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Self-Assembly of cis and trans Forms of the Copper(II) Complex with 1-Aminocyclopropane-1-carboxylate into Discrete Trimers in the Solid State

Nenad Judaš*,[†] and Nenad Raos[‡]

Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, HR-10000 Zagreb, Croatia, and Institute for Medical Research and Occupational Health, HR-10000 Zagreb, Croatia

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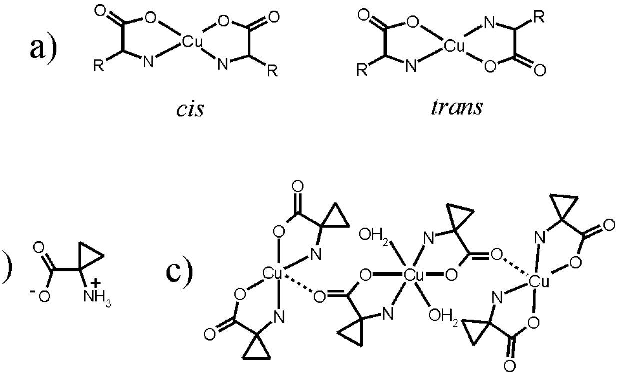
A copper(II) complex with 1-aminocyclopropane-1-carboxylic acid assembles by apical Cu···O bonds and hydrogen-bonding interactions into discrete trimeric units that exhibit both cis and trans binding modes.

Scheme 1



The studies of the biological role of copper have led to the recognition of several coordination modes of copper(II) involving biomolecules[1] such as amino acids[2] or oligopeptides.[3] Specifically, such studies have revealed two distinct coordination environments in complexes with chelating amino acidato ligands. The trans geometry places the two nitrogen atoms of the chelate ligands at the opposite sides of the coordination plane,[4] defined by the four donor atoms, while in the cis geometry, the atoms are on the same side of the plane (Scheme 1a).[5] Available structural data indicate that for a certain amino acidato ligand both forms of the complex appear in the solid state, but never simultaneously.[4,5] In each case, the complex molecules exhibit a propensity to assemble, through a combination of hydrogen bonds, as well as apical Cu···O bonds. Usually, such coordination-driven self-assembly proccesses[6] involving apical Cu···O bonds lead to the formation of sheetlike polymeric structures in the solid state. Our initial interest in the solid-state structures of copper(II) amino acidates was driven by the observation that the complex invloving glycine, a nonchiral amino acid, will undergo a thermaly driven cis-to-trans conversion in the solid state.[7] With the intention to establish the factors that lead to such solid-state reactivity, we have decided to address the symmetry of the lignad. In that context, we have recognized 1-aminocyclopropane-1-carboxylic acid (acc) as a ligand that exhibits the same symmetry properties as glycine (Scheme 1b).[8]

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* To whom correspondence should be addressed. Fax: +385 1 4606 341. Tel: +385 1 4606 368. E-mail: judas@chem.pmf.hr.

[†] University of Zagreb.

[‡] Institute for Medical Research and Occupational Health.

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10.1021/ic060780y CCC: $33.50

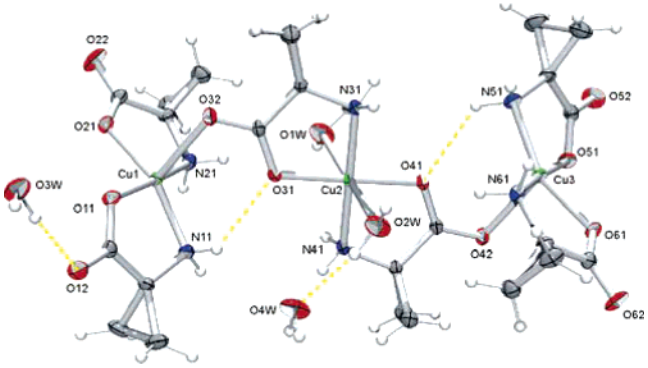

Figure 1. Ortep representation of the trimeric unit in **1**. Non-hydrogen atoms are shown as ellipsoids at the 30% probability level.

Notably, there have been previous reports on the synthesis of acc complexes of transition metal cations, but no structural characterization was performed.[9] We now report that copper(II) and acc assemble in the solid state to provide a trimeric structure unique to copper(II) amino acidates (Scheme 1c).[4,5,10] Specifically, the trimeric complex $[Cu(acc)_2]_3{\cdot}4H_2O$ (**1**) reveals the simultaneous occurrence of both cis and trans forms of the complex in a single crystal.

