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Squarato-metal(II) complexes: Part 5[†]. Polynuclear copper(II) complexes bridged by squarate and croconate dianions

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ABSTRACT

Two polynuclear Cu(II) complexes namely 1-D polymeric $\{[Cu(DPA)(\mu 1,2\text{-}C_4O_4)(H_2O)]\cdot 2H_2O\}_n$ (**1**) and the tetranuclear $\{[Cu_2(DPA)_2(\mu\text{-}1,1,2,3\text{-}C_5O_5)(H_2O)](ClO_4)_2\cdot H_2O\}_2$ (**2**) where DPA = bis(2-pyridylmethyl) amine, $C_4O_4^{2-}$ = squarate dianion, and $C_5O_5^{2-}$ = croconate dianion were synthesized and structurally characterized by X-ray crystallography. The $C_4O_4^{2-}$ and $C_5O_5^{2-}$ dianions are bridging the Cu^{2+} centers *via* a μ-1,2-bis(monodentate) and μ-1,2,3-bis(bidentate)-μ-1-(monodentate) bonding modes in complexes **1** and **2**, respectively. A new coordination bonding mode is reported for the bridged croconate in the later complex. Hydrogen bonds stabilize the supramolecular 2D and 3D systems in the complexes. Magnetic susceptibility measurements for the 1D-polymeric complex **1** reveal insignificant coupling between the Cu(II) ions, whereas the tetranuclear croconato complex **2** exhibits moderate antiferromagnetic coupling between the central Cu(II) ions ($J = -9.4\ cm^{-1}$) and weak antiferromagnetic coupling between the terminal Cu(II) ions ($J = -5.1\ cm^{-1}$).

The coordination chemistry of transition metal ions with benzenoid aromatic oxocarbon dianions, $C_nO_n^{2-}$ ($n = 4$, squarate; $n = 5$, croconate) has attracted considerable attention as these ligands are highly symmetrical and possess extensively delocalized π–electrons over the cyclic ring and the oxygen atoms. In addition to the mononuclear species that can be obtained with these ligands, polynuclear metal complexes with different nuclearity and dimensionality (1D, 2D and 3D) were also isolated. The diverse polydentate nature of the ligands is considered to be the main reason for the construction of polynuclear and polymeric coordination compounds. Both ligands exhibit a variety of coordination modes when they bind metal ions. For instance the bridging squarate dianion acts as *trans*-μ_2-bis- (**I**) and *cis*-μ_2-bis- (**II**) [1–8], μ_3-tris- (**III**) [9,10], μ_4-tetrakis- (**IV**) [11,12] and μ_6-hexakis-monodentate (**V**) ligand [13] (Scheme 1). The corresponding bridging croconate dianion exhibits more complex bonding modes varying from μ_2-bis(monodentate) (**VI** and **VII**) [14,15], μ_3-bidentate-monodentate (**VIII** and **IX**) [16,17], μ_4-bis(bidentate) (**X** and **XI**) [1,18–20,23], μ_5-tris(bidentate) (**XII**) [18], bis(monodentate)-bidentate (**XIII**) [18], bis(bidentate)-monodentate (**XIV** and **XV**) [21–23], bridging bis(monodentate)-bidentate (**XVI**) [24] to bridging bis(monodentate)-bis(bidentate) (**XVII**) [17,21,25]. These modes are illustrated in Scheme 2.

In the squarato 3d metal complexes, the bite angle is too large and hence no chelating or bis(bidentate) coordination modes were observed [11]. These binding modes were observed only with heavier metal ions due to the reduction of the bite parameters [26–28]. In many of the benzenoid metal complexes, the lattice or coordinated water molecules undergo H-bonding of the type O-H···O between the free benzenoid oxygen atoms and hydrogen of the water molecules resulting in the formation of supramolecular structures [2–6,8,14,17]. In general, the majority of bridging structurally characterized squarato- and croconato-complexes derived from paramagnetic metal ions reveal weak antiferromagentic coupling [2–6,9,12,19,20].

