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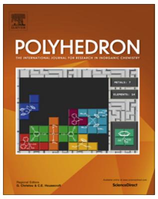

Copper(II) complexes of 7-amino-2-methylchromone and 7-aminoflavone: Magneto-structural, spectroscopic and DFT characterization

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ABSTRACT

Four new complexes of copper(II) consisting of two different chromone derivatives with carbonyl and amine donor atoms: 7-aminoflavone (**L**^{1}) and 7-amino-2-methylchromone (**L**^{2}), were synthesized and characterized by X-ray diffraction, UV–Vis, FT-IR, EPR spectroscopy, MS and elemental analysis. The complexes were synthesized using 2:1 ligand-to-metal ratio, but while three products [Cu(**L**^{2})$_2$Cl$_2$]$_2$ (**1b**), Cu(**L**^{1})$_2$(ClO$_4$)$_2$(H$_2$O)$_2$ (**2a**), Cu(**L**^{2})$_2$(ClO$_4$)$_2$(H$_2$O)$_2$ (**2b**) maintained the applied stoichiometry, the fourth compound showed an unexpected 1:1 ratio and was identified as [Cu(**L**^{1})Cl$_2$]$_n$ (**1a**). In all four compounds, the chromone derivatives were found to act as monodentate *O*- or *N*-ligands. Interestingly, in a doubly chloro-bridged dinuclear complex **1b** each Cu(II) cation interacts with one **L**^{2} ligand through the carbonyl *O*-donor, and with another **L**^{2} molecule through the amine *N*-donor, so the complex adopts a square pyramid geometry. According to a single-crystal X-ray diffraction analysis the complex **2b** is a distorted mononuclear octahedron with the central Cu(II) cation interacting only with oxygen donors (two perchlorate anions, two **L**^{2} ligands, and two water molecules). The structural characteristics of **1a** and **2a** complexes were elucidated from EPR measurements, where their g-tensor components were compared to those observed for **1b** and **2b**, the structures of which were determined by X-ray diffraction method. DFT calculations were performed to estimate the most favored mode of coordination, whereas comparative Hirshfeld surface studies were used to characterize intermolecular interactions in the studied complexes. Magnetic interactions of **1a** and **2a** were also analyzed.

1. Introduction

Natural or synthetic derivatives of 4*H*-1-benzopyran-4-one, 2-phenyl-4*H*-1-benzopyran-4-one and 2*H*-1-benzopyran-2-one (chromone, flavone and coumarin, respectively) are oxygen-containing heterocyclic compounds, which play a key role in initiating the process of free radical formation [1], and are known for being effective monodentante or bidentante chelators. Their actual mode of coordination to a given cation is enforced by additional functional groups. Binding of such ligands (as either *N*- or *O*-donors) to metal ions like Fe(II), Fe(III) and Cu(I) gives rise to complexes having antioxidant properties, however, this process may generate more radicals [2–5]. Certain complexes (most often those of zinc(II) and copper(II)) are significantly more effective scavengers of free radicals than the flavonoids alone [6] and have a wide spectrum of interesting biological and pharmacological properties [7–11], including anti-inflammatory activity and high fluorescence quantum yield [12–14].

Copper(II) is an essential component of many redox metalloenzymes, like cytochrome c oxidase (in mitochondria), superoxide dismutase (also in humans), azurin (in bacteria), and plastocyanin (in plants), and of the oxygen transport proteins such as hemocyanin (in some invertebrate animals). These enzymes are crucial for many important processes, including protection against

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reactive oxygen species (ROS), single electron transport, pigment formation, as well as in production of certain hormones and neurotransmitters. Copper is one of the most important microelements for human body, with a recommended intake of 0.9 mg/day. Its homeostasis must be tightly regulated, because, both, deficiency and too high level of copper(II) often lead to pathological conditions, e.g., neurodegenerative disorders, Menkes' disease, Wilson's disease, or occipital horn syndrome. Therefore, the recommended daily intake average human diet which provides substantial amounts of copper, typically stands at 2–5 mg/day [15–18].

