

## High-spin binuclear Co(II) complexes with a pendant octaazamacrocyclic and carboxylates

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(Received 24 September 2007)

**Abstract:** Three new binuclear Co(II) mixed-ligand complexes with *N,N',N'',N'''*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc) and mono- or dicarboxylate ligands were prepared and some of their physical properties were determined. The general formulas:  $[\text{Co}_2(\text{HCOO})_2\text{tpmc}](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ ,  $[\text{Co}_2(\text{CH}_3\text{COO})_2\text{tpmc}](\text{ClO}_4)_2$  and  $[\text{Co}_2(\text{tpht})\text{tpmc}](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  (tphtH<sub>2</sub> = terephthalic acid) were proposed on the basis of elemental analyses (C,H,N) and molar conductivity. UV/Vis absorption and IR spectra, magnetic and CV measurements were used to study their geometries and properties. For the monocarboxylate complexes, an *exo* coordination of Co(II) with four nitrogens from tpmc and bis-bidentate bonded HCOO<sup>-</sup>/CH<sub>3</sub>COO<sup>-</sup> in the *trans* position is assumed. Tpmc adopts the chair conformation. For the dicarboxylate complex, it is supposed that a terephthalate dianion, as well as methylene chains from cyclam bridge two Co(II) atoms, while tpmc is in the boat conformation. The complexes were stable against chemical and electrochemical oxidation of Co(II) to Co(III). The data are compared with those for the previously published Cu(II) complexes containing the corresponding ligands and mutual similarities or differences were considered. Finally, some antibacterial activity of the complexes was found.

**Keywords:** Co(II) mixed-ligand complexes, *N,N',N'',N'''*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane, acetate, formate, terephthalate.

### INTRODUCTION

Magnetic interactions between paramagnetic ions in bi- or polynuclear complexes containing bridged ligands have been the subject of numerous investigations, in order to obtain information for the design of inorganic–organic materials and active sites in functional biological substances.<sup>1,2</sup> A large number of mono-, bi- and tetranuclear mixed-ligand complexes containing pendant macrocycle *N,N',N'',N'''*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc) (Fig. 1)<sup>3</sup> and one or two additional ligands of various type have hitherto been described. Most of them were Cu(II) and some of them Co(II) complexes.<sup>3–16</sup> In bi- and te-

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doi: 10.2298/JSC0712295V

tranuclear complexes, depending on the number, sort and size of the donor atoms of the additional ligands, the central metal atom and the reaction conditions, different modes of macrocyclic conformations were found (Scheme 1). The macrocyclic ligand adopts a boat conformation when the additional ligand is bonded in a bridged manner (Schemes 1a and 1d) and a chair conformation when two other ligands are independently bonded in the *trans* position (Schemes 1b and 1c). The latter situation was observed in the case of voluminous additional ligands or if an excess of this ligand was added during preparation. The majority of Co(II) complexes with tpmc were stable against oxidation by air oxygen and toward hydrolysis.<sup>4–6</sup> This unexpected property is ascribed to the hydrophobic environment formed by macrocycle around the metal ion. However, by chemical oxidation of  $\mu$ -carbonato or  $\mu$ - $\alpha$ -aminoisobutyrate binuclear Co(II)tpmc complexes using H<sub>2</sub>O<sub>2</sub>, mixed-valence Co(2)/Co(3) complexes were formed.<sup>5,6</sup>

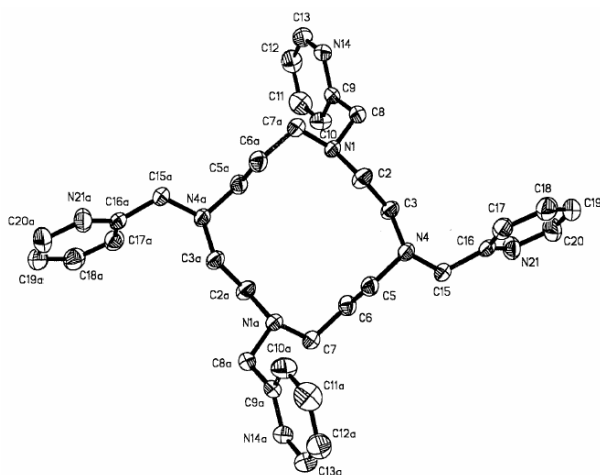
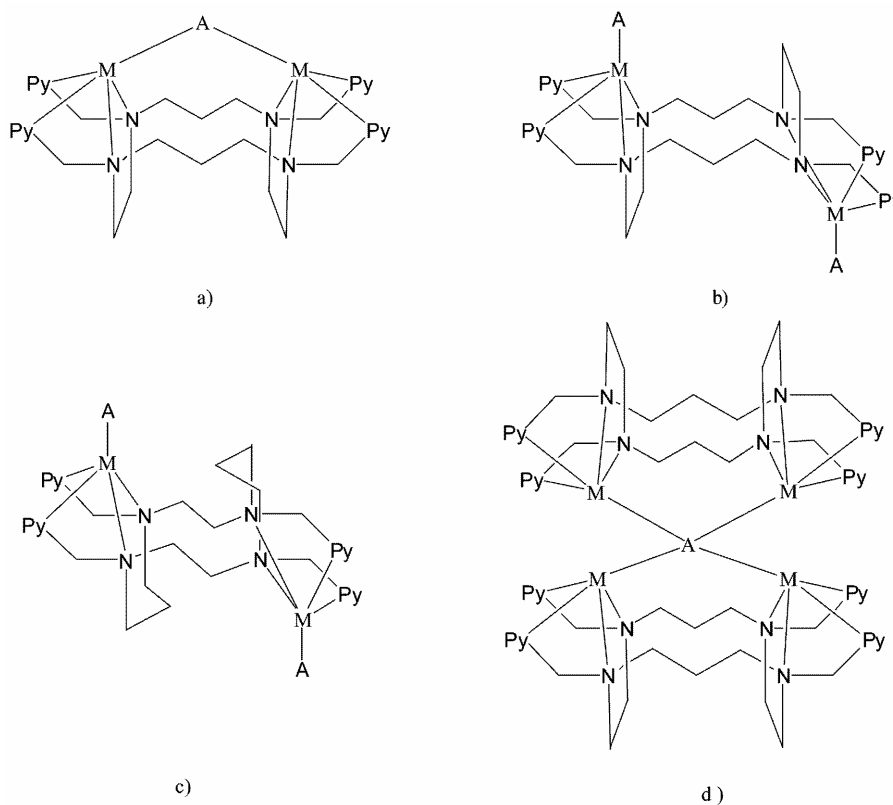


Fig. 1. Structure of the octaazamacrocyclic ligand tpmc.

