** consists of neutral  $[\text{Co}(\text{Hmps})(\text{H}_2\text{O})\text{Br}_2]$  molecules, the structure of which is shown in Fig. 2, while pertinent structural data are listed in Table I. The central atom of the complex, Co(II), is situated in a deformed octahedral environment defined by the two *cis*-oriented bromide ions (one in the axial and one in the equatorial position), tridentately coordinated Hmps ligand in the equatorial coordination plane, and a water molecule in the axial position.

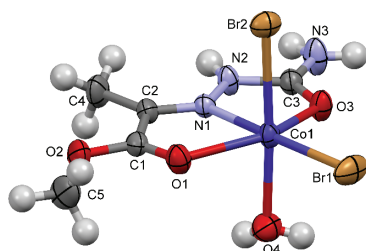


Fig. 2. Molecular structure of  $[\text{Co}(\text{Hmps})(\text{H}_2\text{O})\text{Br}_2]$  (**2**).

Hmps is coordinated in an  $\text{O}_2\text{N}$  tridentate mode, through ester oxygen atom O1, azomethine nitrogen atom N1 and carbonyl oxygen atom O3. The shortest metal–ligand bond is formed between Co(II) and azomethine nitrogen atom, while slightly longer bonds involve coordinated ligand oxygen atoms and water oxygen. Due to the larger size of bromide ion, two corresponding bond lengths are significantly longer, and the one comprised of bromide ion in the axial position is by *ca.*  $0.2\text{ \AA}$  longer compared to the one involving equatorial bromide. The largest angular deviations of the coordination polyhedron are related to the ligand bite-angles of *ca.*  $73^\circ$ , which makes that all equatorial *cis*-angles significantly deviate from the ideal values ( $90^\circ$ ). On the contrary, *cis*-angles comprised of the axial atoms only marginally depart from  $90^\circ$ .

Intraligand bond lengths could be compared with those in structurally characterized Cu(II) (CSD refcodes: CUYHAF<sup>25</sup> and QITNUE<sup>20</sup>) and Mn(II) (CSD refcode: LAPWUU<sup>26</sup>) complexes with a similar ligand – pyruvic acid semicarbazone,

TABLE I. Selected bond lengths (Å) found in **2** and relevant structures extracted from the CSD

Bond	Compound							
	<b>2</b>	CUYHAF <sup>25</sup>	QITNUE <sup>20</sup>	QITNUE <sup>20</sup>	LAPWUU <sup>26</sup>	LAPWUU <sup>26</sup>	EVOPEL <sup>47</sup>	EVOPEL <sup>47</sup>
Br1–Co1	2.4368(5)							
Br2–Co1	2.6085(5)							
Co1–O1	2.194(2)							
Co1–O3	2.144(2)							
Co1–O4	2.162(2)							
Co1–N1	2.115(2)							
O1–C1	1.279	1.280	1.270	1.266	1.271	1.337	1.337	1.337
O2–C1	1.23	1.230	1.232	1.235	1.224	1.206	1.214	1.214
C1–C2	1.524	1.519	1.519	1.519	1.522	1.503	1.505	1.505
N1–C2	1.298	1.261	1.266	1.27	1.269	1.295	1.291	1.291
N1–N2	1.347(3)	1.374	1.352	1.36	1.365	1.363	1.363	1.363
N2–C3	1.369(4)	1.346	1.362	1.374	1.365	1.386	1.386	1.386



as well as with ethyl pyruvate semicarbazone (CSD refcode: EVOPEL<sup>47</sup>). The comparisons are summarized in Table I. It could be seen that the coordinated oxygen atom of pyruvic acid semicarbazone forms shorter C–O bond when compared with the uncoordinated oxygen atom, which is contrary to the trend observed in complex **2**. However, this could be explained by the different chemical environment of these oxygen atoms in the two ligands. The other bond lengths are within the reasonable range, with the exception of O3–C3 bond, which in the structure CUYHAF is *ca.* 0.05 Å longer than those observed in the others.

