Cobalt(II) complexes with aromatic carboxylates and $N$-functionalized cyclam bearing 2-pyridylmethyl pendant arms

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Abstract: Novel binuclear Co(II) complexes with $N$-functionalized cyclam, $N,N',N''$,$N'''$-tetrakis(2-pyridylmethyl)tetraazacyclotetradecane (tpmc) and one of the aromatic mono- or dicarboxylato ligands (benzoate, phthalate or isophthalate ions) were prepared. They were analyzed and studied by elemental analyses (C, H, N), electrical conductivities, VIS and IR spectroscopy and magnetic as well as cyclic voltammetric measurements. In $[\text{Co}_2(C_6H_5COO)_{2}\text{tpmc}]\left(ClO_4\right)_{2}.3H_2O$, the benzoate ligands are most probably coordinated as chelates in the trans-position to each Co(II) and the macrocycle adopts a chair conformation. In the complexes $[\text{Co}_2(Y)\text{tpmc}]\left(ClO_4\right)_{2}.zH_2O$, ($Y = \text{phthalate or } i\text{-phthalate dianizon}, z = 2, 4$), it is proposed that the isomeric dicarboxylates are bonded combined as bridges and chelates. The composition and the assumed geometries of the complexes are compared with the, earlier reported, corresponding Cu(II) complexes. Cyclic voltammetry measurements showed that the compounds are electrochemically stable.

Keywords: Co(II) complexes, $N$-functionalized cyclam, 2-pyridylmethyl pendant arms, aromatic carboxylates.

INTRODUCTION

Cyclam and its $N$-substituted derivatives is an attractive field of investigation, due to their coordination properties towards various metal ions and possible application in medicine.1–3 By substitution of the cyclam amine protons with 2-, 3- or 4-pyridylmethyl groups, different ligands were isolated producing complexes with properties depending on the number of pendant groups and their position.4,5 Among them, only $N,N',N''$,$N'''$-tetrakis(2-pyridylmethyl)tetraazacyclotetracene (tpmc) was fully $N$-functionalized. In spite of the fact that this ligand was prepared6 in 1986 and the synthesis is improved7 in 1997, its X-ray structural analysis was only recently done.8 It showed that the macrocycle adopted a trans-IV confor-

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mation according to Bosnich classification. The pendant 2-pyridylmethyl groups occupied equatorial positions, while the N atoms were pointed out of the cavity with exodentate geometry, although endodentate geometry is theoretically possible as well (Scheme 1). A similar, but not identical, exodentate geometry was found in tetrakis-(2-hydroxyethyl)cyclam and tetrakis-(3-hydroxypropyl)cyclam. These data confirmed that interconversion between endo and exodentate geometry is possible. In the meantime, a great number of transition metal complexes, predominantly Cu(II) and Co(II) were described. Binuclear Co(II)tpmc complexes with aminocarboxylato anions were air stable, as well as to O\textsubscript{2} oxidation. This unexpected property is the result of the hydrophobic environment formed by the macrocycle around Co(II). By chemical oxidation of μ-CO\textsubscript{3}\textsuperscript{2–} or μ-α-aminoisobutirato Co(II)tpmc binuclear complexes using H\textsubscript{2}O\textsubscript{2}, mixed-valence Co(II)/Co(III) complexes were isolated. On the other hand, Co(II) complexes with H-phthalate, isophthalate and terephthalate bridged anions, were found to produce interesting magnetic interactions. The majority of Co(II) complexes with 1,2-benzenedicarboxylic acid contained a H-phthalate monoanion and only a few of them a phthalate dianion.

The aim of this work was to prepare Co(II)tpmc complexes with benzoate, phthalate and isophthalate anions and compare their composition and possible geometries with the corresponding reported Cu(II)tpmc complexes containing the same type of ligands.

**EXPERIMENTAL**

**Preparation**

**CAUTION!** Prechlorate salts of metal complexes with organic ligands are potentially explosive and should be stored and handled with extreme care!