A carboxylate group as a bridged ligand is present in several metalloenzymes. Due to the various coordination modes of mono- or polycarboxylato ligands and, consequently, the diversity of the possible geometries, the study of magnetic interactions in such complexes is very attractive. In a series of octahedral Co(II) complexes with the general formula  $[\text{Co}_2(\mu\text{-CH}_3\text{CO}_2)_2\text{Z}_2(\mu\text{-A})]^+$  ( $\text{Z} = \text{N}, \text{N}', \text{N}''$ -trimethyl-1,4,7-triazacyclononane;  $\text{A} = \text{OH}^-, \text{Cl}^-, \text{Br}^-$ ) weak antiferromagnetic interactions were found due to three factors: (1) smaller orbital contribution to the overall magnetic moment, (2) intermolecular antiferromagnetic and/or (3) intramolecular magnetic coupling between the Co(II) ions.<sup>17</sup>

In last two decades, complexes with mono- or dicarboxylato ligands, both aliphatic and aromatic, were intensively studied. In binuclear Co(II) complexes of the general formula  $[\text{Co}_2(\text{Y})\text{tpmc}]^{3+}$ ,  $\text{HY} = \text{glycine}, (\text{S})\text{-alanine}, (\text{S})\text{-}\alpha\text{-aminoisobutyric acid}, \alpha\text{-aminoisobutyric acid}, \beta\text{-aminoisobutyric acid}, \beta\text{-aminobutyric acid}$

and (*S*)-phenylalanine, the aminocarboxylate anions are coordinated through the  $\text{COO}^-$  group.<sup>5,6,14</sup> The results of electronic spectroscopy, as well as magnetic measurements, corresponded to high-spin, pentacoordinated Co(II) complexes with a square pyramidal geometry. The IR spectroscopic data suggested that in the case of all the complexes both oxygen atoms of the carboxylato groups participate in the coordination. The value  $\Delta\nu$  decrease in the row (*S*)-alanine > > glycine >  $\beta$ -aminobutyric acid >  $\alpha$ -aminoisobutyric acid >  $\beta$ -aminoisobutyric acid > (*S*)- $\alpha$ -aminobutyric acid, indicating the diminution of the bond strength in the same order. For the complex with (*S*)-phenylalanine, it was supposed that hexa-coordination and bis(bidentate)-bridged coordination occurred.



Scheme 1. Simplified coordination modes found in: a), b) c) dinuclear complexes, M = Co(II) and Cu(II); d) tetranuclear complexes, M = Cu(II) with aliphatic/aromatic carboxylates (A).

In addition, Co(II) or Cu(II) tpmc complexes with dicarboxylates (oxalate, malonate and the dianion of bicyclo[2.2.1]-hept-5-en-*endo*-2,3-*cis*-dicarboxylate) were also described.<sup>7-9</sup> According to X-ray analysis, in the  $[\text{Co}(\text{ox})\text{tpmc}](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$  complex, the geometry of 4N and 2O ligators around both Co(II) centres was distorted octahedral.<sup>8</sup> The oxalate dianion is bonded asymmetrically: two O atoms

from different carboxylic groups are coordinated to two different Co(II) ions; the third oxygen is simultaneously bonded to both Co ions and the last remained uncoordinated. The  $\nu(\text{C}=\text{O})$  band at  $1670\text{ cm}^{-1}$  observed in the IR spectrum of the complex confirmed that one O atom remained uncoordinated. The electronic spectrum is consistent with octahedral high-spin Co(II) complexes. The variation of the  $\mu_{\text{eff}}$  values from  $0.78\text{--}4.66\ \mu_{\text{B}}/\text{Co}$  in the temperature range  $4.2\text{--}292\text{ K}$  suggests the existence of weak antiferromagnetic interactions.

On the contrary, the absence of a free carbonyl group band in the IR spectrum of  $[\text{Co}_2(\text{mal})\text{tpmc}](\text{ClO}_4)_2$  (mal = the dianion of malonic acid) suggests that all O atoms of the carboxylate ligand are included in the coordination.<sup>9</sup> The UV/Vis spectrum of  $[\text{Co}_2(\mu\text{-L})\text{tpmc}](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$ <sup>7</sup> (L = the dianion of the above-mentioned bicyclic ligand) is typical for high-spin Co(II) complexes of low symmetry. Based on IR and UV/Vis spectroscopic data, it was concluded that in a series of bi- or tetranuclear Cu(II) tpmc complexes with mono- ( $\text{HCOO}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{C}_6\text{H}_5\text{COO}^-$ ) or dicarboxylato (hydrogenphthalate, isophthalate and terephthalate) bridged ligand, with the  $\text{CuN}_4\text{O}$  chromophore, all the carboxylate oxygen atoms participated in coordination.<sup>10–12</sup> Preliminary X-ray analysis of  $[\text{Cu}_4\text{ipht}(\text{tpmc})_2](\text{ClO}_4)_6$  (ipht = the isophthalate dianion) confirmed that the aromatic carboxylato ligand connected two  $[\text{Cu}_2(\text{tpmc})]^{2+}$  units, engaging both  $\text{COO}^-$  groups (Fig. 2).<sup>11</sup> The complex  $[\text{Cu}_2(\text{HCOO})\text{tpmc}][\text{Cu}_2(\text{CH}_3\text{COO})\text{tpmc}](\text{ClO}_4)_6 \cdot 6\text{H}_2\text{O}$  contained two different binuclear cations in the same crystal lattice.<sup>15</sup> Based on X-ray analysis,  $\mu\text{-O,O'}$  coordination of formate/acetate anions were found. In the complexes  $[\text{Co}_2(\text{baib})(\text{C}_6\text{H}_5\text{COO})_3]^+$  and  $[\text{Co}_2(\text{bhmp})(\text{C}_6\text{H}_5\text{COO})_2]^+$  (baib = 1,3-bis[(2-dimethylaminoethyl)iminomethyl]benzene, bhmp = 2,6-bis[bis(2-hydroxyethyl)aminomethyl]-4-methylphenol), containing the  $\mu$ -bonded  $\text{C}_6\text{H}_5\text{COO}^-$  ligand, weak antiferromagnetic interactions were observed.<sup>18,19</sup> In the complex  $[\text{Cu}_2(\text{tpht})(\text{bpy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  (bpy = 2,2'-bipyridine), strong antiferromagnetic interactions of an intermolecular nature are found.<sup>20</sup> A series of binuclear complexes of the general formula  $[\text{Co}_2(\text{tpht})\text{A}'_4](\text{ClO}_4)_2$ ;  $\text{A}' = \text{phen}$ , bpy and substituted bpy, with bridged terephthalate was also published.<sup>21</sup> In the coordination polymer  $[\{\text{Co}_3(\mu\text{-tpht})_2(\mu\text{-OH})_2(\text{phen})_2\}_n]$  (phen = phenanthroline), the trimer unit contains two carboxylate and two hydroxo bridges.<sup>22</sup> X-ray structural analysis confirmed that the geometry around Co(I) is square planar, while it is square pyramidal around Co(II) and Co(III). In the interval  $300\text{--}41\text{ K}$ , ferromagnetic, but in the range  $41\text{--}4\text{ K}$ , antiferromagnetic types of interactions were found.