Intramolecular contacts within the crystal structure **2** could be summarized in the fingerprint plots shown in Fig. 3.

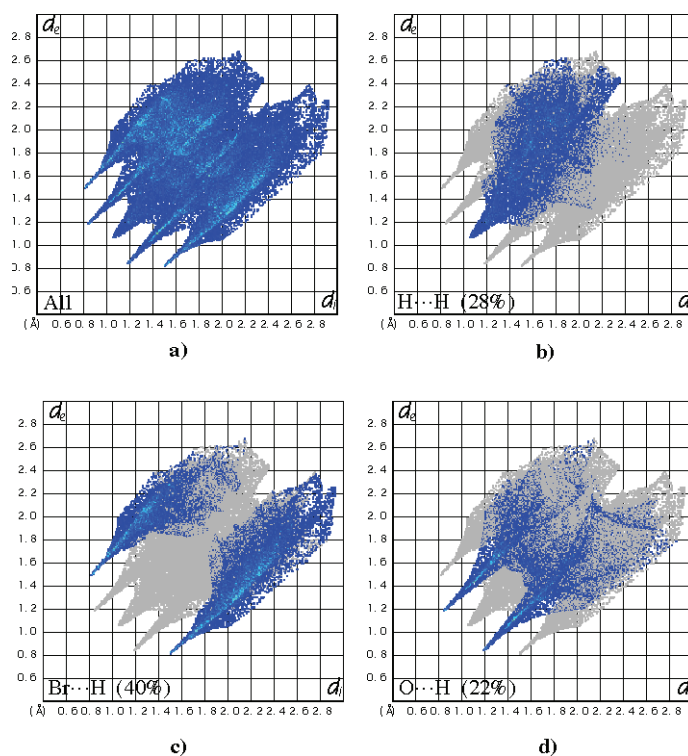


Fig. 3. The fingerprint plots for  $[\text{Co}(\text{Hmps})(\text{H}_2\text{O})\text{Br}_2]$  (**2**).

Decomposition of the Hirshfeld surface (HS) into element-specific contacts reveals that  $\text{Br}\cdots\text{H}$  contacts are dominant, comprising 39.6 % of the HS, and mediated through  $\text{O4-H4A}\cdots\text{Br1}^i$ ,  $\text{O4-H4A}\cdots\text{Br2}^i$ ,  $\text{N2-H2}\cdots\text{Br2}^{\text{iii}}$  and  $\text{N3-H3A}\cdots\text{Br2}^{\text{iii}}$  hydrogen bonds (symmetry codes are given in Table II). Apart from the omnipresent  $\text{H}\cdots\text{H}$  contacts (28 %), 21.6 % of the HS is mapped with  $\text{O}\cdots\text{H}$  contacts, expressed through  $\text{O4-H4B}\cdots\text{O2}^{\text{ii}}$  and  $\text{N3-H3B}\cdots\text{O3}^{\text{iv}}$ .

TABLE II. Hydrogen-bond geometry in complex **2**

$D-H\cdots A$	Distance, Å			Angle, °	Symmetry operation on $A$
	$H\cdots A$	$D\cdots A$	$D-H$		
$O4-H4A\cdots Br1^i$	2.75(3)	3.326(2)	0.78(2)	133(3)	$x, -y+3/2, z-1/2$
$O4-H4A\cdots Br2^i$	2.80(2)	3.462(2)	0.78(2)	144(4)	$x, -y+3/2, z-1/2$
$O4-H4B\cdots O2^{ii}$	2.60(2)	3.340(3)	0.78(2)	161(4)	$x-1, y, z$
$N2-H2\cdots Br2^{iii}$	2.47(2)	3.288(2)	0.85(2)	162(3)	$-x+1, -y+1$
$N3-H3A\cdots Br2^{iii}$	2.85(3)	3.576(3)	0.86(2)	143(3)	$-x+1, -y+1$
$N3-H3B\cdots O3^{iv}$	2.17(2)	2.967(3)	0.85(2)	156(3)	$-x, -y+1, -z+1$

