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# Bonding $\mu_{1,3}$- (*trans*) *vs* $\mu_{1,2}$- (*cis*) in squarato-bridging dinuclear copper(II) complexes derived from pyridyl amine ligands

Franz A. Mautner [a,*], Masahiro Mikuriya [b], Yuko Naka [b], Febee R. Louka [c], Salah S. Massoud [c,*]

[a] Institut für Physikalische and Theoretische Chemie, Technische Universität Graz, A-8010 Graz, Austria
[b] Department of Chemistry and Research Center for Coordination Molecule-based Devices, School of Sciences and Technology, Kwansei Gakuin University, 2-1 Gakuen, Sanda 669-1337, Japan
[c] Department of Chemistry, University of Louisiana at Lafayette, P.O. Box 44370, Lafayette, LA 70504, USA

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ABSTRACT

A series of *trans*- and *cis*-dinuclear squarato-bridged copper(II) complexes $[Cu_2(dpya)_4(\mu_{1,3}\text{-}C_4O_4)](ClO_4)_2\cdot MeOH$ (**1**), $[Cu_2(bdmpzpy)_2(\mu_{1,3}\text{-}C_4O_4)(H_2O)_2](ClO_4)_2\cdot 5H_2O$ (**2**) and $[Cu_2(pmea)_2(\mu_{1,2}\text{-}C_4O_4)](ClO_4)_2\cdot 1.5H_2O$ (**3**) derived from di-, tri- and tetra-dentate pyridyl amine ligands ($C_4O_4^{2-}$ is the 3,4-dihydroxycyclobut-3-en-1,2-dione dianion = squarate dianion, dpya = di-2-pyridylamine, bdmpzpy = 2,6-bis[(2,5-dimethyl-1H-pyrazolyl)methyl]pyridine, pmea = bis(2-pyridylmethyl)-2-(2-pyridylethyl)amine) were synthesized and structurally characterized by single crystal X-ray crystallography. In this series, structures consist of the $ClO_4^-$ groups as counter ions and the $C_4O_4^{2-}$ is bridging two Cu(II) ions in a μ-1,3-bis(monodentate) (**1** and **2**) and a μ-1,2-bis(monodentate) (**3**) bonding modes. The coordination environment around the Cu(II) centers in these complexes is a five-coordinate with a distorted square geometry where the intra-dinuclear Cu···Cu distances across the bridged squarato ligand are in the range 7.26–7.82 Å in the *trans* $\mu_{1,3}$- complexes **1** and **2**, and 6.76 Å in the corresponding *cis* $\mu_{1,2}$- complex **3**. The magnetic measurements in the 4.5–300 K temperature range reveal weak antiferromagnetic coupling in the three complexes ($|J| = 2.4\text{–}12.4\ cm^{-1}$).



## 1. Introduction

The symmetrical nature, the π-electron delocalization and the richness of electron density on the squarate dianion, $C_4O_4^{2-}$ (3,4-dihydroxycyclobut-3-ene-1,2-dionate) as well as the presence of four donor oxygen atoms enhance the capability of this molecule to simultaneously bind more than one metal ion and hence acting as a bridging ligand. These properties led to the isolation of many coordination polynuclear and polymeric metal complexes, which have been structurally characterized [1–22]. With 3d metal ions the squarate dianion cannot act as a bis-bidentate linker by forming chelated metal complexes because of its very large bite angle. However, bis-bidentate complexes were observed only with heavier metal ions due to the reduction of the bite parameters [23]. In general, reactions of divalent metal ions of the 1st row of d-bock elements with squarate dianion tend to form mono-dentate coordination mode [1–21]. Five types of bridging-squarato mono-dentate coordination modes have been identified. These bonding modes are illustrated in Scheme 1. The most common of these modes are μ-1,3- (*trans*) (**I**) [1–4,6–15] and μ-1,2- (*cis*) (**II**) [5,9–17]. Bonding modes such as μ-1,2,3- (**III**) [18,19], μ-1,2,3,4- (**IV**) [20,21] and μ-1,1,2,3,3,4 (**V**) [22] were reported but they are very rare. Bis(bidentate)-squarato bridging complex (**VI**) was also observed with $MoO_2^{2+}$ [23]. These bonding modes are illustrated in Scheme 1. In some cases, bonding through μ-1,3- and μ-1,2-coordination modes have led to the formation of polymeric species [1–5]. The bridging squarato bonding modes in these complexes are mainly determined by the structure of the blocking ligand(s) coordinated to the central metal ion, the electronic nature and the geometrical environment around the metal ion. For example the influence of the metal ion was examined in a number of complexes [4,7,9]. The *trans*-squarato $[Cu_2(TPA)_2(\mu_{1,3}\text{-}C_4O_4)](ClO_4)_2$ (TPA = tris(2-methylpyridyl)amine) was isolated, and when $Cu^{2+}$ was replaced with $Ni^{2+}$, the corresponding *cis*-squarato was obtained [9]. Also, when 4,4′-bipyridine was used as a blocking ligand *trans*-squarato polymeric species were obtained with $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$ and $Ni^{2+}$ complexes [4] and similar geometrical products were observed in $[M(\mu_{1,3}\text{-}C_4O_4)(OH_2)_2(DMF/H_2O)_2]_n$ complexes [7].

