

Cu(II) complexes with a pendant octaazamacrocyclic and μ -bonded aromatic carboxylates

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Abstract: Three new cationic mixed-ligand Cu(II) complexes with *N,N,N',N''*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc) and bridging aromatic mono- or dicarboxylate ligands were prepared. Elemental analysis, conductometric and magnetic measurements, as well as electronic and IR spectroscopy were employed for their characterization. It is proposed that the complexes [Cu₂(C₆H₅COO)tpmc](ClO₄)₃MeOH and [Cu₂(Hph)tpmc](ClO₄)·3H₂O (H₂pht = phthalic acid) are binuclear with μ -coordination of the carboxylate monoanions. The third complex, [Cu₄ipht(tpmc)₂](ClO₄)₆NaClO₄·2MeCN (H₂ipht = isophthalic acid) is one of the rare tetranuclear Cu(II)-tpmc complexes with an aromatic dicarboxylate ion bridging two Cu₂tpmc units. This was also confirmed by preliminary results of the determination of the crystal structure.

Keywords: copper(II) complexes, octaazamacrocyclic, benzoate, phthalate, isophthalate.

INTRODUCTION

Binuclear and multinuclear metal complexes with polyatomic ligands are an attractive field of investigation. The physical and magnetic properties of the compounds, the role of the metallic centers in biological processes and in homogeneous catalysis have been the subject of numerous investigations.^{1–11} Among bridged ligands many carboxylate ligands have been used, since they can coordinate in different ways, *i.e.* monodentates, bidentates or polydentates.^{2,11} Phthalato, isophthalato and terephthalato dianions contain two carboxylate groups, which give a great contribution to the magnetic interactions between two metallic centers even at long distances.^{1–11} With phthalato anions, Cu(II) easily forms polymeric structures with interesting magnetic properties, but polymerization is suppressed in the case of hydrogenphthalate.⁶ Dimerization of the complex with bridging isophthalato anions has also been studied with Cu(II).⁶ In the case of terephthalato Cu(II)

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complexes, polymerization is facilitated and depending on the reaction conditions dimerization or polymerization is achieved.

Complexes of transition metals with tpmc are interesting in terms of their structure, stability, spectral, redox and magnetic properties. Among them Cu(II) complexes are the most investigated.^{12–18} Tpmc in the absence of other ligands with Cu(II) can form two different complexes: mononuclear, when Cu(II) ions are coordinated in the centre of the cyclam ring-endo coordination, or binuclear, when Cu(II) ions are bonded outside the cyclam ring-exo coordination, with the chair conformation.¹² A great number of the described complexes containing one or two additional ligands besides tpmc are binuclear. Tpmc with pendant N-donor arms can accommodate to different additional ligands in a variety of coordination ways giving stable complexes. If only one such ligand is present (*e.g.*, X⁻, OH⁻, CO₃²⁻, C₂O₄²⁻, CNO⁻, CH₃COO⁻, HCOO⁻, urea, thiourea, semicarbazide, thiosemicarbazide...) the tpmc ligand adopts the boat conformation and bridges two Cu(II).^{12–16} In the case of more voluminous ligands or in the presence of excess of the additional ligand during preparation (I⁻, Br⁻, N₃⁻, SeCN⁻, SCN⁻...), they are coordinated to Cu(II) in the *trans* position and the macrocycle adopts the chair conformation.^{13,16} Only two tetranuclear Cu(II) complexes with tpmc and malonate- or bicyclo-[2,2,1]-hept-5-endo-2,3-*cis* dicarboxylate anions^{14,17} are known so far. The dicarboxylate ligands in these cases engages all four oxygens with Cu(II) atoms in two tpmc units. X-Ray analysis of the mixed-ligand complex cations containing bridging acetato and formato ions in the same crystal lattice [Cu₂(CH₃COO)tpmc][Cu₂(HCOO)tpmc](ClO₄)₆·6H₂O¹⁸ showed asymmetrical coordination of carboxylate. One oxygen is bonded in the axial and the other in the equatorial position. This manner of coordination has previously been found in the compound with an NO₃⁻ bridge.¹² On the other hand, complexes of Cu(II) with dibenzoic acids are interesting because of their magnetic properties and possible application as new materials in the electronic industry.