The ligand tpmc and Co(ClO\textsubscript{4})\textsubscript{2}·6H\textsubscript{2}O were prepared according to described procedures. All other chemical were commercial products of p.a. grade of purity.
[Co₂(C₇H₆COO)₂tpmc][ClO₄]₂·3H₂O (1): Co₂(ClO₄)₂·6H₂O (50.5 mg; 0.138 mmol) and benzoic acid (13.3 mg; 0.10 mmol) previously neutralized with 0.1 mol/dm³ NaOH solution to pH 6.2 (controlled with pH strips for pH 5.4–7.0) were refluxed in 6.5 cm³ of the mixture CH₃CN–H₂O (8:5; v/v). The reaction mixture was then heated for 1 h in a water bath (≈75 °C). A suspension of tpmc (38.6 mg; 0.068 mmol) in water was added and the heating prolonged for a further 5 h, whereby the colour turned from pink to intense purple. Then the reaction mixture was concentrated to about 1/4 of the initial volume, vacuum filtered, covered with needle-pierced parafilm and left in a refrigerator overnight. The bright purple crystals were removed by vacuum filtration, washed several times with iced water and dried in desiccator over CaCl₂. A small amount of violet crystalline Co₂(OH)tpmc(ClO₄)₃ was always present as an impurity (less than 1 %). Yield: 38 mg (48 %). Anal. Calcd. for Co₂C₄₈H₆₀O₁₅N₈Cl₂ (FW = 1177.83): C, 48.95; H, 5.13; N, 9.51. Found: C, 48.44, H, 5.31; N, 9.84. Solubility: well soluble in CH₃CN, DMF and CH₃OH, insoluble in H₂O.

[Co₂(pht)tpmc][ClO₄]₂·2H₂O (2): Solution of Co(ClO₄)₂·6H₂O (50.2 mg; 0.137 mmol) in water (0.7 cm³), and of KHpt (21.4 mg; 0.105 mg) in CH₃CN (1.7 cm³) were mixed and refluxed with stirring for 1 h on a water bath (≈ 70 °C). A suspension of tpmc (38.6 mg; 0.068 mmol) in 3.2 cm³ of the solvent mixture CH₃CN–H₂O (5:1; v/v) was added and the heating continued for a further 4.5 h, whereby the colour turned from pink to purple-violet. Then the mixture was concentrated to 1/3 of the initial volume and left in a refrigerator overnight. The purple-violet crystals which appeared were treated as for complex (1). Yield: 35 mg (48 %). Anal. Calcd. for Co₂C₄₂H₅₂O₁₄N₈Cl₂ (FW = 1081.70): C, 46.64; H, 4.84; N, 10.37. Found: C, 46.59, H, 4.93; N, 10.67. Solubility: well soluble in CH₃CN, DMF, insoluble in CH₃OH and H₂O.

[Co₂(ipht)tpmc][ClO₄]₂·4H₂O (3): Co(ClO₄)₂·6H₂O (51.4 mg; 0.140 mmol) and isophthalic acid (16.95 mg; 0.105 mmol) previously neutralized with 0.1 mol/dm³ NaOH solution to pH 6.6 (test strips of pH 6.0–7.4 were used) were dissolved in 6.5 cm³ of a mixture CH₃CN–H₂O (8:5; v/v) and refluxed. The further procedure was similar to that for complex (2), except the reaction mixture was concentrated to about 1/2 of the initial value. Rose crystals were isolated. Yield: 66 mg (87 %). Anal. Calcd. for Co₂C₄₂H₅₆O₁₆N₈Cl₂ (FW = 1117.73): C, 45.13; H, 5.05; N, 10.02. Found: C, 45.05; H, 5.12; N, 10.32. Solubility: sparingly soluble in DMF, DMSO and CH₃CN, insoluble in common solvents. All three complexes were stable up to 250 °C.

