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Polynuclear copper(II) complexes bridged by polycarboxylates of aromatic and *N*-heterocyclic compounds

Salah S. Massoud [a,*], Febee R. Louka [a], Mohammed A. Gazzaz [a], Maher M. Henary [b], Roland C. Fischer [c], Franz A. Mautner [d,*]

[a] Department of Chemistry, University of Louisiana at Lafayette, P.O. Box 43700 Lafayette, LA 70504-4370, USA
[b] Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095-1569, USA
[c] Institut für Anorganische Chemie, Technische Universität Graz, A-8010 Graz, Austria
[d] Institut für Chemische Technologie von Materialien, Technische Universität Graz, Stremayrgasse 16, A-8010 Graz, Austria

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ABSTRACT

Two categories of polynuclear Cu(II) complexes bridged by multicarboxylate compounds 2,5-pyridine dicarboxylic acid ($H_2Py^{2,5\text{-dc}}$), 2,4-pyridine dicarboxylic acid ($H_2Py^{2,4\text{-dc}}$), 2,3-pyrazine dicarboxylic acid ($H_2Pyaz^{2,3\text{-dc}}$) and terephthalic acid (H_2tp) have been isolated with the tripod N4-donor ligands tris(2-pyridylmethyl)amine (TPA) and tris(2-isopropyl-2-aminoethyl)amine (iptren). The trinuclear bridged-carboxylato species were obtained with TPA: $[(TPA)Cu\text{-}(\mu_2\text{-}Py^{2,4\text{-dc}})_2Cu(H_2O)_2\text{-}Cu(TPA)](ClO_4)_2{\cdot}2H_2O$ (**1**), $[Cu(TPA)\text{-}Cu(\mu_2\text{-}Py^{2,5dc})_2\text{-}Cu(TPA)](ClO_4)_2$ (**2**) and $[(TPA)Cu\text{-}(\mu_2\text{-}Pyaz^{2,3\text{-dc}})_2Cu(ClO_4)_2\text{-}Cu(TPA)][Cu(TPA)(H_2O)]_2(ClO_4)_4{\cdot}4H_2O$ (**3**), and the dinuclear species $[Cu_2(iptren)_2(tp)](ClO_4)_2$ (**4**) and $[Cu_2(iptren)_2(Pyaz^{2,5\text{-dc}})](ClO_4)_2{\cdot}H_2O$ (**5**) with iptren. The synthesized complexes were characterized by elemental microanalyses, conductivity measurements, IR and UV–Vis spectroscopic techniques as well as by single crystal X-ray crystallography. The nature of polycarboxylate compounds used and the coligands skeletal structure play crucial role in adopting certain carboxylate-bonding mode and the nuclearity of the coordination product.

1. Introduction

Polycarboxylic acid compounds have been extensively used for the design and the construction of many metal–organic-frameworks (MOFs) and metal–organic coordination compounds, not only for their versatile physical properties and potential applications but also for their various fascinating architecture topologies [1–21]. The rich coordination chemistry of the carboxylate containing compounds results from the tendency of the carboxylate groups in binding and bridging metal ions in different coordination modes which of course depend on the nature of the polycarboxylic acid compounds and its flexibility as well as their ability to form hydrogen bonds, metal ions, reaction conditions, solvent used and pH of the reaction. The electronic nature of the coordinated metal ion permits these molecules to adapt special geometrical and topological coordination features and hence to exhibit chemical and physical characteristics that make them interesting for a wide range of potential applications. Some of these applications may include removal and recovery of toxic metal ions and remediation of heavy metals contaminating soil washings [22], gas storage, gas adsorption [23–25], molecular recognition processes in biological systems and in medicine [9,26,27], catalysis [28], electrical conductivity [29], host–guest exchange chemistry [30], nonlinear optics [31] and magnetism [32].

Aromatic and heterocyclic-*N*-donor compounds bearing multicarboxylate groups provide special interest in the construction of polynuclear and polymeric coordination metal(II/III) complexes, where the rigidity incorporated into the aromatic or heterocyclic rings, and the flexibility of the carboxylate groups may lead to the generation of "unpredictable" topological compounds, especially with the involvement of the heterocyclic-*N*-donor atom(s) in the coordination with metal ions. Symmetrical and asymmetrical benzene-dicarboxylate (1,4-, 1,3-, 1,2-) [1,2,4–8], -tricarboxylates (1,2,3-, 1,3,5- and 1,2,4-) [7,13,33] and -tetracarboxylate (1,2,4,5-) [3,33–36] as well as 1,4,5,8-naphthalene-tetracarboxylate [13] have been extensively used. Heterocyclic bases containing polycarboxylic groups such as pyridine-dicarboxylate [13,14,17], -tri, and -tetra-carboxylate [10,17,33,37,38], pyrazine-dicarboxylate (2,5- and 2,3-) [15,18,24,39], imidazole-4,5-dicarboxylate