Compound **1** was prepared in the form of blue crystals (68% yield) from an aqueous ethanolic solution (30 mL, 1:1 v/v) containing 0.102 g (5.11 mmol) of copper(II) acetate monohydrate and 0.102 g (1.01 mmol) of acc. The copper salt was dissolved in boiling aqueous ethanol and added dropwise to a boiling solution of the acc ligand in aqueous ethanol. The color of the solution turned indigo blue, and after 2 days, a fine crystalline precipitate of **1** was filtered off.[11] Single crystals of **1** suitable for X-ray diffraction were obtained from a saturated ethanolic solution by evaporation.[12]

The crystal structure of **1** reveals the formation of discrete trimeric complexes by the linear assembly of $Cu(acc)_2$ building blocks via Cu···O and hydrogen bonding (Figure 1). In the central building block, the acc ligands adopt a trans geometry and the axial coordination of two water molecules provides a slightly distorted octahedral environment for the copper(II) ion Cu2. The nonchelating oxygen atoms of the *trans*-$Cu(acc)_2$ coordinate to copper atoms within peripheral *cis*-$Cu(acc)_2$ units to form trimers (Cu···O distances (Å): Cu1···O32, 2.35; Cu3···O42, 2.31). In that way, the coordination environment of the metal in peripheral units is distorted square pyramidal. The trimers are additionally stabilized by two intramolecular N−H···O hydrogen bonds, wherein acc ligands from peripheral units act as hydrogen bond donors and the oxygen atoms of the central building block act as acceptors (N···O distances (Å): N11···O31, 2.94; N51···O41, 3.09).

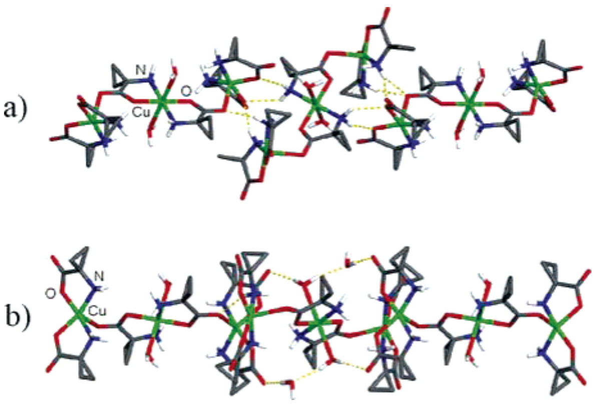

Figure 2. Wireframe representation of the structure of **1**, displaying (a) the formation of layers via N−H···O hydrogen bonding and (b) stabilization of the layers via O−H···O hydrogen bonds.

The trimer molecules self-assemble in the crystal by *inter*molecular N−H···O hydrogen bonds forming the layers that spread perpendicular to the crystallographic *z* direction (Figure 2a). Specifically, the layers are based on a three-point recognition motif involving clusters of three amino groups and three carboxylate oxygens in neighboring trimer units. In that way, the combination of three amino moieties represents a recognition site for a five-coordinate cis complex (Figure 2a). The structure of each layer is additionally supported by O−H···O hydrogen bonds established between water molecules coordinated to the copper(II) ion of the central trans building block and noncoordinated water molecules, as well as noncoordinated carboxylate oxygen atoms of the trimer (Figure 2b).

From the surface of each layer protrude the cyclopropane rings of the amino acidato ligands alongside with noncoordinated carboxylato oxygen atoms and water molecules. The latter join through O−H···O bonds forces connecting the neighboring layers via finite motifs of 16 hydrogen bonds that involve coordinated and noncoordinated water molecules, as well as noncoordinated carboxylate oxygen atoms. Each motif contains a sequence of 12 consecutive hydrogen bonds (Figure 3).[13]

The formation of finite trimeric moieties in solid **1** contrasts the previously reported behavior of solid copper(II) amino acidato complexes. Specifically, the Cu···O and N−H···O forces, which stabilize the trimer of **1**, lead generally to the formation of infinite polymeric structures.[14]

To elucidate factors that lead to the preferred formation of a finite structure, as compared to a polymer, we analyzed

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(9) During the revision of the manuscript, a structure has been reported of a monomeric coppr(II) complex involving 2,2′-dipyridyl and acc as ligands: Ghattas, W.; Gaudin, C.; Giorgi, M.; Rockenbauer, A.; Simaan, A. J.; Réglier, M. *Chem. Commun.* **2006**, 1027.