**Measurements**

Elemental analyses (C, H, N) were carried out by standard micromethods in the Center for Instrumental Analyses of Iowa State University, Ames, USA. The electronic spectra were recorded using a GBC UV/VIS spectrophotometer. The IR spectra (KBr disc technique) were recorded on a Perkin–Elmer 31725XFTIR spectrophotometer. Magnetic susceptibilities were measured with a MSB-MKI magnetic balance. The data were corrected for diamagnetic susceptibilities using Pascal’s constants. The molar electrical conductivities in DMF were measured at 20 ± 2 °C on a Jenway 4010 conductometer. The electrochemical measurements were performed using a Metrohm 797 in a standard three-electrode cell: Pt as the auxiliary, AgCl/Ag as the reference electrode and a glassy carbon as the working electrode.

**RESULTS AND DISCUSSION**

The type and the yield of the complexes described in this paper depended on various factors: temperature, ratio and order of added reactants, solvent mixture employed, pH at which the aromatic carboxylate was neutralized, etc. It was found that the optimal conditions are as given in the Experimental. Namely, Co(II) perchlorate with tpmc alone always forms a violet µ-OH⁻ binuclear complex. On the other hand, aromatic carboxylates have a tendency to bind Co(II) in polymeric complexes. The best way of preparation of mixed-ligand complexes was to use CH₃CN–water mixtures as the solvent, KHpt salt for complex (2), to neutralized
the carboxylate to a pH close to $pK_a + 2$ for the complexes (1) and (3), to add tpmc as the last reactant and to increase the temperature. Such procedures resulted in better solubility and donor ability of the reactants, shifted the equilibrium towards the desired compounds and partially avoided side products.

The proposed composition and formulas of the complexes were based on elemental analysis (C, H, N) and molar electrical conductivities in DMF (Table I). The electrical conductivities of complexes (1) and (2) were consistent with a 1:2 electrolyte, while for complex (3), the $\Delta_M$ value was slightly lower than for such an electrolyte type.

<p>| Table I. Conductivities, $\mu_{\text{eff}}$/Co atom at room temperature and VIS absorption spectral data |</p>
<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Delta_M^{20\degree C}$/S mol$^{-1}$ cm$^2$ in DMF</th>
<th>$\mu_{\text{eff}}$ per Co atom/$\mu_B$</th>
<th>VIS spectra in DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>143</td>
<td>4.81</td>
<td>516</td>
</tr>
<tr>
<td>(1:2)*</td>
<td></td>
<td>479 $sh^#$</td>
<td>66</td>
</tr>
<tr>
<td>(2)</td>
<td>172</td>
<td>4.74</td>
<td>523</td>
</tr>
<tr>
<td>(1:2)</td>
<td></td>
<td>487 $sh$</td>
<td>74</td>
</tr>
<tr>
<td>(3)</td>
<td>116 between 1:1 and 1:2; but closer to 1:2</td>
<td>5.01</td>
<td>508</td>
</tr>
<tr>
<td></td>
<td></td>
<td>485 $sh$</td>
<td>89</td>
</tr>
</tbody>
</table>

*Literature ranges$^{17}$ for 1:1 electrolyte type is 65–90 S mol$^{-1}$ cm$^2$; for 1:2 is 130–170 S mol$^{-1}$ cm$^2$  

A variety of different coordination modes and conformation of such ligands in binuclear complexes are found: unidentate, $\eta^\text{n}$ – chelate, bisbidentate, combined chelate-bridged, unsymmetrical, etc. Some of the oxygens may remain non-coordinated, shared by both metallic centers, or may be included in hydrogen bonds.$^{18}$ Determination of the precise manner of coordination for multidonor aromatic dicarboxylates is only possible on the basis of X-ray crystal analysis.