Crystal structures of complexes **3** and **4** are comprised of the same complex cation  $[Co(Hmpt)_2]^{2+}$  and different counterions:  $[CoCl_4]^{2-}$  in **3** and  $Br^-$  in **4** (Fig. 4). The crystal structure of **3** contains voids occupied by disordered water molecules (not located), while  $Me_2CO$  molecules are present in **4** as a crystalline solvent. In both complexes, Co(II) is situated in a deformed octahedral environment, formed by two meridionally placed Hmpt ligands.

The ligand is coordinated as a tridentate NOS ligator, through the ester oxygen atom, azomethine nitrogen atom and sulfur atom. This coordination mode is expected for Hmpt, although it has not been observed so far in its complexes. Namely, the only two structurally characterized complexes with Hmpt are Cu(I) compounds (CSD refcodes: SOJVES and SOJVIW),<sup>28</sup> where the *S*-monodentate coordination mode of this ligand is observed.

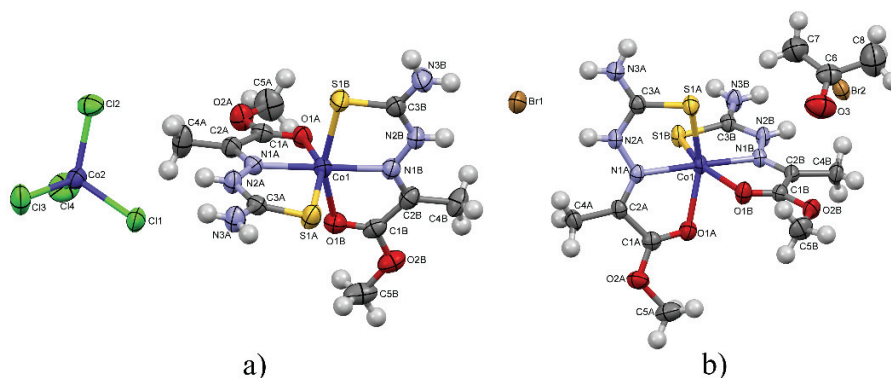


Fig. 4. Molecular structures of: a)  $[Co(Hmpt)_2][CoCl_4]\cdot 2H_2O$  (**3**); b)  $[Co(Hmpt)_2]Br_2\cdot Me_2CO$  (**4**). The positions of the water molecules were not determined by crystallographic analysis.

In addition, the number of crystal structures of complexes with structurally related, N-substituted methyl pyruvate thiosemicarbazones is scarce. There are three Cu(I) complexes (CSD refcodes: FOSTAJ, FOSTEN and FOSTOX),<sup>29</sup> where both sulfur atom and azomethine nitrogen atoms are involved in coordin-

ation, and one Zn(II) complex (CSD refcode: OGIMOG),<sup>48</sup> where NOS tridentate coordination is found, analogous to that observed in **3** and **4**.

Tridentate coordination of Hmpt results in two fused five-membered metallo-cycles. The thiosemicarbazide metallocycles are not planar, and their conformation and degree of pucker vary notably, not only between **3** and **4** but also between two meridionally coordinated ligands A and B in the cation of one compound. The Cremer & Pople puckering parameters<sup>49</sup> are summarized in Table S-II of the Supplementary material. It could be seen that Co1–S1A–C3A–N2A–N1A ring in **4** most severely deviate from planarity by having the highest value of puckering amplitude  $Q_2 = 0.3725(14)$  Å, while other rings have  $Q_2$  in the range 0.1230(18)–0.1979(16) Å.

