



Influence of meridional N₃-ligands on supramolecular assembling and redox behavior of carboxylatocopper(II) complexes

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ABSTRACT

Mononuclear phenylglyoxylato- and 4-R-benzoatocopper(II) complexes with two different 1,3-bis(2-arylimino)isoindoline ligands (aryl = pyridyl, or benzimidazolyl) have been synthesized and characterized. Coordination mode of the carboxylate ligands is very similar (monodentate) in each case, while redox behavior of the copper center is dependent on the aryl- and 4-R-substituents. The supramolecular assembly in the solid state via hydrogen bonds and π -stacking between the ligands can be influenced by the aryl-group and carboxylate ligand.

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Mixed-ligand copper complexes with carboxylate ligands are of perpetual interest due to their interesting structural properties [1,2], therapeutic potential [3] or biomimetic activities [3–5]. *O*-Benzoylsalicylato- and salicylatocopper(II) complexes with the rigid, meridional N₃-ligand 1,3-bis(2-pyridylimino)isoindoline (HL¹, Scheme 1) [6] have been structurally characterized as products from the oxygenation of the corresponding flavonolato- and methylchromatocopper(II) complexes [6,7]. These compounds served as functional models for the copper-containing 2,4-flavonol dioxygenase enzyme [8]. Acetatocopper(II) complexes with other tridentate isoindoline derivatives were also studied as selective peroxylation catalysts for olefins [9]. An interesting, common feature of the structurally characterized complexes is that the carboxylate is coordinated to the copper exclusively as a monodentate ligand in spite that the isoindoline-based ligands allow other bidentate ligands such as flavonol and methylchromone to occupy one quasi-equatorial and one apical position in a square-pyramidal geometry, or another isoindoline [10] to form hexacoordinate, bis-chelate copper(II) complexes. The aim of the present work was to apply the two different isoindolines, 1,3-bis(2-pyridylimino)isoindoline (HL¹) [11] and 1,3-bis(2-benzimidazolylimino)isoindoline (HL²) [11], and the carboxylate ligands shown in Scheme 1 in order to possibly alter the carboxylate coordination mode by electronic and steric effects. As it will be shown the binding mode does not change significantly for a wide spectrum of ligand combinations,

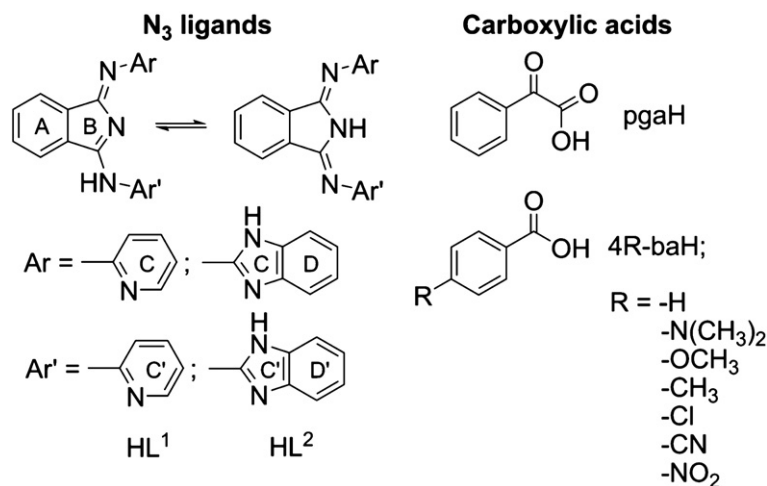
instead systematic change in the supramolecular assembling of the mononuclear complexes is experienced along with changes in the Cu²⁺/Cu⁺ redox potential and reversibility.

The complexes were synthesized according to the procedure in Scheme 2 [12]. Crystallization of the solid products from DMF provided single crystals of **1**, **2**·2DMF and **4**·DMF that were suitable for X-ray crystallography [13–15]. Structure of **1** is shown in Fig. 1a. The Cu(II) center adopts distorted SPY-5 geometry, the basal square plane is constituted of three nitrogens of L¹ (N1, N3 and N5) and one carboxylate oxygen (O1) of pga. The copper atom is out of the N1,N3,N5 plane by 0.128 Å. The steric hindrance of the two pyridyl arms on L¹ pushes the O1 atom out from the fourth equatorial position leading to distortion of the geometry toward TBPY-5 (the τ -value is 0.21 [16]). The apical position is occupied by a water molecule. The distance of the pga O2 atom from the Cu(II) center (2.993 Å) excludes bonding interaction thus the carboxylate is coordinated to the metal as a monodentate ligand. The $\Delta = 184 \text{ cm}^{-1}$ energy difference between the ν_{as} and ν_{s} vibration modes of the carboxylate group that were observed in the FTIR spectrum of **1** (Fig. S1, FTIR data: ref. [12]) also indicates monodentate coordination mode in agreement with the X-ray structural information.

The presence of water ligand, carboxylate and carbonyl oxygen atoms and exocyclic imine nitrogens on L¹ may lead to H-bonding interactions. These interactions are observed in the crystal structure of **1** and indicated with dashed lines in Fig. 1b. For clarity, the pattern of the intermolecular H-bonds is depicted for one of the two individual molecules in the unit cell. Each mononuclear complex is bound to three adjacent ones by four intermolecular

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Scheme 1. Structure of the applied ligands.