The electronic absorption maxima and molar extinction coefficients ($\varepsilon$) for the complexes (1)–(3) (Table I) are typical for high-spin Co(II) complexes of low symmetry with the maxima originating from d–d transitions.$^{19,20}$ They are comparable with some familiar binuclear Co(II)tpmc complexes with bridged aliphatic (oxalato or malonato)$^{12b,13c}$ and bicyclic dicarboxylates$^{13c}$ in which the central ion is hexacoordinated. The similar VIS spectral features and $\varepsilon$ values suggest that the same chromophore, CoN$_4$O$_2^-$, is present in all the mentioned complexes. Moreover, asymmetrical coordination in the case of the symmetrical C$_2$O$_4^{2-}$ bridged ligand with one non-coordinated oxygen was confirmed by X-ray analysis.$^{13c}$ In this case, non-equal Co–O bond distances and deviations in the angles around the central ion were found, with the Co atoms pushed out of the basal plane formed by 2N atoms from cyclam and 2 from the pendant arm pyridine. The geometry was pseudo octahedral.
TABLE II. Some IR spectral data for free carboxylato ligands and for the corresponding (1)–(3) complexes

<table>
<thead>
<tr>
<th>Ligand/complex</th>
<th>(\nu_{\text{asym}}(\text{OCO})/\text{cm}^{-1})</th>
<th>(\nu_{\text{sym}}(\text{OCO})/\text{cm}^{-1})</th>
<th>(\Delta\nu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_6\text{H}_5\text{COONa})(^{(1)})</td>
<td>1580</td>
<td>1413</td>
<td>167</td>
</tr>
<tr>
<td></td>
<td>1533</td>
<td>1420</td>
<td>113</td>
</tr>
<tr>
<td>(\text{K}_2\text{pht})(^{(2)})</td>
<td>1563</td>
<td>1384</td>
<td>179</td>
</tr>
<tr>
<td></td>
<td>1544</td>
<td>1423</td>
<td>121</td>
</tr>
<tr>
<td>(\text{Na}_2\text{ipht})(^{(3)})</td>
<td>1564</td>
<td>1395</td>
<td>169</td>
</tr>
<tr>
<td></td>
<td>1538</td>
<td>1425</td>
<td>113</td>
</tr>
</tbody>
</table>

** Data taken from Refs. 15 and 21

In the IR spectra of the complexes (1)–(3), corresponding bands were found from: \(\nu(\text{ClO}_4)\) at \(\approx 1090 \text{ cm}^{-1}\) (very strong, broad) and \(\delta(\text{ClO}_4)\) at \(625 \text{ cm}^{-1}\) (medium, sharp), in the range of \(3580–3280 \text{ cm}^{-1}\) (medium, very broad) \(\nu\) of crystal water, skeletal vibration of the pyridine ring belonging to tpmc included in the coordination at \(1605 \text{ cm}^{-1}\) (strong, sharp). The vibrations originating from carboxylato ligands in the complexes, \(\nu(\text{OCO}^-)\) symmetrical and asymmetrical and \(\Delta\nu = \nu_{\text{asym}}(\text{OCO}^-) – \nu_{\text{sym}}(\text{OCO}^-)\), together with those for the corresponding alkaline salts are given in Table II. These data give information about the manner of carboxylate ligand coordination.\(^{21}\) Much lower values of \(\Delta\nu\) for all three complexes compared with their alkaline salts were found, suggesting that the carboxylato ligands were chelates. As in complex (1) two benzoato ligands were found per one tpmc and two Co(II), and there were no bands arising from free carbonyl groups in its IR spectrum, it could be expected that for each metal one carboxylate was coordinated in the \textit{trans} position, using both oxygens forming 4-membered rings. For the complexes (2) and (3), a combined chelate-bridged manner of coordination is proposed. The smaller value of \(\Delta\nu\) for the complex having \(i\)-phthalate ions than that containing phthalate ions, could indicate that the Co–O bonds in complex (3) were longer and weaker than in complex (2).\(^{18,21}\) This is somewhat unexpected due to the lower donor ability of carboxylates in the \textit{ortho} position and the steric hindrance in comparison with those in the \textit{meta} position. Nevertheless, it seems that the macrocyclic ligand, its conformation and hydrophobic cavity favored, a shorter Co···Co distance in the dimmeric complex (2) and slightly stronger Co–O bonds in the phthalato than in the isophthalato complex. More rigid, and voluminous bridges, such as bicyclic dicarboxylato ligands, were found to stabilized binuclear Co(II)tpmc complexes.\(^{13e}\) A bond for \(\nu(\text{C}=\text{O})\) was absent from its IR spectrum. In this case there were no possibilities for participation of any oxygens in H-bond formation, as there were no crystal solvent molecules. It is proposed that bis(bidentate)-bridged coordination of bicyclic dicarboxylate was achieved, using oxygens from different COO\(^{-}\) groups for binding to each Co(II), thus forming 7-membered rings, rather than 4-membered ones. With the \(\mu\)-malonato ligand, as it
is aliphatic, and causes smaller constrain as the mentioned one, the possibility for more flexible geometry than in the case of aromatic dicarboxylates and bicyclic ligand exists. It is capable of forming two 4-membered rings with Co atoms using both O atoms from the same COO\(^-\) groups, which was proposed for the corresponding complex with tpmc\(^1\)\(^{13}\). As for the \(\mu\)-oxalato complex,\(^1\)\(^{13}\) X-ray analyses confirmed the formation of one 4- and one 5-membered ring.