Continuing our investigations, three mixed complexes with aromatic carboxylates and the octaazamacrocyclic ligand *N,N',N'',N'''*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane will be described in the present paper.

EXPERIMENTAL

Safety note! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with extreme caution! Only small amounts of material should be prepared!

Syntheses

The ligand tpmc¹⁹ and the starting [Cu₂tpmc](ClO₄)₄¹² were obtained according to the procedures described in the literature.

[Cu₂(C₆H₅COO)tpmc](ClO₄)₃·MeOH (A). To a solution containing 50 mg (0.05 mmol) of [Cu₂tpmc](ClO₄)₄ in 5 cm³ of a MeOH–H₂O (5:1, v/v) mixture, a solution of benzoic acid (9 mg, 0.07 mmol) in 3 cm³ of MeOH, previously neutralized with NaOH (0.1 mol/dm³) to pH 6.2, was added dropwise. When the mixture was refluxed for 2 h on a water bath (80 °C) it gradually turned from violet to blue. After concentration on a water bath to about 4 cm³, the container was covered with needle-pierced parafilm and left in a refrigerator for several days. The blue product was filtered off by suction, washed with MeOH and recrystallized from

MeOH–H₂O (10:1, v/v). The final microcrystals were washed with cold methanol and left in a desiccator (over CaO). Yield 35 mg (66 %). Calculated for Cu₂C₄₂H₅₃N₈Cl₃O₁₅ (FW = 1143.30): C 44.12; H 4.67; N 9.80; Cu 11.11 %. Found: C 44.41; H 4.69; N 9.71; Cu 10.65 %.

[Cu₂(Hpth)tpmc](ClO₄)₃·3H₂O (B). To a solution of 50 mg (0.05 mmol) of [Cu₂tpmc](ClO₄)₄ in MeCN (5 cm³), a solution of KHpth (14 mg, 0.07 mmol) in water (4 cm³) was added dropwise. The further procedure was similar to that for complex A, but recrystallization was not necessary. The blue crystals are washed with cold ethanol and kept in a desiccator. Yield 46 mg (82 %). Calculated for Cu₂C₄₂H₅₅N₈O₁₉Cl₃ (FW = 1209.42): C 41.71; H 4.58; N 9.26; Cu 10.51 %. Found: C 41.33; H 4.80; N 9.57; Cu 10.13 %.

[Cu₄ipth(tpmc)₂](ClO₄)₆·NaClO₄·2MeCN (C). 50 mg (0.05 mmol) of [Cu₂tpmc](ClO₄)₄ was dissolved in 4 cm³ of MeCN. Isophthalic acid (12 mg, 0.07 mmol) was dissolved in 5 cm³ of a mixture of MeCN–H₂O (3:2, v/v), neutralized to pH 6.7 with NaOH (0.1 mol/dm³) and added dropwise to the first solution. The further procedure and the reaction conditions are similar to those for complex B. For faster crystallization, a small amount of solid NaClO₄ was added. Yield 41 mg (75 %). Calculated for Cu₄C₈₀H₉₈O₃₂N₁₈Cl₇Na (FW = 2349.21): C 40.90; H 4.20; N 10.73; Cu 10.82 %. Found: C 41.32; H 4.14; N 10.42; Cu 10.64 %.

Measurements

Elemental analyses (C, H, N) were achieved by standard micromethods in the Centre for Instrumental Analysis, Faculty of Chemistry, Belgrade. The Cu analyses were made using a Perkin-Elmer AAS-5100/PC atomic absorption spectrophotometer. The electronic absorption spectra were recorded in MeCN using a GBC UV/VIS 911 A spectrophotometer. The IR spectra (KBr discs or Nujol mull) were recorded in the range 400–4000 cm⁻¹ using Perkin-Elmer FTIR 31725X spectrophotometer. The electrical conductivity was measured by a Janway 4010 conductometer. Molar conductivity values for all the complexes were measured in MeCN at room temperature (20±2 °C). The concentration was about 10⁻³ mol/dm³ for A, B and 5×10⁻⁴ mol/dm³ for complex C. The magnetic susceptibility was determined by the SQUID technique. The data were corrected for diamagnetic susceptibilities using Pascal's constants.²⁰