It is not straightforward to describe the deformation of coordination polyhedra comprised of different atom types belonging to organic ligands, as distortion from ideal octahedron involves changes in both octahedral bond lengths and angles. To evaluate numerically the degree of polyhedral deformation, various indices of polyhedral distortion were calculated and are listed in Table S-III of the Supplementary material. Although two coordination octahedra have quite similar average bond lengths, other parameters indicate that the coordination octahedron in **4** is more deformed (larger distortion index, quadratic elongation and bond angle variance).

Intra-ligand bond lengths do not vary significantly among **3** and **4** and are in agreement with those found in the free form of the ligand Hmpt·0.5H<sub>2</sub>O (CSD refcode: KAGDUR).<sup>18</sup> Structural parameters of the complexes **3** and **4**, as well as the ligand Hmpt are summarized in Table S-IV, while the geometry of hydrogen bonding is given in Table S-V of the Supplementary material.

#### CONCLUSIONS

These obtained results show that tridentate O<sub>2</sub>N (Hmps) and ONS (Hmpt) ligands form different types of complexes with CoX<sub>2</sub>·*n*H<sub>2</sub>O (X = Cl, Br), under the same reaction conditions. Namely, with Hmps, mono(ligand) complexes [Co(Hmps)(H<sub>2</sub>O)X<sub>2</sub>] are formed from the acetone solution, irrespective of the metal salt to ligand molar ratio. On the contrary, the same reaction with Hmpt yielded in the formation of bis(ligand) dicationic complexes [Co(Hmpt)<sub>2</sub>] [CoCl<sub>4</sub>]·2H<sub>2</sub>O and [Co(Hmpt)<sub>2</sub>]Br<sub>2</sub>·Me<sub>2</sub>CO. Effective magnetic moments of Hmps complexes have values near the upper limit ( $5\mu_B$ ), while the values for Hmpt complexes are near the lower limit ( $4.4\mu_B$ ) of the range for high spin Co(II) complexes. Eventually, it was shown that in the reaction of Hmpt and CoX<sub>2</sub>·*n*H<sub>2</sub>O in acetone, unlike in methanol,<sup>31</sup> the hydrolysis Hmpt and formation of Co(III) complex with H<sub>2</sub>pt did not occur.

## SUPPLEMENTARY MATERIAL

Additional analytical and crystallographic data are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request. Crystallographic and refinement details are deposited in the Cambridge Crystallographic Data Centre under CCDC 1920679–1920681, obtainable free of charge from <https://www.ccdc.cam.ac.uk/structures/>.

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## ИЗВОД

ПРВИ КОМПЛЕКСИ КОБАЛТА СА СЕМИ/ТИОСЕМИКАРБАЗОНОМ  
МЕТИЛ-ПИРУВАТА – СИНТЕЗА, ФИЗИЧКО-ХЕМИЈСКА И  
СТРУКТУРНА КАРАКТЕРИЗАЦИЈА

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Реакцијом ацетонских раствора  $\text{CoX}_2 \cdot n\text{H}_2\text{O}$  ( $X = \text{Cl}, \text{Br}$ ) са семи/тиосемикарбазоном метил-пирувата ( $\text{Hmps}$ ,  $\text{Hmppt}$ ), добијени су први комплекси  $\text{Co(II)}$  са овим лигандима, формула  $[\text{Co}(\text{Hmps})(\text{H}_2\text{O})\text{X}_2]$  ( $X = \text{Cl}$  (**1**),  $\text{Br}$  (**2**)),  $[\text{Co}(\text{Hmppt})_2][\text{CoCl}_4]$  (**3**) и  $[\text{Co}(\text{Hmppt})_2]\text{Br}_2 \cdot \text{Me}_2\text{CO}$  (**4**), при чему су **1** и **2** први комплекси  $\text{Hmps}$  са металима уопште. Сва добијена једињења су окарактерисана елементалном анализом, кондуктометријом, магнетним мерењима и IR спектроскопијом. Комплекси **1** и **2** имају вредности  $\mu_{\text{eff}}$  које су блиске горњој граници ( $5\mu_{\text{B}}$ ), а комплекси **3** и **4** доњој граници  $\mu_{\text{eff}}$  вредности карактеристичних за високоспинске  $\text{Co(II)}$  комплексе ( $4,4\mu_{\text{B}}$ ). За комплексе **2–4** урађена је и рендгенска структурна анализа, која је показала да се оба лиганда координују као тридентати, у неутралној форми, преко естарског атома кисеоника, иминског атома азота и атома кисеоника уреидо фрагмента ( $\text{Hmps}$ ), односно атома сумпора тиоуреидо групе ( $\text{Hmppt}$ ). Координациони полиедар металног атома је деформисани октаедар. Комплекс **2** има *cis*-Br конфигурацију, а комплекси **3** и **4** *mer*-конфигурацију.