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

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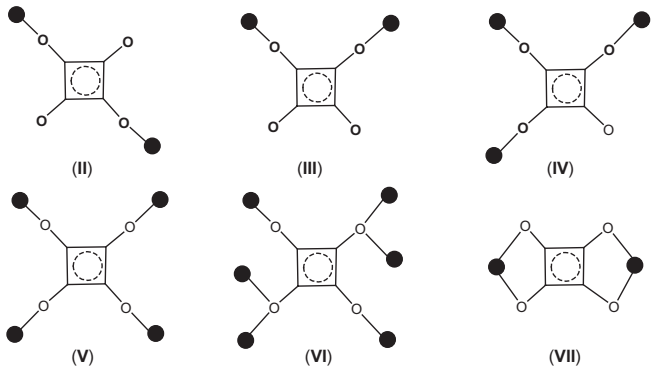



**Scheme 1.** Different coordination modes in bridging squarato-metal(II) complexes.

In squarato-bridged-$M^{II}$ complexes, the average intradimer separation distances between the metal centers vary from ca 5 Å in *cis*, μ-1,2-bonding to 8 Å in the *trans*, μ-1,3-bonding [5,6,8–21]. The magnetic measurements on structurally characterized squarato-bridged dinuclear nickel(II) and copper(II) complexes reveal weak antiferromagnetic interactions between the paramagnetic centers with the singlet–triplet exchange constant, $|J|$ in the range 0–26 $cm^{-1}$ [8–14,16,17]. However, some deviations from this trend were observed and very weak ferromagnetic interactions has been reported in $[Cu_2(bpcam)_2(\mu_{1,3}\text{-}C_4O_4)(H_2O)_4]\cdot 10H_2O$ (bpcam = bis(2-pyrimidyl)amidate) [12].

In a continuous effort to understand the factors that might affect the coordination mode of bonding in the squarato-bridged metal(II) complexes and its impact on the magnetic properties of the complexes, the present study was undertaken. Three ligands based pyridyl groups with structures vary from simple bi- (dpya), sterically tri- (bdmpzpy) to tetra-dentate tripod (pmea) amines were selected (Scheme 2) and their corresponding dinuclear squarato-bridged Cu(II) were synthesized. An attempt was made to correlate the magnetic properties of the complexes to the bonding mode of the bridged-squarate as a function of the structural skeletons of the coligand(s).

## 2. Experimental

### 2.1. Materials and physical measurements

Di(2-pyridyl)amine (dpya) and 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid, $H_2C_4O_4$) was purchased from Aldrich Chem. comp. All other materials were reagent grade quality. Infrared spectra were recorded on JASCO FT/IR-480 plus spectrometer as KBr pellets. Electronic spectra were recorded using Agilent 8453 HP diode UV–Vis spectrophotometer. $^1H$ and $^{13}C$ NMR spectra were obtained at room temperature on a Varian 400 NMR spectrometer operating at 400 MHz ($^1H$) and 100 MHz ($^{13}C$). The molar conductivity of a solution sample was determined from $\Lambda_M = (1.0 \times 10^3\ \kappa)/M$, where κ = cell constant and M is the molar concentration of the complex. The measurements were performed using Mettler Toledo Seven Easy conductometer 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 USA. Magnetic susceptibilities of compounds were measured on polycrystalline powder at Kwansei Gakuin University with a Quantum Design MPMS-XL SQUID susceptometer working in the range 4.5–300 K under a magnetic field of 0.5 T. Diamagnetic corrections were performed by using Pascal's Tables.