Preliminary X-ray analysis

Single crystals of compound C were obtained by the diffusion method. In a small (0.5 cm³) container, 0.25 cm³ of a saturated solution of substance C in MeCN was added together with one drop of water. In the other container of 5 cm³ volume, 3 cm³ of MeOH were added. Both containers were put into a small desiccator (∅ = 9 cm) over CaO. After two days blue plate-like single crystals of suitable dimensions appeared.

For the intensity data collection a Bruker AXS four-circle diffractometer equipped with CCD 1000 K area detector and a flat graphite monochromator (MoK_α radiation, λ = 0.71073 Å), sample to detector distance of 60 mm, and series of φ and ω scans were applied. The data were collected at room temperature (298 K) using a crystal of about 0.05×0.18×0.25 mm size (Miller indices range: -35 <h <36, -11 <k <10, -41 <l <15).

The structure was solved by direct methods (SHELXS97)²¹ and refined by full-matrix least-squares methods of F² (SHELXL97).²²

It must be emphasised that the investigated compound turned out to be very sensitive to X-rays with a highly pronounced time decay; therefore only approx. one half of the collected data were suitable for further treatment and the obtained intensities were unusually low. As a consequence, the refinement resulted in high agreement indices [R₁ = 0.209; goodness-of-fit, S(F²) = 1.541] and some unreliable bond distances and atomic displacement parameters. In addition, the very probable disorder of the ClO₄⁻ ions and lattice solvent (MeCN) can also contribute to the high R-value. At the present level of precision and accuracy it was impossible to locate the NaClO₄ and MeCN known to be present in the crystal lattice from the results of chemical analysis. Therefore, part of the crystal data listed in the next paragraph are given for the formula [Cu₄ipth(tpmc)₂](ClO₄)₆. Nevertheless, some essential data concerning the coordination of the copper(II) and the bonding mode of the ipth ions were established unambiguously.

Crystal data: C₇₆H₉₂Cl₆Cu₄N₁₆O₂₈, M_r = 2144.52, monoclinic, space group C2/c, a = 37.23 (4), b = 11.580 (13), c = 43.38 (4) Å, β = 104.436 (12)°, V = 18111 (33) Å³, Z = 8, F(000) = 8816, ρ_x = 1.573 gcm⁻³, μ(Mo K_α) = 1.190 mm⁻¹, number of collected reflections: 16680, number of independent reflections: 8041, number of strong reflections with I > 2σ(I): 3920.

RESULTS AND DISCUSSION

All three compounds are soluble in MeCN and DMSO and insoluble or sparingly soluble in most other ordinary solvents. The complexes are stable in air and on heating up to $t = 210\text{ }^{\circ}\text{C}$. (The stability at higher temperatures was not tested since the complexes, as perchlorates, are potentially explosive). The formulae of the complexes are based on elemental analyses (C, H, N, Cu) and molar conductivity measurements. They corresponded to binuclear complexes for A and B, and tetranuclear for complex C. The molar conductivities are given in Table I. For complex A, the value of $310\text{ S cm}^2\text{ mol}^{-1}$ is between 1:2 and 1:3 electrolytes,²³ but closer to a 1:3 type. The large value obtained for complex B could be a consequence of the presence of 3 moles of crystal water in this compound. The Λ_M value of $800\text{ S cm}^2\text{ mol}^{-1}$ for complex C is very high, corresponding to an electrolyte type more than 1:5. It can correspond to a 1:6 electrolyte type, although in the literature there is no precise data for such an electrolyte type.^{14,17} The molar conductivity of 10^{-3} mol/dm^3 NaClO_4 (present in the crystal lattice of the complex) is itself $135\text{ S cm}^2\text{ mol}^{-1}$, which contributes a great deal to the total molar conductivity of compound C. On the other hand, a complex cation of 6+ charge is very voluminous and expected to be of low mobility. From this point of view the molar conductivity of the complex C is still very high.