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## REFERENCES

1. S. Padhyé, G. B. Kauffman, *Coord. Chem. Rev.* **63** (1985) 127 ([https://dx.doi.org/10.1016/0010-8545\(85\)80022-9](https://dx.doi.org/10.1016/0010-8545(85)80022-9))
2. J. S. Casas, M. S. García-Tasende, J. Sordo, *Coord. Chem. Rev.* **209** (2000) 197 ([https://dx.doi.org/10.1016/S0010-8545\(00\)00363-5](https://dx.doi.org/10.1016/S0010-8545(00)00363-5))
3. T. S. Lobana, R. Sharma, G. Bawa, S. Khanna, *Coord. Chem. Rev.* **253** (2009) 977 (<https://dx.doi.org/10.1016/J.CCR.2008.07.004>)
4. H. Beraldo, D. Gambino, *Mini-Rev. Med. Chem.* **4** (2004) 31 (<https://dx.doi.org/10.2174/1389557043487484>)
5. C. B. Scarim, D. H. Jornada, M. G. M. Machado, C. M. R. Ferreira, J. L. dos Santos, M. C. Chung, *Eur. J. Med. Chem.* **162** (2019) 378 (<https://dx.doi.org/10.1016/j.ejmech.2018.11.013>)

6. B. Atasever, B. Ülküseven, T. Bal-Demirci, S. Erdem-Kuruca, Z. Solakoğlu, *Invest. New Drugs* **28** (2010) 421 (<https://dx.doi.org/10.1007/s10637-009-9272-2>)
7. D. X. West, S. B. Padhye, P. B. Sonawane, in *Complex Chem. Struct. Bond.*, Vol. 76, Springer, Berlin, 1991, pp. 1–50 ([https://dx.doi.org/10.1007/3-540-53499-7\\_1](https://dx.doi.org/10.1007/3-540-53499-7_1))
8. C. Santini, M. Pellei, V. Gandin, M. Porchia, F. Tisato, C. Marzano, *Chem. Rev.* **114** (2014) 815 (<https://dx.doi.org/10.1021/cr400135x>)
9. L. Feng, W. Shi, J. Ma, Y. Chen, F. Kui, Y. Hui, Z. Xie, *Sens. Actuators, B* **237** (2016) 563 (<https://dx.doi.org/10.1016/j.snb.2016.06.129>)
10. A. V. Ablov, N. I. Belichuk, L. F. Chapurina, *Zh. Neorg. Khim.* **15** (1970) 112
11. A. V. Ablov, N. V. Gerbelev, N. Y. Negryatse, M. D. Revenko, *Zh. Neorg. Khim.* **15** (1970) 123
12. A. V. Ablov, N. V. Gerbelev, *Zh. Neorg. Khim.* **15** (1970) 1854
13. G. L. Sawhney, J. S. Bajjal, S. Chandra, K. B. Pandeya, *Acta Chim. Acad. Sci. Hung.* **108** (1981) 325
14. M. D. Timken, S. R. Wilson, D. N. Hendrickson, *Inorg. Chem.* **24** (1985) 3450 (<https://dx.doi.org/10.1021/ic00215a030>)
15. I. F. Burshtein, N. V. Gerbelev, O. A. Bologna, A. Y. Kon, T. I. Malinovskii, *Met. Khim.* **3** (1990) 1162
16. I. F. Burshtein, N. V. Gerbelev, A. Y. Kon, O. A. Bologna, T. I. Malinovskii, *Zh. Strukt. Khim.* **28** (1987) 188
17. D. Kovala-Demertzi, J. Wiecek, J. C. Plakatouras, Z. Ciunik, *CrystEngComm* **10** (2008) 1291 (<https://dx.doi.org/10.1039/B809216H>)