* Corresponding authors. Tel.: +1 337 482 5672; fax: +1 337 482 5676 (S.S. Massoud). Tel.: +43 316 873 8234; fax: +43 316 4873 8225 (F.A. Mautner).
E-mail addresses: ssmassoud@louisiana.edu (S.S. Massoud), mautner@tu-graz.at (F.A. Mautner).

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[12,13,16,26,40], pyrazole-3,5-dicarboxylate [15] have also been used in the construction of polynuclear and multidimensional network complexes of interesting structural properties.

In this study, we examine how the polycarboxylate positions in the hetereocyclic bases and the nature of the coligands might affect the structural bonding of the polynuclear coordination products. Therefore a new series of Cu(II)-multicarboxylate complexes have been synthesized using the tripod ligands (tris(2-pyridylmethyl) amine, TPA and tris(isopropyl-2-ethyl)amine, iptren) and the multicarboxylic compounds: 2,5-pyridine dicarboxylic acid ($H_2Py^{2,5\text{-dc}}$), 2,4-pyridine dicarboxylic acid ($H_2Py^{2,4\text{-dc}}$), 2,3-pyrazine dicarboxylic acid ($H_2Pyaz^{2,3\text{-dc}}$), 2,5-pyrazine dicarboxylic acid ($H_2Pyaz^{2,5\text{-dc}}$) and terephthalic acid (H_2tp). The structural formulas of the amines and the carboxylic acids used in this study are shown in Scheme 1.

2. Experimental

2.1. Materials and physical measurements

All chemicals and carboxylic acids used in this study were purchased from TCI-America, whereas (tris(2-isopropyl)-2-aminoethyl)amine was obtained from Aldrich Chem. Comp. Tris(2-pyridylmethyl)amine (TPA) was synthesized according to literature methods [41]. The polycarboxylic acid compounds were converted to the corresponding sodium salts by treating the acid with slight excess of aqueous sodium hydroxide solution followed by slow evaporation. Infrared spectra were recorded on a JASCO FT/IR-480 plus spectrometer as KBr pellets. Electronic spectra were recorded using an Agilent 8453 HP diode UV–Vis spectrophotometer. The conductivity measurements were performed using Mettler Toledo Seven Easy conductivity meter and the cell constant was determined by the aid of 1413 μS/cm conductivity standard. Elemental analyses were performed at the Atlantic Microlaboratory, Norcross, Georgia U.S.A.

Caution! Salts of perchlorate and their metal complexes are potentially explosive and should be handled with great care and in small quantities.

2.2. Preparation of the complexes

2.2.1. [(TPA)Cu-(μ_2-$Py^{2,4\text{-dc}}$)$_2$Cu(H_2O)$_2$-Cu(TPA)](ClO_4)$_2$·2H_2O (**1**)