TABLE I. Positions of the absorption maxima, λ_{max} , molar absorptivity coefficients (ϵ) of the electronic absorption spectra, molar conductivities, Λ_M , and magnetic moments, μ_{eff} , at room temperature

Complex	λ_{max} (ϵ) [nm ($\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$)]	Λ_M /[$\text{S cm}^2\text{ mol}^{-1}$] (electrolyte type)	μ_{eff} [BM/Cu]
A	671 (365);450 sh (105)	310 (between 1:2 and 1:3)	1.88
B	658 (335);859 sh (151)	435 (1:3)	1.74
C	676 (652);900 sh (405)	800 (1:6)	1.76
$[\text{Cu}_2\text{tpmc}](\text{ClO}_4)_4^*$	670 (312)	510 (1:4)	1.90
$[\text{Cu}_2(\text{HCOO})\text{tpmc}](\text{ClO}_4)_3^*$	649 (333)	395 (1:3)	2.34
$[\text{Cu}_2(\text{CH}_3\text{COO})\text{tpmc}](\text{ClO}_4)_3^*$	655 (301)	-	1.81

*Data taken from references,^{12,15,18} sh-shoulder

The position of the absorption maxima and molar absorptivity coefficients of the complexes together with some data for comparison are given in Table I. The origins of the absorption maxima are d-d transitions. The electronic absorption spectrum of complex A was recorded immediately after dissolution (see Table I). After 1 h standing at room temperature, the shape and the positions of the maxima and the shoulder are changed suggesting substitution of the bridged ligand or a different conformation of the complex. In the fresh solution of the complex A a bathochromic shift of 22 nm was observed in comparison to an earlier described formato-bridged complex. This is consistent with the presence of an aromatic ring in complex A, causing a weaker ligand field. A shift toward higher wavelengths was also observed in earlier described acetato analogue,¹² belonging to the same homologous series. In the spectra of B and C, maxima characteristic for penta-coor-

dinated Cu(II) with a distorted square pyramid and the CuN_4O chromophore were observed.^{12,14,16–18} These spectra were time insensitive. The very high value of ϵ found for complex C maybe a consequence of the asymmetry and is consistent with a tetranuclear structure. Additional proof that the structure is tetranuclear is that similar ϵ values were found earlier for the tetranuclear μ -bicyclo-[2,2,1]-hept-5-en-endo-2,3-*cis*. dicarboxylato and μ -malonato complexes.^{14,17}

In the IR spectra of all three compounds the following bands were found: in the range of 3100–3000 cm^{-1} $\nu(\text{C-H})$ from aromatic rings which can overlap with $\nu(\text{O-H})$ from the crystal H_2O (as in the case of complex B); a sharp band at 1610 cm^{-1} from skeletal vibrations of the pyridine ring, a broad intensive band at about 1100 cm^{-1} from $\nu(\text{ClO}_4^-)$ and a sharp medium band from $\delta(\text{ClO}_4^-)$ at 630 cm^{-1} ; in the 1600–1450 cm^{-1} region bands from $\nu(\text{C=C})$ of pyridine and aromatic rings are observed while the bands in the range of 1300–1100 cm^{-1} originate from $\delta(\text{C-H})$ of the aromatic rings. In the spectra of all three complexes there is a band around 470 cm^{-1} which originates from $\nu(\text{C-N})$ and a band about 420 cm^{-1} from $\nu(\text{Cu-O})$. The comparison of the spectra of the complexes and corresponding alkaline salts in the range 1670–1350 cm^{-1} , where $\nu_{\text{asym}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ appear, is given in Table II. The change of the $\Delta\nu$ value ($\nu_{\text{asym}} - \nu_{\text{sym}}$) of the complex in comparison with the value for the salt confirms that the ligand is coordinated to the metal^{25,26} through COO^- groups. It is obvious that ν_{asym} and ν_{sym} are shifted toward lower values in comparison with the corresponding salts, which is the case when COO^- participates in H-bonds formation or when the coordination is achieved through both oxygens.²⁵ Due to steric hindrance, the possibility of H-bond formation in the complexes is small, which also proves the proposed coordination mode of the ligands. In complex A, both oxygens of COO^- are engaged in coordination thus forming a bridge between two Cu(II) from the same tpmc unit (Fig. 1), probably in the same way as in the case of HCOO^- and CH_3COO^- .^{12,18} The presence of two carboxylato groups in complexes B and C at different position in the aromatic ring enables the possibility for participation of all four oxygens for various bridged or chelate coordination.^{24–26} Only in the spectrum of B there are bands at 1713 cm^{-1} and 1298 cm^{-1} , corresponding to $\nu_{\text{asym}}(\text{COOH})$ and $\nu_{\text{sym}}(\text{COOH})$, which