18. M. Belicchi-Ferrari, G. G. Fava, P. Tarasconi, *J. Chem. Soc. Dalt. Trans.* (1989) 361 (<https://dx.doi.org/10.1039/DT9890000361>)
19. M. Belicchi-Ferrari, G. G. Fava, G. Pelosi, P. Tarasconi, *Polyhedron* **19** (2000) 1895 ([https://dx.doi.org/10.1016/S0277-5387\(00\)00454-X](https://dx.doi.org/10.1016/S0277-5387(00)00454-X))
20. Y. M. Chumakov, V. I. Tsapkov, E. Jeanneau, A. P. Gulea, *J. Struct. Chem.* **54** (2013) 577 (<https://dx.doi.org/10.1134/S0022476613030165>)
21. M. Belicchi-Ferrari, G. G. Fava, C. Pelizzi, G. Pelosi, P. Tarasconi, *Inorg. Chim. Acta* **269** (1998) 297 ([https://dx.doi.org/10.1016/S0020-1693\(97\)05795-2](https://dx.doi.org/10.1016/S0020-1693(97)05795-2))
22. R. Chikate, P. Sonawane, A. Kumbhar, S. Padhye, R. J. Butcher, *Inorg. Chim. Acta* **205** (1993) 59 ([https://dx.doi.org/10.1016/S0020-1693\(00\)87355-7](https://dx.doi.org/10.1016/S0020-1693(00)87355-7))
23. M. B. Ferrari, G. G. Fava, C. Pelizzi, P. Tarasconi, *J. Chem. Soc. Dalt. Trans.* (1992) 2153 (<https://dx.doi.org/10.1039/DT9920002153>)
24. J. Wiecek, V. Dokorou, Z. Ciunik, D. Kovala-Demertzi, *Polyhedron* **28** (2009) 3298 (<https://dx.doi.org/10.1016/j.poly.2009.05.012>)
25. G. G. Taran, N. M. Samus, I. D. Samus, V. E. Zavodnik, V. K. Bel'skii, V. G. Bodyu, *Izv. Akad. Nauk Mold. SSR. Ser. Fiz.-Tek. Mat. Nauk* **27** (1984) 2
26. W. Liufang, P. Zhouren, W. Xin, Y. Shuyan, L. Qinhuai, W. Qi, *Polyhedron* **12** (1993) 1505 ([https://dx.doi.org/https://doi.org/10.1016/S0277-5387\(00\)84590-8](https://dx.doi.org/https://doi.org/10.1016/S0277-5387(00)84590-8))
27. C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, *Acta Crystallogr., B* **72** (2016) 171. (<https://dx.doi.org/10.1107/S2052520616003954>).
28. M. Belicchi-Ferrari, G. G. Fava, M. Lanfranchi, C. Pelizzi, P. Tarasconi, *Inorg. Chim. Acta* **181** (1991) 253 ([https://dx.doi.org/10.1016/S0020-1693\(00\)86818-8](https://dx.doi.org/10.1016/S0020-1693(00)86818-8))
29. M. Belicchi-Ferrari, F. Bisceglie, E. Buluggiu, G. Pelosi, P. Tarasconi, *Polyhedron* **28** (2009) 1160 (<https://dx.doi.org/10.1016/j.poly.2009.01.013>)
30. M. Belicchi-Ferrari, F. Bisceglie, E. Buluggiu, G. Pelosi, P. Tarasconi, *Polyhedron* **29** (2010) 2134 (<https://dx.doi.org/10.1016/j.poly.2010.04.009>)