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

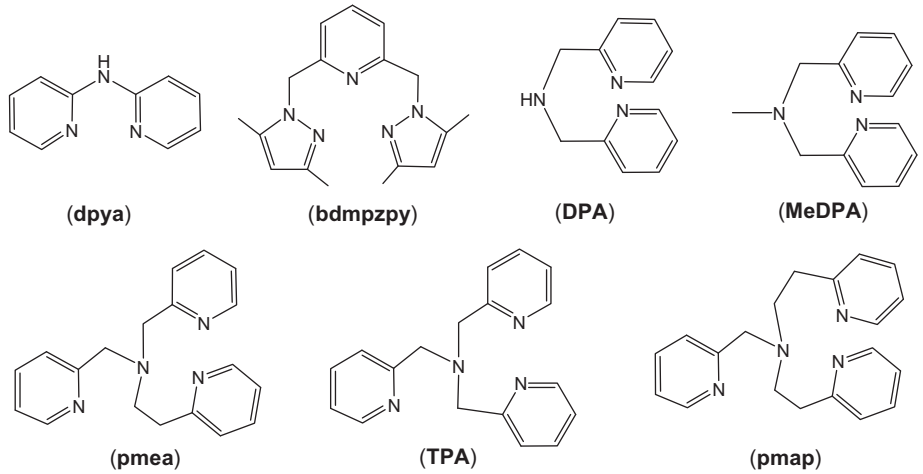
### 2.2. Synthesis of the ligands and complexes

#### 2.2.1. Bis(2-pyridylmethyl)-2-(2-pyridylethyl)amine (pmea) and 2,6-bis[(2,5-dimethyl-1H-pyrazolyl)methyl]pyridine (bdmpzpy)

These ligands were synthesized, purified and characterized according to the published procedures [24,25].

#### 2.2.2. $[Cu_2(dpya)_4(\mu_{1,3}\text{-}C_4O_4)](ClO_4)_2\cdot MeOH$ **(1)**

To a hot mixture of copper(II) perchlorate hexahydrate (0.190 g, 0.50 mmol) and di(2-pyridyl) amine (0.172 g, 1.0 mmol) dissolved in 20 mL $H_2O$, disodium squarate was added (0.081 g, 0.50 mmol). The resulting solution was heated for 15 min, filtered through celite and allowed to crystallize at room temperature. After one week, the green crystals which separated were collected by filtration, washed with 4 mL of cold propan-2-ol then ether and air dried (overall yield: 251 mg, 87%). Crystals suitable for X-ray structure determination were obtained from dilute aqueous solution. Characterization: *Anal.* Calc. for $C_{38}H_{56}Cl_2Cu_2N_{10}O_{17}$ (1154.88 g/mol): C, 46.80; H, 3.49; N, 14.55. Found: C, 46.48; H, 3.36; N, 14.49%. Selected IR bands ($cm^{-1}$): $\nu$(O–H) stretching 3448 (m, br); $\nu$(C=C) 1638 (m), $\nu$(CO) 1584 (m), 1524 (m), 1474 (vs), 1376 (w), 1237 (m); $\nu$(Cl–O) ($ClO_4^-$) (split) 1120 (m) and 1086 (m). UV–Vis in $H_2O$: $\lambda_{max}$ in nm ($\varepsilon_{max}$ $M^{-1}\,cm^{-1}$, per Cu atom): in $CH_3CN$ (sat): 490 sh, ~625 (sh), ~750 (w,b).




**Scheme 2.** Structure formulas of some pyridyl amine ligands used in this study and in other related studies.