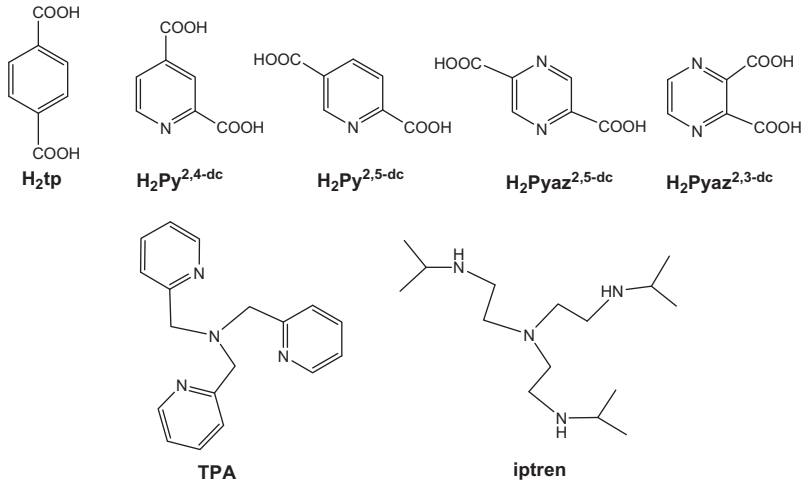
To a mixture of tris(2-pyridylmethyl)amine, TPA (0.146 g, 0.50 mmol) and Cu(ClO_4)$_2$·6H_2O (0.109 g, 0.50 mmol) dissolved in MeOH (20 mL), pyridine-2,4-dicarboxylic acid disodium salt (Na_2-$Py^{2,4\text{-dc}}$) (0.054 g, 0.25 mmol) dissolved in 5.0 mL H_2O was added drop by drop. The resulting solution was heated for 5 min on a steam-bath, filtered through Celite and then was allowed to stand at room temperature. After two days, the resulting crude solid was collected by filtration and recrystallized from H_2O to produe aqua blue single crystals of X-ray quality. These were collected by filtration, washed with propan-2-ol, Et_2O and dried in air (overall yield: 0.105 g, 61% based on $Na_2Py^{2,4\text{-dc}}$). Characterization: $C_{50}H_{50}Cl_2Cu_3N_{10}O_{20}$ (1372.58 g/mol): *Anal.* Calc.: C, 43.75; H, 3.67; N, 10.20. Found: C, 43.42; H, 3.59; N, 10.60%. Selected IR bands: 3567 (w, br) [ν(O–H) stretching)]; 1636 (s) [ν(CO)]; 1606 (s), 1559 (m), 1480 (m), 1443 (m), 1311 (s), 1329 (s); 1082 (vs), 1051 (m) [ν(Cl–O) (ClO_4^-)]. UV–Vis (CH_3CN): λ_{max}, nm (ε_{max} M^{-1} cm^{-1} per Cu atom): ~660 (72), 870 (148, br). Molar conductivity, Λ_M in CH_3CN = 269 Ω^{-1} cm^2 mol^{-1}.

2.2.2. [Cu(TPA)-Cu(μ_2-$Py^{2,5dc}$)$_2$-Cu(TPA)](ClO_4)$_2$ (**2**)

This complex was synthesized using a procedure similar to that described for complex **1**, except 2,5-pyridine dicarboxylate ($Py^{2,5dc}$) was used instead of the corresponding 2,4-pyridine dicarboxylate (overall yield: 67%). Single aquamarine crystals of the complex were obtained upon crystallization from H_2O. Characterization: $C_{50}H_{42}Cl_2Cu_3N_{10}O_{16}$ (1300.51 g/mol): *Anal.* Calc.: C, 46.18; H, 3.26; N, 10.77. Found: C, 46.00; H, 3.35; N, 10.82%. Selected IR bands: 1608 (s) [ν(CO)]; 1481 (m), 1439 (s), 1360 (s); 1078 (vs) [ν(Cl–O) (ClO_4^-)]. UV–Vis (CH_3CN): λ_{max}, nm (ε_{max} $M^{-1}cm^{-1}$ per Cu atom):~460 (sh), 650 (sh), 867 (155). Λ_M (CH_3CN) = 272 Ω^{-1} cm^2 mol^{-1}.

2.2.3. [(TPA)Cu-(μ_2-$Pyaz^{2,3\text{-dc}}$)$_2$Cu(ClO_4)$_2$-Cu(TPA)][Cu(TPA)(H_2O)]$_2$(ClO_4)$_4$·4H_2O (**3**)

To a mixture of tris(2-pyridylmethyl)amine, TPA (0.146 g, 0.50 mmol) and Cu(ClO_4)$_2$·6H_2O (0.109 g, 0.50 mmol) dissolved in MeOH (20 mL), 2,3-pyrazine-dicarboxylic acid ($H_2Pyaz^{2,3\text{-dc}}$) (0.054 g, 0.25 mmol) which was neutralized with LiOH (0.012 g, 0.5 mmol) dissolved in 5.0 mL H_2O was added drop by drop. The resulting solution was heated for 5 min on a steam-bath, filtered through Celite and then was allowed to stand at room temperature. The resulting precipitate, which was obtained after four days was collected by filtration and recrystallized from H_2O to produe aqua blue single crystals of X-ray quality. These were collected by filtration, washed with propan-2-ol, Et_2O and dried in air. (overall yield: 62 mg, 25% based on $H_2Pyaz^{2,3\text{-dc}}$) Characterization: $C_{84}H_{88}Cl_6Cu_5N_{18}O_{38}$ (2516.19 g/mol) *Anal.* Calc.: C, 40.10, H, 3.53,



Scheme 1. Structure formulas of the tripod tetradentate amine ligands and polycarboxylic acids used in this study.