31. M. Belicchi-Ferrari, G. G. Fava, G. Pelosi, M. C. Rodriguez-Argüelles, P. Tarasconi, *J. Chem. Soc. Dalt. Trans.* (1995) 3035 (<https://dx.doi.org/10.1039/DT9950003035>)
32. S. Ianelli, G. Minardi, C. Pelizzi, G. Pelizzi, L. Reverberi, C. Solinas, P. Tarasconi, *J. Chem. Soc. Dalt. Trans.* (1991) 2113 (<https://dx.doi.org/10.1039/DT9910002113>)
33. Rigaku Oxford Diffraction, *CrysAlis<sup>Pro</sup> Software system*, Rigaku Corporation, Oxford, 2018
34. G. M. Sheldrick, *Acta Crystallogr., A* **71** (2015) 3 (<https://dx.doi.org/10.1107/S2053273314026370>)
35. G. M. Sheldrick, *Acta Crystallogr., C* **71** (2015) 3 (<https://dx.doi.org/10.1107/S2053229614024218>)
36. C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **44** (2011) 1281. (<https://dx.doi.org/10.1107/S0021889811043202>)
37. A. L. Spek, *Acta Crystallogr., C* **71** (2015) 9 (<https://dx.doi.org/10.1107/S2053229614024929>)
38. A. L. Spek, *Acta Crystallogr., D* **65** (2009) 148 (<https://dx.doi.org/10.1107/S090744490804362X>)
39. C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler, P. A. Wood, *J. Appl. Crystallogr.* **53** (2020) (<https://dx.doi.org/10.1107/S1600576719014092>)
40. I. J. Bruno, J. C. Cole, M. Kessler, J. Luo, W. D. Sam Motherwell, L. H. Purkis, B. R. Smith, R. Taylor, R. I. Cooper, S. E. Harris, A. Guy Orpen, *J. Chem. Inf. Comput. Sci.* **44** (2004) 2133. (<https://dx.doi.org/10.1021/CI049780B>)
41. K. Momma, F. Izumi, *J. Appl. Crystallogr.* **44** (2011) 1272 (<https://dx.doi.org/10.1107/S0021889811038970>)
42. M. A. Spackman, J. J. McKinnon, *CrystEngComm* **4** (2002) 378 (<https://dx.doi.org/10.1039/B203191B>)
43. M. J. Turner, J. J. McKinnon, S. K. Wolff, D. J. Grimwood, P. R. Spackman, D. Jayatilaka, M. A. Spackman, *CrystalExplorer17*, University of Western Australia, 2017
44. W. J. Geary, *Coord. Chem. Rev.* **7** (1971) 81 ([https://dx.doi.org/10.1016/S0010-8545\(00\)80009-0](https://dx.doi.org/10.1016/S0010-8545(00)80009-0))
45. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley-Interscience, New York, 1988, p. 731
46. G. Just, S. Kim, *Can. J. Chem.* **55** (1977) 427 (<https://dx.doi.org/10.1139/v77-063>)
47. C. C. Corrêa, J. E. J. C. Graúdo, L. F. C. de Oliveira, M. V. de Almeida, R. Diniz, *Acta Crystallogr., E* **67** (2011) o1882 (<https://dx.doi.org/10.1107/S160053681102530X>)
48. M. Belicchi-Ferrari, F. Bisceglie, G. Pelosi, P. Tarasconi, R. Albertini, S. Pinelli, *J. Inorg. Biochem.* **87** (2001) 137 ([https://dx.doi.org/10.1016/S0162-0134\(01\)00321-X](https://dx.doi.org/10.1016/S0162-0134(01)00321-X))
49. D. Cremer, J. A. Pople, *J. Am. Chem. Soc.* **97** (1975) 1354 (<https://dx.doi.org/10.1021/ja00839a011>).