Substituents on the phenyl group of aromatic dicarboxylato ligands could influence the intensity of the magnetic interactions in polynuclear complexes. For instance, in the series of the complexes  $[\text{Co}_2(\text{tcpht})(\text{A})_4]^{2+}$ , (tcpht = tetrachlorophthalate;  $\text{A} = \text{phen}$ , 5-nitro-phen or bpy), magnetic measurements were studied in the interval  $77\text{--}300\text{ K}$ .<sup>23</sup> Antiferromagnetic spin-interchanges were found between the Co(II) ions. It is considered that they could be a result of the influence

of the phthalate group and/or the chloro substituents on it. Namely, the four Cl atoms with their negative inductive effect caused a decrease of electronic density in the bridge and thus of the strength of the electron–electron interactions, lowering the energetic level of the bridged orbitals and thus increasing the difference in energy between the orbitals of the metal and the bridge. The final effect was delocalization of the metal orbitals towards the O atom from the bridge and a decrease of the antiferromagnetic interactions.

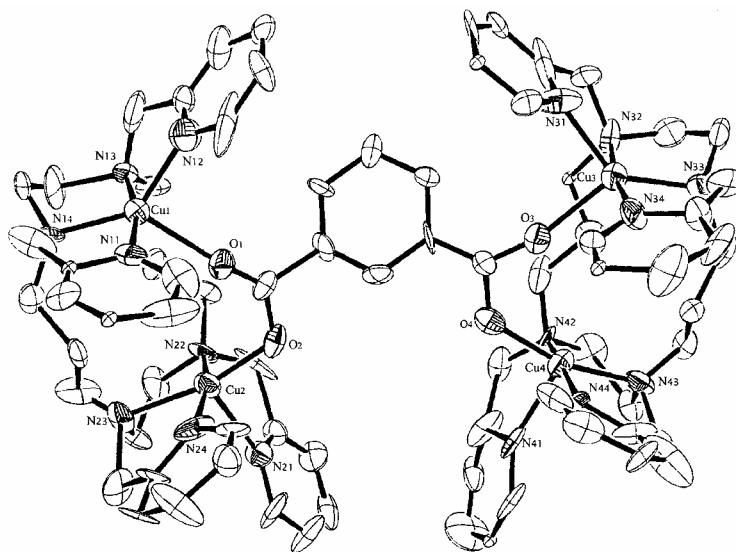


Fig. 2. Structure of the complex cation  $[\text{Cu}_4\text{ipht}(\text{tpmc})_2]^{6+}$ .

#### EXPERIMENTAL

##### Synthesis

The ligand *N,N',N'',N'''*-tetrakis-(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc) and  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  were prepared according to described procedures.<sup>3,24</sup> Piperidine terephthalate was isolated by the reaction of the total neutralization of terephthalic acid with piperidine.<sup>25</sup> This facilitates the solubility of the obtained salt and thus the coordination of terephthalate. The other chemicals used were commercial products of *p.a.* grade of purity and were used without further purification. CAUTION! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with extreme caution!

$[\text{Co}_2(\text{HCOO})_2\text{tpmc}](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  (**1**): To a solution of  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (50 mg ; 0.137 mmol) in 2.0 cm<sup>3</sup> of  $\text{CH}_3\text{OH}$ , a solution of  $\text{HCOONa}$  (7 mg ; 0.103 mmol) in 0.2 cm<sup>3</sup>  $\text{H}_2\text{O}$  and 2 drops of conc.  $\text{HCOOH}$  were added. The reaction mixture was stirred and refluxed for 1 h on a water bath ( $\approx 70^\circ\text{C}$ ), followed by the addition of a tpmc (38 mg; 0.067 mmol) suspension in 3 cm<sup>3</sup> of  $\text{CH}_3\text{OH}$ . The reaction was prolonged for a further 1.5 h and then the mixture was concentrated by heating at  $70^\circ\text{C}$  to about 1/2 of its initial volume, covered with parafilm and left at room temperature until crystals deposited. The deep purple microcrystals were separated by suction, washed properly with several portions of cold  $\text{CH}_3\text{OH}$  and dried in a desiccator above silica gel. Yield: 48 mg (70 %). Anal. Calcd. for  $\text{Co}_2\text{C}_{36}\text{H}_{54}\text{O}_{16}\text{N}_8\text{Cl}_2$ : C, 41.43; H, 5.22; N, 10.74. Found: C, 41.46; H, 4.89; N, 10.77.