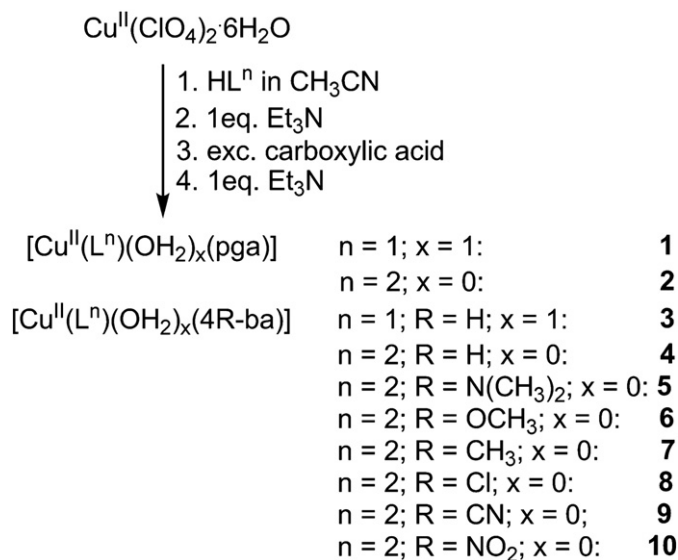
H-bonds of two types: O2[⋯]H2w–O4 and N4[⋯]H1w–O4. Based on the distances and angles (caption of Fig. 1) these two interactions are close in energy and belong to the medium-strength category [17]. The interactions assist in building of a double-chain network of **1** that is further supported by “intra-chain” π -stacking between the A and C, or C' (Scheme 1) heterocyclic moieties of L¹. The geometrical parameters describing the π -stacking are listed in Table 1 (X is the distance between the centroids of the stacked aromatic rings, d is the perpendicular distance between their mean planes, δ is the offset between the centers measured along one of the planes, α is the angle between the line connecting centroids (X) and the normal to the plane of the aromatic system (d), and β is the dihedral angle between the planes in a stack, according to Scheme S1). Somewhat similar interactions were reported for the [Cu(4'-MeL¹(H₂O)₂)⁺ complex (4'-MeL¹ = 1,3-bis{2-(4-methylpyridyl)imino}isoindolate) with TPBY-5 geometry [18]. In the case of **1** a further, sheet-like arrangement of the “double-chains” is observed as shown in Fig. 1c. The chains are anchored by π - π interactions between the benzene rings of the pga ligands (for parameters see Table 1) that lead to a highly organized supramolecular assembly.

In comparison, in single crystals of **2** from DMF the complex adopts a significantly distorted SP-4 geometry with an N₃O donor set (Fig. 2a) where the Cu atom is out of the N1,N3,N5 plane by

0.293 Å. The O2 atom of the pga ligand is found at 2.616 Å from the Cu(II) center that does not support significant bonding interaction. The $\Delta = \nu_{\text{as}}(\text{CO}_2) - \nu_{\text{s}}(\text{CO}_2)$ value from FTIR data (Fig. S2) is smaller (171 cm⁻¹) than in the case of **1** in accordance with the smaller observed Cu–O2 distance.

The presence of NH functions on L² of **2** and the absence of water ligand lead to changes in the intermolecular interactions in comparison with **1**. The N4 and N7 atoms form almost linear H-bonds with two O-atoms (O4 and O5) of DMF molecules (Fig. 2a). Between two 2:2DMF assemblies offset π -stacking forces make contact due to interactions of A and C or C' rings of the two L² moieties (Table 1). These pairs of two independent molecules along with the H-bonded DMF molecules are positioned across a center of pseudosymmetry at the center of the unit cell or at the half of axis a (Fig. 2b). Such interactions were shown to imprint chiral information on supramolecular dimers of Pd complexes with β -pinene containing isoindolines [19]. Furthermore, there are short intermolecular contacts between methyl H-atoms (H34A) of DMF molecules and a neighboring carboxylic O2 atom of a dimeric assembly that render a chain of dimers together (Fig. 2c), where the L² ligands in antiparallel conformation are strongly slipped ($\delta = 2.54$ Å) therefore only weak (if any) stacking can be presumed (Table 1).

Complex **4** crystallizes from DMF with one solvent per complex molecule that is H-bonded to the N7 atom of the L² ligand via H7 (Fig. 3a). The Cu(II) center is four-coordinate, surrounded by a N₃O donor set. The geometry is distorted square-planar where the O1 points out of the plane due to strong steric hindrance of the L² ligand (H-atoms on C21 and C15). To show that the distortion of the SPY-4 geometry is dominantly governed by the steric hindrance of the two *in-plane* H-atoms a brief structural analysis was done with carboxylate complexes that contain L¹ [6], 4'-Me-L¹ [9], L², or 1,3-bis(2-thiazolylimino)isoindolate (L³) [9]. Ligands L¹, L² and L³ have *in-plane* H \cdots H distances that span a range between 3.33 and 4.85 Å (Table S1). A negative relationship was found between the distance of the quasi-equatorial carboxylate O atom from the line of the two *in-plane* H-atoms and the H \cdots H distance (Fig. S3), e.g. the least distorted SPY-4 geometries were found with L³, where the H \cdots H distance is the longest. The Cu atom in **4** is above the N1,N3,N5 plane by 0.361 Å. The Cu1–O2 distance (2.614 Å) is indicative of monodentate coordination of the benzoate ligand. Note that the $\Delta = \nu_{\text{as}}(\text{CO}_2) - \nu_{\text{s}}(\text{CO}_2)$ value from FTIR (Fig. S2) is 162 cm⁻¹, unusually small for a monodentate carboxylate ligand. However, the 4·DMF assemblies form H-bonded dimers in which the N4–H4A \cdots O2' interactions are relatively strong, based on their distance and linearity (Fig. 3a, caption). This interaction can be accounted for the small difference in $\nu(\text{CO}_2)$. The L² moieties are arranged antiparallel in the



Scheme 2. Synthesis and numbering of the mixed-ligand complexes.

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