The values of \(\mu_{\text{eff}}/\text{Co atom of complexes (1)} - (3)\) at room temperature (Table I) fall in the range previously found for the majority of hexacoordinated high-spin Co(II) analogous complexes (4.7 – 5.2 \(\mu_B\)) with an orbital contribution to the magnetic moment. Magnetic interactions transmitted through phenyl dicarboxylate bridges are usually weak.\(^2\)\(^2\) In the case of pentacoordinated \(\mu-O,O'\)-aminocarboxylato Co(II)tpmc complexes in which a weak magnetic interaction was noticed, the magnetic moments at room temperature were in the range 3.96 – 4.72 \(\mu_B\) and slightly varied with decreasing temperature.\(^1\)\(^{3a,b}\) Only in the \(\mu\)-oxalato complex\(^1\)\(^{13}\) was weak antiferromagnetic coupling found, which was explained by the mechanism of super-exchange, most probably facilitated via the common oxygen atom.

The electrochemical behavior for the complexes (1) and (2) was investigated in the range of \(-0.7\) V to \(+1\) V and for complex (3) in the range of \(-1\) V to \(+1\) V (the scan rate was 50 mV s\(^{-1}\)). Their practically identical cyclic voltammograms demonstrate that no decomposition of the complexes occurs in the given ranges, indicating their electrochemical stability. On holding at the potential at \(-1\) V and \(+1\) V for complexes (1) and (2), and at \(-0.7\) V and \(+1\) V for complex (3), no peaks appeared which additionally proved their electrochemical stability.

Scheme 2. Suggested structure of the \([\text{Co}_2(C_6H_5\text{COO})_2\text{tpmc}]^{2+}\) from complex (1) in a chair conformation.
On the basis of the experimental results given above, and by analogy with previously isolated Co(II) complexes containing two additional ligands in addition to tpmc, the most probable structure of the complex (1) is presented in the Scheme 2. Comparing analogous Co(II) and Cu(II) complexes,\textsuperscript{15} it is evident that Cu(II) is pentacoordinated forming a binuclear \( \mu\text{-C}_6\text{H}_5\text{COO}^- \) complex (even in the presence of a large excess of benzoate) with the tpmc being a boat conformation, while in complex (1), two \( \text{C}_6\text{H}_5\text{COO}^- \) were coordinated to each Co(II) in the trans-position, and the tpmc adopted a chair conformation. On the contrary, complexes (2) and (3), according to elemental analyses, electrical conductivities and magnetic data, corresponded to a binuclear Co(II) structure, where the tpmc achieved a boat conformation (Scheme 3a). Pht\textsubscript{2}– or ipht\textsubscript{2}– ligands form bridges in one of the most probable ways presented in Scheme 3b, c and 3d, e, respectively. Taking into account the steric hindrance of tpmc and the bridged ligand(s), the negative inductive effects and the position of the COO– groups, the spectral data of the complexes and their alkaline salts (Tables I and II) compared with some described analogous complexes, the magnetic properties at room temperature, as well as using models, pentacoordination in which some of the oxygens from the dicarboxylate remain non-coordinated, as well as unidentate coordination are excluded. Due to the steric constrains of two adjacent COO– groups, it is supposed that the coordination of bridged pht\textsuperscript{2}– presented in Scheme 3c for complex (2), engages two oxygens from different carboxylic groups, thus forming 7-membered rings, is more probable than for 3b in which 4-membered rings are formed. In some familiar Co(II) tpmc complexes, as was found earlier,\textsuperscript{13} tpmc could change the distance between the metal centers, adapting itself to being a bridged ligand with O-donors of various sizes. Finally, the great stability of the complexes (2) and (3), electrochemically as well as towards air and pure \( \text{O}_2 \) oxidation, which was not observed for some pentacoor-