Herein, we report the synthesis, structural characterization and magnetic properties of the two polynuclear Cu(II) complexes that result from interaction of the squarate ($C_4O_4^{2-}$) or the croconate ($C_5O_5^{2-}$) dianions with copper(II) perchlorate in the presence of bis(2-pyridylmethyl)amine (DPA): 1-D polymeric $\{[Cu(DPA)(\mu 1,2\text{-}C_4O_4)(H_2O)]\cdot 2H_2O\}_n$ (**1**) [29] and the tetranuclear $\{[Cu_2(DPA)_2(\mu 1,1,2,3\text{-}C_5O_5)(H_2O)](ClO_4)_2\cdot H_2O\}_2$ (**2**) [30].

The IR spectra of the complexes display a broad absorption band in the region 3500–3400 cm^{-1} due to the stretching ν(O-H) vibration of lattice and coordinated water molecules. The strong band observed at 1096 cm^{-1} in **2** was assigned to ν(Cl–O) of the ionic perchlorate. The IR spectrum of the squarato complex **1** also displays strong intensity bands over the 1600–1460 cm^{-1} region. These bands have been

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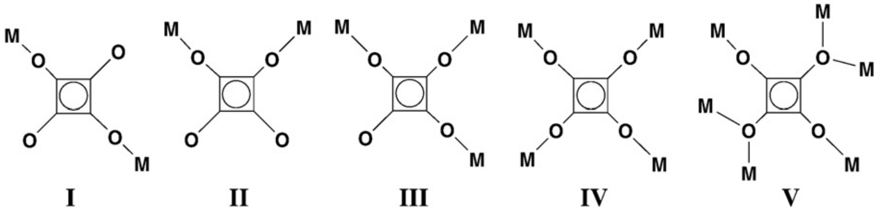


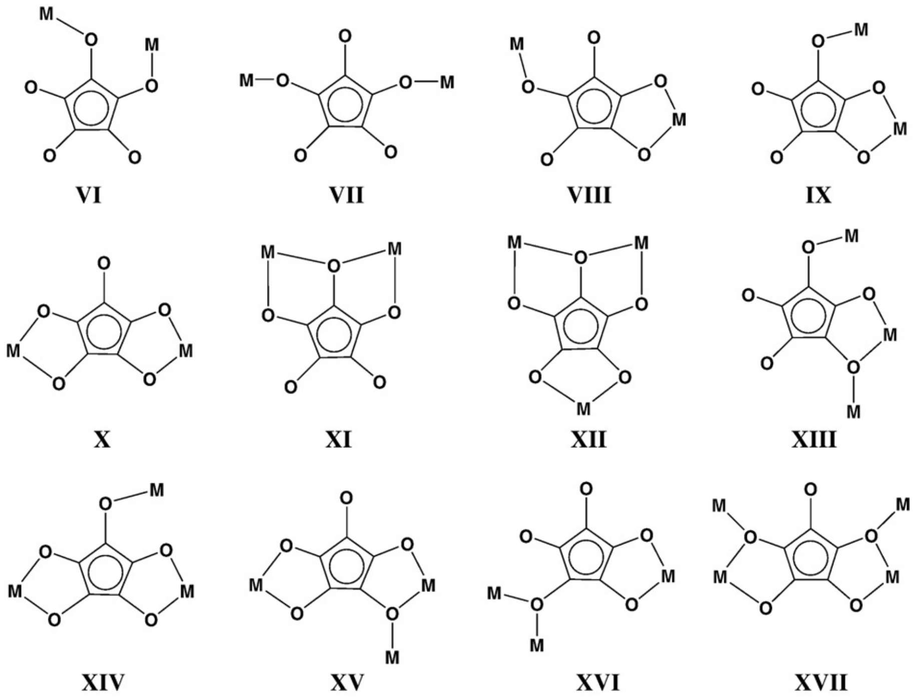
Scheme 1. The coordination bonding modes in bridging squarato complexes.

tentatively assigned to a mixture of C–O and C–C stretching vibration modes of the bridging squarate ligand [12a,31]. The IR features of the croconato complex **2** exhibit a series of bands that are associated with the chelating croconate ligand. The coordinated carbonyl groups are characterized by a strong absorption at 1607 cm^{-1}. The very strong absorption bands located around 1490–1440 cm^{-1} region are assigned to the mixture of ν(C–O) and ν(C–C) stretching vibration modes [20,32] and these are in agreement with those characteristic for $(CO)_n^{2-}$ salts [33].