$[Co_2(CH_3COO)_2tpmc](ClO_4)_2$  (**2**):  $Co(CH_3COO)_2 \cdot 4H_2O$  (34.5 mg; 0.112 mmol) was dissolved in 3.5 cm<sup>3</sup> of the mixture  $CH_3OH/H_2O$  (6:1; v/v) and a suspension of *tpmc* (38 mg; 0.067 mmol) in 3.0 cm<sup>3</sup> of  $CH_3OH$  was added. The purple reaction mixture was stirred at room temperature for 1 h. When 0.5 cm<sup>3</sup> of a saturated aqueous solution of  $NaClO_4$  was added, deep purple crystals appeared. The stirring was continued for the following 2 h. The further procedure was the same as for complex **1**. Yield: 52 mg (77 %). Anal. Calcd. for  $Co_2C_{38}H_{50}O_{12}N_8Cl_2$ : C, 45.66; H, 5.04; N, 11.20. Found: C, 45.41; H, 5.14; N, 10.91.

$[Co_2(tpht)tpmc](ClO_4)_2 \cdot 4H_2O$  (**3**): A suspension of *tpmc* (38 mg, 0.067 mmol) in 3.0 cm<sup>3</sup> of  $CH_3OH$  was mixed with a solution of  $Co(ClO_4)_2 \cdot 6H_2O$  (50 mg, 0.137 mmol) in 3.0 cm<sup>3</sup> of  $CH_3OH$ . The deep purple reaction mixture was stirred at room temperature for 1 h, and then a solution of piperidine terephthalate (34 mg, 0.105 mmol) in 4 cm<sup>3</sup> of  $CH_3OH$  was added and the stirring prolonged for the following 2 h. The further procedure was the same as for complexes **1** and **2**. Yield: 60 mg (79 %). Anal. Calcd. for  $Co_2C_{42}H_{56}O_{16}N_8Cl_2$ : C, 44.77; H, 5.10; N, 9.95. Found C, 45.02; H, 5.09; N, 9.87.

All three complexes were stable up to 250 °C (check with hot plate equipped with microscope). Some of the physical properties of the complexes are presented in Table I.

TABLE I. Values of molar electrical conductivity (type of electrolyte) in  $CH_3CN$  and solubility data of the complexes

Cmpd.	$\Lambda_M / S \text{ cm}^2 \text{ mol}^{-1}$ at 25 °C	Solubility
<b>1</b>	276 <sup>a</sup> (1:2)	$CH_3CN$ , DMF, $CH_3OH$ , $H_2O$
<b>2</b>	217 <sup>a</sup> (1:2)	$CH_3CN$ , $H_2O$ , sparingly in DMF, $CH_3OH$ , $C_2H_5OH$ , DMSO
<b>3</b>	–	$CH_3CN/H_2O$ (1:1, v/v), sparingly in DMF, $CH_3CN$ , DMSO, insoluble in $CH_3OH$ , $H_2O$

<sup>a</sup>Literature ranges: 120–160  $S \text{ mol}^{-1} \text{ cm}^2$  and 220–300  $S \text{ mol}^{-1} \text{ cm}^2$  for 1:1 and 1:2 type of electrolytes, respectively<sup>26</sup>

#### Methods and applied instruments

Elemental analysis (C, H, N) was performed by standard micromethods in the Centre for Instrumental Analysis of the Faculty of Chemistry, University of Belgrade.

The UV/Vis spectra of complexes ( $1 \times 10^{-3} \text{ mol dm}^{-3}$ ) **1** and **2** were recorded in  $CH_3CN$  and of complex **3** in a  $CH_3CN/H_2O$  (1:1, v/v) mixture using a GBC UV/Vis 911 A spectrophotometer.

The IR spectra (KBr disk technique) were recorded on Perkin–Elmer FTIR 31725X spectrophotometer in the range 400–4000  $\text{cm}^{-1}$ .

The molar conductivity of complexes **1** and **2** (see Table I) was determined in  $CH_3CN$  solution ( $1 \times 10^{-3} \text{ mol dm}^{-3}$ ) at  $25 \pm 2$  °C with a Hanna Instruments HI 8820N conductometer. Complex **3** was not sufficiently soluble in common solvents and hence its conductivity was not determined.

Magnetic measurements were performed at room temperature ( $25 \pm 2$  °C) on a magnetic balance, MSB-MKI, Sherwood Scientific Ltd., England. The data are corrected for diamagnetic susceptibilities using the Pascal's constants.<sup>28</sup>

#### Cyclic voltammetry (CV)

The electrochemical measurements were performed at room temperature ( $20 \pm 2$  °C) using a Metrohm 797 apparatus in a standard three-electrode cell: Pt as the auxiliary electrode, standard  $Ag/AgCl$  as the reference and a glassy carbon electrode as the working one. The concentration of the solutions was  $\approx 5 \times 10^{-4} \text{ mol dm}^{-3}$ . The measurements were performed on 30 cm<sup>3</sup> of the complex solution in  $CH_3CN$  (complexes **1** and **2**) and in a mixture  $CH_3CN-H_2O$  (1:1, v/v) (complex **3**). The scan rate was 50  $\text{mV s}^{-1}$ , in the potential interval from  $-1.0$  to  $1.0$  V. Oxygen was removed from the system by bubbling  $N_2$ .

### Biological activity

The biological activity of the simple Co(II) salt, solvent, ligands and the complexes was preliminary tested by the diffusion method through an agar plate. Nutrition, agar (powder) Tripton „Torlak”, was prepared by mixing agar (23.5 g) in water (100 cm<sup>3</sup>) and, after 15 min, careful heating up to boiling until the agar had completely dissolved. After sterilization for 15 min in an autoclave at 120 °C, the nutrition was poured into Petri plates and inoculated with microorganisms from a physiological solution. The paper disks (1 cm in diameter) were previously sterilized using a UV lamp. The complexes were tested against the following strains of microorganisms: *Bacillus subtilis*, *Escherichia coli* ATCC 25923, *Bacillus cereus*, *Pseudomonas aeruginosa* and *Aspergillus niger*. 60 µl (concentration of  $\approx 5 \times 10^{-4}$  mol dm<sup>-3</sup>) of the complex solution or one crystal of the complex (if it was sparingly soluble) were put on the paper discs. The Petri plates were left for 48 hours thermostated at 28 °C and then the diameters of the inhibition zone were measured if microbiological activity was detected.