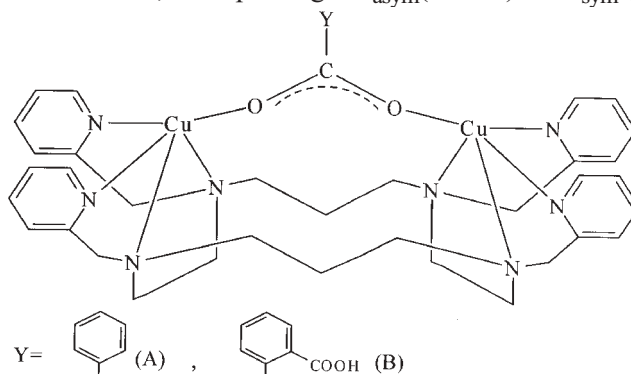


Fig. 1. Suggested structures of the complex cations $[\text{Cu}_2(\text{C}_6\text{H}_5\text{COO})\text{tpmc}]^{3+}$ (A) and $[\text{Cu}_2(\text{Hpth})\text{tpmc}]^{3+}$ (B).

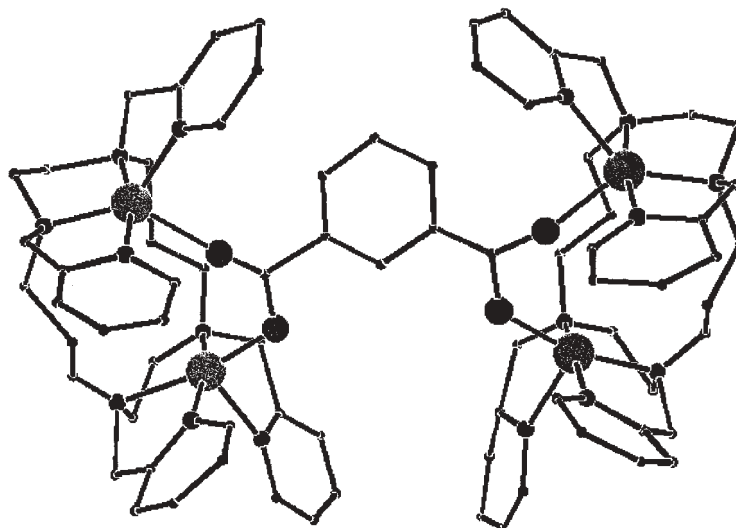


Fig. 2. Schematic drawing of the $[\{Cu_2(tpmc)\}_2(ipht)]^{6+}$ ion in complex C based on the preliminary X-ray structure determination. In order of decreasing radii, the circles represent Cu, O, N and C atoms.

are neither included in coordination nor in H-bonds. The bands for $\nu_{\text{asym}}(\text{COOH})$ and $\nu_{\text{sym}}(\text{COOH})$ are also present in the spectrum of KHpht at 1696 cm^{-1} and 1283 cm^{-1} . The shift in complex B can be explained by the absence of H-bonds due to the steric strains, while in the simple KHpht salt such bonds exist. Very probably the other ionic group (COO^-) is the bridge between two metal atoms (Fig. 1). The absence of a band at about 1700 cm^{-1} in the spectrum of C means that all four oxygens are included in coordination. The formation of H-bonds is difficult for the same reasons as in complex B. Actually, the results of preliminary X-ray structure analysis (Fig. 2) showed that ipht ions act as bis-bidentate ligands with each COO^- group bridging two Cu atoms and with the whole ipht ion bridging two $\text{Cu}_2(\text{tpmc})$ units thus making a tetranuclear complex. As far as we know, no X-ray analysis for tetranuclear Cu_2tpmc complexes has been published.