The visible spectra of the two complexes **1** and **2** recorded in H_2O and/or in CH_3CN reveal the presence of broad absorption maxima around 647 ± 2 nm. These spectral features are most likely consistent with a distorted octahedral geometry for Cu(II) complexes, which are also indicative of a similar ligand field strength around the central Cu^{2+} ion for the two species in solution; i.e., for the same Cu(N$_3$-DPA) (O$_2$-benz)(O-aqua) chromophore.

Single crystal structure determinations (Table S1) reveal that the squarato compound **1** is forming a 1D system, whereas in case of the croconato compound **2** a tetranuclear complex is observed. Complex **1** crystallizes in the acentric monoclinic unit cell P2$_1$ with two independent Cu(II) metal centers. The Cu(II) centers are hexa-coordinated where their CuN$_3$O$_3$ chromophores may be described as elongated square bipyramides with the three N donor atoms of the DPA coligand, and one O of an aqua ligand in basal sites [Cu-N/O bond distances range from 1.992(3) to 2.019(4) Å] and two *trans*-O atoms of the *cis*-squarato bridges in axial sites [Cu-O(axial) from 2.251(3) to 2.370(3) Å] (Fig. 1a, Table S2). The *cis*-squarato bridges form two different 1D chains of polyhedra oriented along the *a*-axis of the monoclinic unit cell (Fig. 1b). The intra-chain Cu···Cu distances are 7.777(16) Å. Hydrogen bonds of types N–H···O and O–H···O form a supramolecular 3D system (Fig. S1, Table S3) as donor atoms act N(amine) of DPA, O(aqua) and O of the two water solvent molecules.

The crystal structure of **2** features centrosymmetric tetranuclear complex cations $[Cu_2(DPA)_2(C_5O_5)(H_2O)]_2^{4+}$, perchlorate counter ions and lattice water molecules. Both Cu(II) centers are hexa-coordinated with CuN$_3$O$_3$ chromophores (Fig. 2). The Cu(1) has a distorted elongated square bipyramid formed by N(1), N(2) and N(3) of DPA blocker, and O(10) of $C_5O_5^{2-}$ ligand in basal sites [Cu-N/O bond distances range from 1.977(3) to 1.985(4) Å] and O(9) and O(10′) in *trans*-axial sites [Cu(1)-O(9) = 2.550(2), Cu(1)-O(10′) = 2.475(2) Å]. Cu(2) is ligated by N(4), N(5) and N(6) of another DPA, O(9) and O(11) of the croconato ligand and O(14) of an aqua ligand. The longer Cu–O bonds are formed by the *trans*-coordinated O(11) and O(14) atoms [Cu(2)-O(11) = 2.529(2), Cu(2)-O(14) = 2.404(3) Å], and the basal Cu(2)-N/O bond lengths are in the range from 1.996(3) to 2.003(3) Å. The croconato bridge occurs *via* the μ1,1,2,3-bridging modes: O(11) is ligated to Cu(2) only, O(9) bridges Cu(1) with Cu(2), O(10) bridges Cu(1) and Cu(1′), whereas O(12) and O(13) are not coordinated to the metal centers [Cu(1)···Cu(1′) = 3.4672(7) and Cu(1)···Cu(2) = 4.3685(7) Å]. Within the tetranuclear subunit the four metal centers, the two croconato bridging anions and the two aqua ligands are coplanar, whereas the four DPA ligands are oriented normal to this central plane. Hydrogen bonds of type N–H···O and O–H···O form a supramolecular 2D system oriented along [1 0 0] and [0 1 1] directions. (Fig. S2, Table 3).



Scheme 2. The coordination bonding modes in bridging croconato-complexes.