### RESULTS AND DISCUSSION

The type and yields of the complexes described in this paper depended on the various factors: temperature, rate and the order of the added reactants, solvent, pH values on which mono-/dicarboxylic acid is neutralized and pH value of the reaction mixture. Co(II) perchlorate in the presence of tpmc always forms the very stable violet  $\mu$ -OH<sup>-</sup> binuclear complex [Co<sub>2</sub>(OH)tpmc](ClO<sub>4</sub>)<sub>3</sub> as a by-product. In a more basic medium, the formation of this product is favoured, while in more acidic medium the carboxylate ligand is protonated causing a decrease in its donor properties. However, the optimal conditions favoured the formation of the complexes **1** and **2** in good yield. In addition, aromatic carboxylic acids have a tendency to form polymeric Co(II) complexes, especially at elevated temperatures. Therefore, the synthesis with terephthalate was performed at room temperature.

The isolated complexes were microcrystalline compounds, of purple or dark purple colour. Their solubility in common solvents is given in Table I. The results of elemental analysis suggested binuclear complexes in all cases. The values of the molar conductivities for complexes **1** and **2** (Table I) corresponded to a 1:2 type of electrolyte.<sup>26</sup> The absorption maxima and intensities of peaks in the Vis spectra of the complexes **1–6** (Table II)<sup>27</sup> were similar and corresponded to d–d transitions in high-spin Co(II) complexes of low symmetry.<sup>28</sup> The  $\epsilon$  values for complex **2** containing CH<sub>3</sub>COO<sup>-</sup> are larger than those for the complex **1** containing HCOO<sup>-</sup> (Table II). This is in accordance with the enhanced asymmetry in complex **2**, due to the stronger steric repulsion between tpmc pyridyl groups and the CH<sub>3</sub> groups of the acetate, than with the H from the formate ions in complex **1**. CT bands in the UV spectra of all the complexes were in the range 240–280 nm ( $\epsilon = 6000$ – $7100$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>). Interpretation of the electronic spectra of Co(II) complexes is usually complicated and the magnetic measurements are additional criterions for the assumption of the coordination geometry, although the variety of the possible magnetic interactions could be problematic.<sup>29</sup>

The values of  $\mu_{\text{eff}}/\text{Co}$  at room temperature were in the range 4.57–5.08  $\mu_{\text{B}}$ , which confirmed the high-spin state of the cobalt(II) and weak magnetic interactions. Similar values were found earlier for some familiar complexes (Table II).

TABLE II. Vis spectral data and magnetic moment values of the synthesized and relevant described complexes

Complex	Maxima and shoulders ( <i>sh</i> )	$\mu_{\text{eff}}$ per Co, $\mu_{\text{B}}$ (25 °C)
	$\lambda_{\text{max}} / \text{nm}$ ( $\epsilon / \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ )	
[Co <sub>2</sub> (HCOO) <sub>2</sub> tpmc](ClO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O ( <b>1</b> )	448(56); 521(67); 552(63) <sup>b</sup>	4.57
[Co <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub> tpmc](ClO <sub>4</sub> ) <sub>2</sub> ( <b>2</b> )	480(60) <i>sh</i> ; 504(70) <i>sh</i> ; 527(73) <sup>b</sup>	5.01
[Co <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> COO) <sub>2</sub> tpmc](ClO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O <sup>a</sup> ( <b>6</b> )	479(66) <i>sh</i> ; 516(75) <sup>c</sup>	4.81
[Co <sub>2</sub> (pht)tpmc](ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O <sup>a</sup> ( <b>4</b> )	487(74) <i>sh</i> ; 523(86) <sup>c</sup>	4.74
[Co <sub>2</sub> (ipht)tpmc](ClO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O <sup>a</sup> ( <b>5</b> )	485(89) <i>sh</i> ; 508(94) <sup>c</sup>	5.01
[Co <sub>2</sub> (tpht)tpmc](ClO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O ( <b>3</b> )	485(100) <i>sh</i> ; 508(106) <sup>d</sup>	5.08

<sup>a</sup>Literature data<sup>27</sup>. Solvents used: <sup>b</sup>CH<sub>3</sub>CN; <sup>c</sup>DMF; <sup>d</sup>mixture CH<sub>3</sub>CN–H<sub>2</sub>O (1:1; v/v)

In the IR spectra of complexes **1–3**, some common characteristic bands were observed: at 3590–3220 cm<sup>-1</sup> broad and strong, arising from  $\nu(\text{O–H})$  of the crystal H<sub>2</sub>O molecules in the complexes; at  $\approx 1610$  cm<sup>-1</sup> strong, sharp, assigned to the valence skeletal vibrations of the pyridine ring; at  $\approx 1100$  cm<sup>-1</sup> broad, the strongest band, and at  $\approx 630$  cm<sup>-1</sup> medium, sharp, due to the  $\nu(\text{ClO}_4^-)$  and  $\delta(\text{ClO}_4^-)$  of uncoordinated ClO<sub>4</sub><sup>-</sup>, respectively.<sup>30</sup> The positions of the bands due to asymmetrical ( $\nu_a$ ) and symmetrical ( $\nu_s$ ) skeletal vibrations of carboxylic groups in the spectra of complexes and their corresponding alkaline salts are presented in Table III, together with the  $\Delta\nu$  values (equal to  $\nu_a - \nu_s$ ). Contrary to aliphatic  $\mu$ -aminocarboxylato Co(II)tpmc complexes,<sup>4,5</sup> for which the positions of  $\nu_a$  and  $\nu_s$  are shifted to lower frequencies upon coordination and, consequently, the  $\Delta\nu$  values in the spectra of the complexes are higher than those for the corresponding salts, for all complexes (**1–6**),  $\nu_s$  is shifted towards higher frequencies and considerably lower  $\Delta\nu$  values were observed. This is ascribed to coordination number 5 for the first type and 6 for the latter complexes. In the new complexes (**1–3**), the  $\Delta\nu$  values were lower than those of the related alkaline salts were. The shift of  $\nu_a(\text{OCO})$  towards lower and  $\nu_s(\text{OCO})$  towards higher frequencies compared with the corresponding alkaline salts could be the consequence of the participation of the COO<sup>-</sup> group in coordination through both oxygen atoms or due to the participation of the uncoordinated carboxylic O atom in hydrogen bond formation. In the complexes, hydrogen bond formation is slightly more difficult than in the alkaline salts, due to steric protection originating from the macrocyclic and carboxylate ligand. For complexes **1** and **3**, containing crystal H<sub>2</sub>O, there is an enhanced possibility for hydrogen bond formation. The results suggest that the mono-/dicarboxylato ligands are bonded as chelates, while in complexes **4–6** as chelates and bridges.<sup>27</sup> The  $\Delta\nu$  values of the complexes decrease with the strength of the Co(II)–O bonds, in the order:  $\mu$ -formate (121 cm<sup>-1</sup>) >  $\mu$ -benzoate (113 cm<sup>-1</sup>) >  $\mu$ -acetate (99 cm<sup>-1</sup>) or  $\mu$ -phthalate (120 cm<sup>-1</sup>) >  $\mu$ -isophthalate (113 cm<sup>-1</sup>) >  $\mu$ -terephthalate (106 cm<sup>-1</sup>), respectively. Moreover, the strength of this bond parallels the strength of the monocarboxylic acids (Table IV) in complexes **1–3**.