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(11) Elemental analysis of the obtained **1** provided satisfactory results (%): $C_{calc} = 33.39$ ($C_{exp} = 32.91$), $H_{calc} = 5.14$ ($H_{exp} = 5.07$), $N_{calc} = 9.74$ ($N_{exp} = 9.07$), $Cu_{calc} = 22.08$ ($Cu_{exp} = 24.49$); IR: 3324 ν(NH); 1618 ν(C=O); 1654 cm^{-1} ν(C=O); UV: $\lambda_{max} = 629$ nm.

(12) Crystal Data (**1**): Monoclinic, space group $P2_1/c$, unit cell parameters (Å, deg): $a = 10.1556(9)$, $b = 17.1039(14)$, $c = 20.4373(17)$, $\beta = 101.340(7)$, $V = 3480.7(5)$ Å^3, $Z = 4$, $R = 0.039$ for 5079 reflections with $I \geq 2\sigma(I)$. CCDC reference code: 288147.

(13) Thallapally, P. K.; Katz, A. K.; Carrell, H. L.; Desiraju, G. R. *Chem. Commun.* **2002**, 344.

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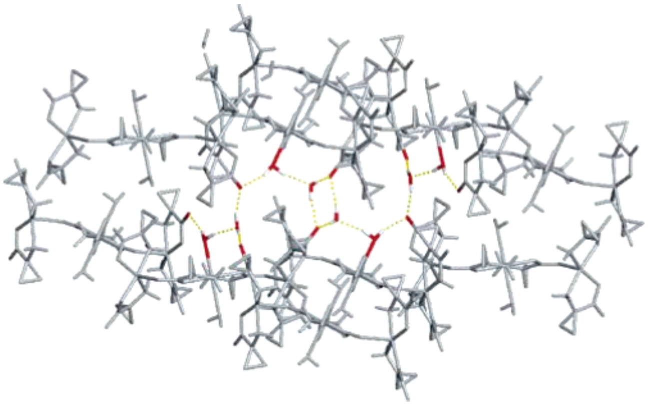

Figure 3. Wireframe representation of the finite sequence of 16 O−H···O hydrogen bonds in the crystal structure of **1**.

excluded volumes in the vicinity of copper atom sites. The analysis was performed by the overlapping spheres method.[15] The volume excluded within a sphere situated on the apical coordination site of copper(II) at a distance of 2.5 Å from the metal ion was calculated. The value of the volume was found to be dependent on cis or trans geometry, as well as on the symmetry properties of the coordination environment, specifically on which side of the coordination plane the sphere is positioned. Notably, assuming a sphere of a 3 Å radius, the excluded volumes of cis moieties are larger on the side lacking any additional ligands (79.8 and 72.9 Å^3 for Cu1 and Cu3, respectively) than on the side of the coordination plane containing the apically coordinated ligand (29.3 and 29.6 Å^3 for Cu1 and Cu3, respectively). However, for the Cu2 atom, in the trans moiety of the trimer, the excluded volumes on both sides of the coordination plane are comparable (42.1 and 39.1 Å^3). The same trend of values is observed in case of a sphere with a 4 Å radius.[16] The results suggest the formation of a polymeric structure in **1** is made difficult by steric hindrance involved in the binding of additional ligands to the apical sites of the cis moieties.

In summary, **1** exhibits structural properties that deviate from previously observed ones in copper(II) amino acidato complexes in two aspects. First, the complex exists in both cis and trans form in the same crystal. Second, in **1** the apical Cu···O bonds that typically result in polymerization[4,5,10] lead to the formation of discrete trimers, suggesting that such weak coordination bonds could have potential in the construction of finite polynuclear complexes.[17,18] The formation of sheetlike structures, characteristic of copper(II) amino acidato complexes, is still achieved in **1**, although by way of hydrogen-bonding interactions only, rather than a combination of apical Cu···O bonding and hydrogen bonds. Further investigations on structural behavior of **1** are currently underway, focusing primarily on thermal behavior with respect to dehydratation and solid-state reactivity.[19]

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Supporting Information Available: Additional spectra of compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Preliminary thermogravimetric measurements reveal that **1** loses water in a broad step that starts at 75 °C and extends well beyond 180 °C, suggesting that a possible cis-to-trans isomerization would be connected by a loss of water molecules.