Scheme 3. Exo coordination mode in binuclear bridged tpmc complexes with a boat conformation (a); the most probable bridged ligand coordination assumed for pht\textsuperscript{2}– (b,c) in the complex ion \([\text{Co}_2\text{(pht)tpmc}]^{2+}\) (2) and for ipht\textsuperscript{2}– (d,e) in \([\text{Co}_2\text{(i-pht)tpmc}]^{2+}\) (3).
dinated \(\mu\)-aminocarboxylato Co(II)tpmc complexes,\(^{13a,b}\) additionally supports the assumption of a bis(bidentate)-bridged stereochemistry for the phthalato and \(i\)-phthalato dianions. As it is known,\(^{15}\) Cu(II)tpmc formed pentacoordinated binclear and tetranuclear complexes with Hpht\(^-\) and \(i\)-pht\(^2-\), respectively. The greater tendency of Co(II), than Cu(II) under the similar conditions, to form hexacoordinated species could explain some of these differences. In conclusion, further effort to grow single crystals suitable for X-ray analysis is in progress. Along with the temperature dependence of the magnetic susceptibility and EPR measurements, as well as their interpretation, this well be an interesting subject for future investigations.

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ИЗВОД

КОБАЛТ(II) КОМПЛЕКСИ СА АРОМАТИЧНИМ КАРБОКСИЛАТИМА И \(\alpha\)-ФУНКЦИОНАЛИЗОВАНИМ ЦИКЛАМОМ КОЈИ ИМА 2-ПИРИДИЛМЕТИЛ ПЕНДАНТНЕ ГРУПЕ

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Добијени су нови динуклеарни Co(II) комплекси са октазамакроцикличним лигандом \(N,N',N'',N''\)-тетракис-(2-пиридилметил)-1,4,8,11-тетраазамакроциклотетраметиламмониум (tpmc) и јединим од ароматичних моно- или дикарбоксилатно лиганда (бензоатном, фталатном или изофталатом). Они су анализирани и окарактерисани помоћу елементалне анализе (C, H, N), електричне проводљивости, VIS и IR спектроскопије као и магнетних и циклично волтаметријских мерења. У \(\text{[Co}_2(C_6H_5COO)_2\text{tpmc]}_2\text{(ClO}_4)_2\cdot3\text{H}_2\text{O}\) бензоатно лиганди су највероватније координацијан бидентатно за сваки Co(II) у \(\text{транспо}^{-}\)-положају, при чему макроциклични лиганд заузима конформацију столице. У комплексима \(\text{[Co}_2(Y)\text{tpmc]}_2\text{(ClO}_4)_2\cdot2\text{H}_2\text{O}\), (\(Y\) = фталатни или изофталатни дијанен, \(z = 2; 4\)) приложено је да су изомери дикарбоксилати комбиновано мостовно и хелатно координацијане. Мерења цикличном волтаметријом су показала да су комплекси електрохемијски стабилни.

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REFERENCES