However, when aromatic dicarboxylates are coordinated, besides their pH values, the mutual interactions between carboxylic groups (inductive, resonance, steric effects and the chelate ring size), as well as the hard–soft relations<sup>29,31</sup> of the ligands and metallic centres have a large influence. Finally, the rest of the molecule also contributes to overall geometry and deviations of some bond distances. The methyl group in the hard base  $\text{CH}_3\text{COO}^-$  with its (+)-inductive effect makes it softer than  $\text{HCOO}^-$ . On a contrary, the phenyl group in  $\text{C}_6\text{H}_5\text{COO}^-$  has a weak (–)-inductive effect, but a positive resonance effect, being a harder base than acetate and softer than formate. In Co(II)/Cu(II)-tpmc complexes, the central atoms are chelate bonded with hard bases, N atoms from the pendant ligand, which increases their hardness. The Co(II)–O strength is also a result of a type of inductive effect, the position of the  $\text{COO}^-$  group at the aromatic ring and the mode of carboxylate bonding. The  $\text{COOH}$  group has a (–)- while  $\text{COO}^-$  a (+)-inductive effect. A coordinated  $\text{COO}^-$  group has a (–)-inductive effect which decreases dramatically with distance. Thus, when two coordinated  $\text{COO}^-$  are 1,2-positioned, the ligand is harder than in the case of 1,3- or 1,4-positioned ones, causing a stronger Co(II)–O bond. Some simplified carboxylate coordination modes are presented in Schemes 3b–3g. In addition, asymmetrical modes are possible, causing distortion of the octahedral and non-equal Co(II)–O bonds in the same molecule. This is obvious for complex **3**, the IR spectra of which distinguished themselves from those of the other complexes in exhibiting multiple  $\nu_a$  and  $\nu_s$   $\text{COO}^-$  bands.

TABLE III. Position of the bands of the asymmetric ( $\nu_a$ ), and symmetric ( $\nu_s$ ) stretching vibrations of the carboxylic group and values of  $\Delta\nu$  ( $\nu_a - \nu_s$ ) in the IR spectra of the alkaline salts of the carboxylic acids and the related complexes ( $s$  = strong;  $m$  = medium intensity)

Cmpd.	$\nu_a / \text{cm}^{-1}$	$\nu_s / \text{cm}^{-1}$	$\Delta\nu / \text{cm}^{-1}$
$\text{HCOONa}$	1567 $s$	1366 $m$	201
$[\text{Co}_2(\text{HCOO})_2\text{tpmc}](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ ( <b>1</b> )	1565 $s$	1445 $m$	120
$\text{CH}_3\text{COONa}$	1578 $s$	1414 $m$	164
$[\text{Co}_2(\text{CH}_3\text{COO})_2\text{tpmc}](\text{ClO}_4)_2$ ( <b>2</b> )	1549 $s$	1450 $m$	99
$\text{Na}_2\text{tpht}$	1561;	1400 $m$	161
$[\text{Co}_2(\text{tpht})\text{tpmc}](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ ( <b>3</b> )	1550 $s$ 1509 $s$ 1529 <sup>a</sup>	1444 $m$ 1403 $m$ 1424 <sup>a</sup>	  106
$\text{K}_2\text{pht}^b$	1563 $s$	1384 $m$	179
$[\text{Co}_2(\text{pht})\text{tpmc}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ ( <b>4</b> )	1544 $s$	1423 $m$	121
$\text{Na}_2\text{ipht}^b$	1564 $s$	1395 $m$	169
$[\text{Co}_2(\text{ipht})\text{tpmc}](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ ( <b>5</b> )	1538 $s$	1425 $m$	113
$\text{C}_6\text{H}_5\text{COONa}^b$	1580 $s$	1413 $m$	167
$[\text{Co}_2(\text{C}_6\text{H}_5\text{COO})_2\text{tpmc}](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ ( <b>6</b> )	1533 $s$	1420 $m$	113

<sup>a</sup>calculated as the average value of two bands; <sup>b</sup>data taken from the literature<sup>27</sup>

All three complexes are stable to oxidation in the open atmosphere, both in the solid state and in solution. This was confirmed by their time independent Vis spectra recorded after bubbling  $\text{O}_2$  through solutions of the complexes.

TABLE IV.  $pK_a$  values of the aliphatic and aromatic mono-/dicarboxylic acids

pK Values	Formic acid	Acetic acid	Benzoic acid	Phthalic acid	Isophthalic acid	Terephthalic acid
$pK_1$	3.75	4.75	4.19	2.91	2.30	3.45
$pK_2$	–	–	–	5.13	4.66	4.45

The electrochemical behaviour of complexes **1–3** was studied in the potential range from 1 to  $-1$  V (scan speed of  $50 \text{ mV s}^{-1}$ ). The CV diagrams of the compounds were practically the same as that of the supporting electrolyte, confirming their great electrochemical stability under the studied conditions. The peaks remained unchanged on repeated cycling, as well as on holding the potential at  $-1$  and  $1$  V. Such properties give the possibility of the application of these complexes as catalysts.