TABLE II. Some IR data for free carboxylate ligands and for the corresponding complexes

Compound	$\nu_{\text{asym}}(\text{OCO})$	$\nu_{\text{sym}}(\text{OCO})$	$\Delta\nu$
$\text{C}_6\text{H}_5\text{COONa}$	1553*	1413*	140
A	1555	1382	173
KHpht	1696**,1587	1405, 1283**	182
B	1713**,1576,1565	1391,1357,1298**	196
Na_2ipht	1564	1395	169
C	1573,1560	1387	180

$\Delta\nu = \nu_{\text{asym}} - \nu_{\text{sym}}$; *Data taken from the literature,^{24,25}; ** $\nu(\text{COOH})$

The difference in the structures of complexes B and C are in accordance with the properties of Hpht^- and ipht^{2-} . When carboxylic groups are in the *ortho*-position there is

steric hindrance for tetranuclear complexes formation, as all four oxygens should be coordinated with two voluminous *tpmc* units. For *ipht*²⁻ these hindrances are lowered by the *meta*-position of *COO*⁻. In addition, the inductive effect of the aromatic ring is slightly negative, the inductive effect of *COOH* is negative, while *COO*⁻ has a positive inductive effect. The donor ability of the acid increases with increasing positive inductive effect. When there is a *COOH* group in the *ortho*-position to the *COO*⁻ group, its donor ability is lowered. However, in *ipht*²⁻ the two *COO*⁻ groups with a positive inductive effect are in the *meta*-position, so their effect on each other is not so pronounced and hence both of them have stronger donor abilities than *Hpht*⁻.^{26,27}

The magnetic moments per Cu atom for the complexes at room temperature given in Table I are consistent with the values found in the literature for simple paramagnetic pentacoordinated Cu(II) complexes. Interpretation of the temperature dependence of the magnetic susceptibilities of Cu(II) complexes containing aromatic carboxylates is somewhat complicated,²⁶ so this will be an interesting subject for a further investigation. In our complexes there are no possibilities for weak inter- and intramolecular anti- or ferromagnetic interactions.

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ИЗВОД

КОМПЛЕКСИ Cu(II) СА ПЕНДАНТНИМ ОКТААЗАМАКРОЦИКЛОМ И μ-ВЕЗАНИМ АРОМАТИЧНИМ КАРБОКСИЛАТИМА

ГОРДАНА ВУЧКОВИЋ,¹ МИРЈАНА АНТОНИЈЕВИЋ² И ДЕЈАН ПОЛЕТИЋ³

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Добијена су три нова комплекса Cu(II) са *N,N,N',N'*-тетраакис(2-пиридилметил)-1,4,8,11-тетраазациклотетрадеканом (*tpmc*) и μ-везаним ароматичним моно- и дикарбоксилатима. Комплекси су окарактерисани елементалном анализом, кондуктометријским и магнетним мерењима, електронском и IR спектроскопијом. За комплексе [Cu₂(C₆H₅COO)*tpmc*](ClO₄)₃·MeOH и [Cu₂(*Hpht*)*tpmc*](ClO₄)₃·3H₂O (*H₂pht* = фтална киселина) претпостављено је да су динуклеарни са μ-координацијом карбоксилато моноанјона. Трећи комплекс [Cu₄*ipht*(*tpmc*)₂](ClO₄)₆·NaClO₄·2MeCN (*H₂ipht* = изофтална киселина) је један од ретких тетрануклеарних комплекса Cu(II) са *tpmc*-ом где је ароматични дикарбоксилато-јон мост између две Cu₂*tpmc* јединице. Ово је потврђено и на основу прелиминарних резултата рендгенске структурне анализе.

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