It is known that HCOOH, CH<sub>3</sub>COOH, C<sub>6</sub>H<sub>5</sub>COOH, and their salts are preservatives in the alimentary industry, while benzenedicarboxylic acids are poisons for microorganisms. Preliminary testing of the microbiological activity of the new complexes, together with familiar Co(II)tpmc complexes recently described,<sup>27</sup> against some Gram(+) and Gram(–)-bacteria and mould was performed in order to check if their activity is modified on coordination. Data for both tests described in the Experimental are presented in Table V. The solvent (CH<sub>3</sub>CN), tpmc, the previously tested Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, the alkaline salts of pht, ipht and tpht, and the complexes **4** and **5** were inactive. Complexes **1–3** and **6** exhibited antimicrobial activity towards particular strains, and C<sub>6</sub>H<sub>5</sub>COOH in all studied cases. Complexes **1**, **2** and **6** gave positive result only when applied in the solid state, providing for their high concentration on dissolution in the nutrition agar. The activity of complexes **1** and **2** is not ascribed to the carboxylato ligands themselves, as their concentration in the applied crystals was too small. The same is supposed for complex **6**, as the concentration of benzoate produced by its dissociation in the used aliquot is negligible. In spite of the fact that the tpht ligand was inactive, complex **3** containing this ligand was active.

Based on all the afore said, the most probable coordination geometry of the complex cations of **1** and **2** is presented in Scheme 2 (as already proposed for the benzoate analogue) and for the complex cation of **3** in Schemes 3g or 3f. The geometry in Scheme 3f has enhanced strain due to the longer Co...Co distance and, thus, much weaker Co(II)–O bonds.

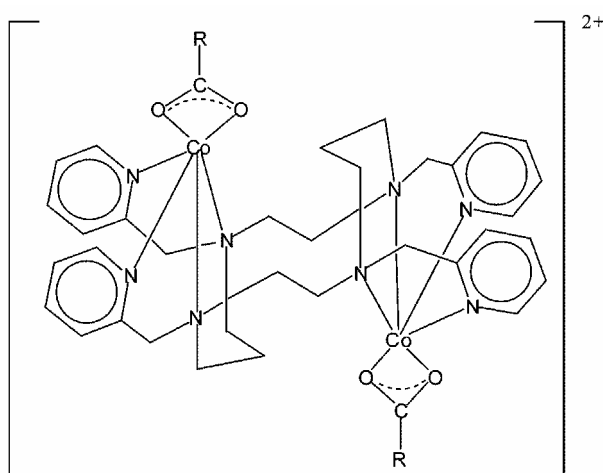
When Co(II) and Cu(II)tpmc related complexes with: HCOO<sup>–</sup>, CH<sub>3</sub>COO<sup>–</sup>, C<sub>6</sub>H<sub>5</sub>COO<sup>–</sup>, dianions of: pht, ipht or tpht<sup>11,27</sup> ligands are mutually compared, it can be concluded that in no case was the same composition obtained. This is the result of specific properties of these metal ions (different electronic configurations, size of the ionic diameter, tendency to form 5- or 6-coordinated species, *etc.*), as well as the changed experimental conditions which were necessary to apply in

each case. With one  $\text{HCOO}^-$  or  $\text{CH}_3\text{COO}^-$  ligand,  $\text{Cu(II)tpmc}$  formed five-coordinated bridged binuclear complexes, but in the case of  $\text{Co(II)}$  *bis*(bidentate), six-coordination of two such ligands was favoured. For  $[\text{Co}_2(\text{pht})\text{tpmc}]^{2+}$ , pht was  $\mu$ -bonded (Schemes 3b or 3c), while in the corresponding  $\text{Cu(II)}$  complex,  $\text{Hpht}^-$  was a bridged ligand, engaging only one  $\text{COO}^-$  group.  $\text{Co(II)}$  formed binuclear complexes with ipht (Scheme 3d or 3e) and tph (Scheme 3g and less probable 3f) when tpmc was present. On the contrary,  $\text{Cu(II)}$  complexes with the same ligands were tetranuclear ones in which four metallic centres were bridged with one dicarboxylate (Scheme 1d). These conclusions were supported by X-ray analyses of  $\text{Cu(II)tpmc}$  complexes with  $\text{ipht}^{2-}$  and recently with  $\text{C}_6\text{H}_5\text{COO}^-$ .<sup>11,32</sup>

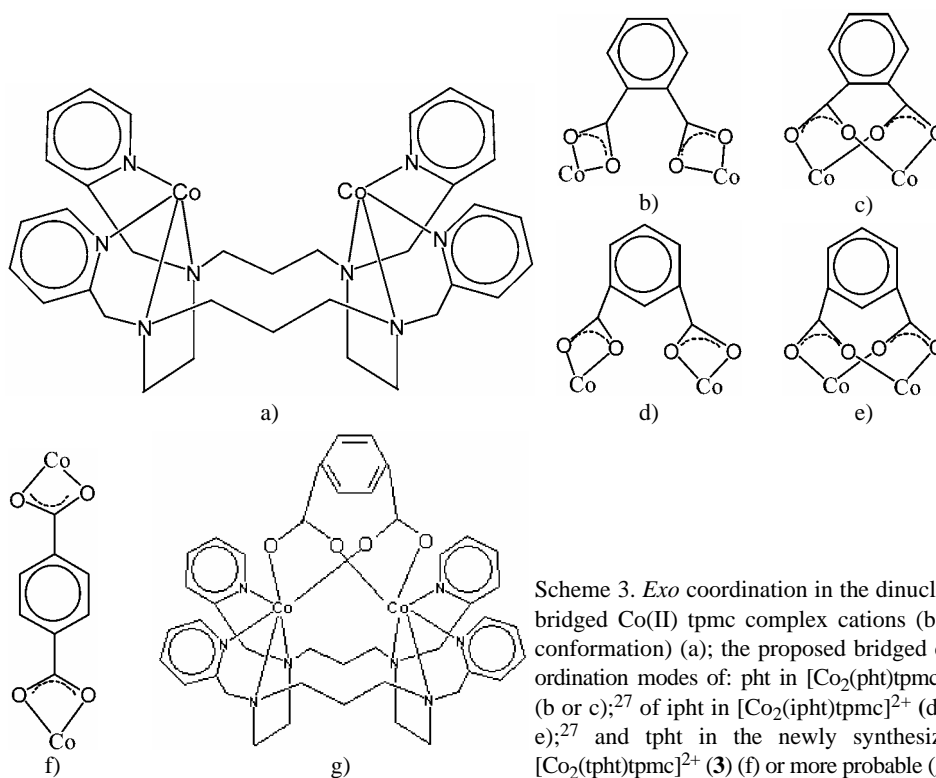
TABLE V. Results of the antimicrobial activity of the tested complexes, ligands and solvents

Cmpd.	<i>B. subtilis</i>	<i>B. cereus</i>	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>A. niger</i>
	Gram(+) bacteria		Gram(-) bacteria		mould
Crystal of $[\text{Co}_2(\text{HCOO})_2\text{tpmc}](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ ( <b>1</b> )	-	++	+	Not tested	-
Crystal of $[\text{Co}_2(\text{CH}_3\text{COO})_2\text{tpmc}](\text{ClO}_4)_2$ ( <b>2</b> )	-	+++	-	Not tested	-
$\text{C}_6\text{H}_5\text{COOH}$	+	+	+	+	+
$[\text{Co}_2(\text{C}_6\text{H}_5\text{COO})_2\text{tpmc}](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}^{\text{a}}$ ( <b>6</b> )	-	+	+++	+	+
KHpht	-	-	-	-	-
$\text{K}_2\text{pht}$	-	-	-	-	-
$[\text{Co}_2(\text{pht})\text{tpmc}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}^{\text{a}}$ ( <b>4</b> )	-	-	-	-	-
$\text{H}_2\text{ipht}$	-	-	-	-	-
$[\text{Co}_2(\text{ipht})\text{tpmc}](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}^{\text{a}}$ ( <b>5</b> )	-	-	-	-	-
$\text{H}_2\text{tph}$	-	-	-	Not tested	-
Crystal of $[\text{Co}_2(\text{tph})\text{tpmc}](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ ( <b>3</b> )	-	+++	+	Not tested	-
Tpmc	-	-	-	-	-
$\text{CH}_3\text{CN}$	-	-	-	-	-

<sup>a</sup>Described complexes<sup>27</sup>; (+) antimicrobial activity with a diameter of the inhibition zone up to 10 mm; (++) antimicrobial activity with a diameter of the inhibition zone up to 30 mm, (+++) antimicrobial activity with a diameter of the inhibition zone larger than 30 mm; (-) antimicrobial activity was not detected



Scheme 2. Simplified structure of the complex cations of the complexes **1** ( $\text{R} = \text{H}$ ) and **2** ( $\text{R} = \text{CH}_3$ ).



Scheme 3. *Exo* coordination in the dinuclear bridged Co(II) tpmc complex cations (boat conformation) (a); the proposed bridged coordination modes of: pht in  $[\text{Co}_2(\text{pht})\text{tpmc}]^{2+}$  (b or c);<sup>27</sup> of ipht in  $[\text{Co}_2(\text{ipht})\text{tpmc}]^{2+}$  (d or e);<sup>27</sup> and tpht in the newly synthesized  $[\text{Co}_2(\text{tpht})\text{tpmc}]^{2+}$  (3) (f) or more probable (g).

### CONCLUSIONS

Three novel Co(II) complexes with pendant octaazamacrocyclic ligand *N,N',N'',N'''*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc) and mono- ( $\text{HCOO}^-/\text{CH}_3\text{COO}^-$ ) or dicarboxylate ligands (terephthalate dianion) were prepared, characterized by some physical properties and valuable methods and techniques (elemental analyses, molar electrical conductivity, spectroscopic data, magnetic measurements, cyclic voltammetry), and compared with the already described Co(II)/Cu(II) analogues. All complexes were binuclear and cationic. For Co(II)tpmc complexes containing two  $\text{HCOO}^-/\text{CH}_3\text{COO}^-$  ligands, bis(bidentate) coordination of the additional ligands in the *trans* position for each metal and the chair conformation of tpmc is predicted, while for the multidonor terephthalate dianion  $\mu\text{-O,O,O',O'}$  coordination is supposed.

*Acknowledgements.* We gratefully acknowledge the financial support of the Ministry of Science (Project No. 142028) of the Republic of Serbia and Dr. Gordana Gojgić-Cvijović for the microbiological screening.

## ИЗВОД

ВИСОКОСПИНСКИ Co(II) КОМПЛЕКСИ СА ПЕНДАНТНИМ  
ОКТААЗАМАКРОЦИКЛОМ И КАРБОКСИЛАТИМАГ. ВУЧКОВИЋ<sup>1</sup>, С. Б. ТАНАСКОВИЋ<sup>2</sup>, З. М. МИОДРАГОВИЋ<sup>1</sup> И В. СТАНИЋ<sup>1</sup><sup>1</sup>Хемијски факултет, Универзитет у Београду, б. бр. 158, 11001 Београд и <sup>2</sup>Фармацеутички факултет,  
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Добијена су три нова динуклеарна Co(II) мешовито-лигандна комплекса са *N,N',N'',N'''*-тетраакис(2-пиридилметил)-1,4,8,11-тетраазациклотетрадеканом (trmc) и моно- или дикарбоксилато лигандима и одређена су нека њихова физичка својства. Опште формуле:  $[\text{Co}_2(\text{HCOO})_2\text{trmc}](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ ,  $[\text{Co}_2(\text{CH}_3\text{COO})_2\text{trmc}](\text{ClO}_4)_2$  и  $[\text{Co}_2(\text{tpht})\text{trmc}](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  (tphtH<sub>2</sub> = терефтална киселина) предложене су на основу резултата анализе (C,H,N) и мерења моларне електричне проводљивости. UV/Vis и IR спектри, магнетна и CV мерења коришћена су за проучавање геометрије и особина ових једињења. За монокарбоксилатне комплексе предложена је *exo* координација Co(II) са четири азотова атома trmc-а и бис-бидентатно везаним HCOO<sup>-</sup>/CH<sub>3</sub>COO<sup>-</sup>) у *trans* положају. Trmc заузима конформацију столице. Претпостављено је да терефталатни дианјон, као и метиленске групе циклума премошћују два атома Co(II), а trmc је у конформацији лађе. Комплекси су стабилни према хемијској и електрохемијској оксидацији Co(II) у Co(III). Подаци су упоређени са раније објављеним Cu(II) комплексима који садрже одговарајуће лиганде и разматране су међусобне сличности и разлике. Најзад, утврђена је извесна антимикробна активност комплекса.

(Примљено 24. септембра 2007)

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