Two chromone-related amine derivatives and their complexes with copper(II) ions have been examined. 7-Aminoflavone (**L^1**) and 7-amino-2-methylchromone (**L^2**) were reacted with $CuCl_2\cdot 2H_2O$ or $Cu(ClO_4)_2\cdot 6H_2O$, and the physicochemical properties of the resultant complexes were compared with those of analogous complexes of 5-amino-8-methylchromone (**L^3**) (Fig. 1).

The crystal structure analysis was extended to include other similar complexes [19–21] and different intermolecular interactions. For selected complexes magnetic measurements were performed to show magneto-structural correlation, while DFT calculations showed the thermodynamically preferred isomers. For compounds with **L^2** or **L^3** ligands, the comparative Hirshfeld surface [22–28] analysis was used to identify characteristic interactions through their crystal structure.

2. Experimental

2.1. Materials and methods

7-Aminoflavone, 7-amino-2-methylchromone, copper(II) chloride dihydrate, copper(II) perchlorate hexahydrate and solvents were purchased from Sigma-Aldrich, Chempur and POCH chemical companies and used without additional purification.

Due to the explosive nature of perchlorate salts copper(II) perchlorate hexahydrate was used with exceptional precautions.

Melting points were determined on a Büchi Melting Point B-540 apparatus in a capillary mode and they were uncorrected.

The infrared transmission spectra of crystalline products were recorded using a Nicolet iS50 FT-IR spectrophotometer equipped with a Specac Quest single-reflection diamond attenuated total reflectance (ATR) accessory. Spectral analysis was controlled by the OMNIC software package.

The FAB-MS spectra were recorded on a Finnigan MAT 95 mass spectrometer (Finnigan MAT, Bremen, Germany). Samples dissolved in DMSO were spiked with 1 µl of 3-nitrobenzylalcohol (NBA) and mixed. For the ionization, a 13 keV beam of cesium ions was used. Spectra were recorded in a positive and a negative ion mode.

Elemental analyses were performed in the Microanalytical Laboratory of the Department of Bioorganic Chemistry (Medical University of Lodz) using a Perkin Elmer PE 2400 CHNS analyzer.

Diffuse reflectance UV–Vis spectra were measured using Nicolet Evolution 220 UV–Vis spectrophotometer (Thermo Scientific) equipped with the integrating sphere (baseline: $BaSO_4$).

X-band EPR spectra of polycrystalline complexes were measured at 295 K using a Bruker Elexys E 500 Spectrometer equipped with an NMR teslamerter and a frequency counter. The experimental spectra were simulated with the DoubletExact program written by Dr Andrew Ozarowski (National High Magnetic Field Laboratory, Tallahassee, USA).

Magnetic measurements in a temperature range 1.8–300 K were performed using a Quantum Design SQUID-based MPMS3-type magnetometer. The SQUID magnetometer was calibrated with the palladium rod sample (Materials Research Corporation, measured purity 99.9985%). Measurements were made at a magnetic field of 0.5 T. Corrections are based on subtracting the sample – holder signal and contribution χ_D estimated from the Pascal constants [29].

2.2. Synthesis of 7-aminoflavone copper complex $[Cu(\mathbf{L^1})Cl_2]_n$ **1a**

A solution of copper(II) chloride dihydrate (17.04 mg, 0.1 mmol) in methanol (1 ml) was added dropwise to a stirred solution of 7-aminoflavone (**L^1**) (47.45 mg, 0.2 mmol) in ethyl acetate (10 ml). The reaction mixture was stirred at room temperature for 24 h. The solid precipitate was filtered off, washed with diethyl ether and dried in the air.

Yield: 49.75 mg (77%). Dark yellow crystals. Mp 214.5–219 °C. IR (KBr): ν (cm^{-1}) 3247m, 3189m, 3112m, 1615s, 1581s, 1549s, 1452s, 1392s, 1059s, 951m, 910m, 860m, 785m, 686m, 671m, 618m, 493w. FAB-MS (m/z): 371.2 $(Cu(\mathbf{L^1})Cl_2)^+$. *Anal.* Calc. for

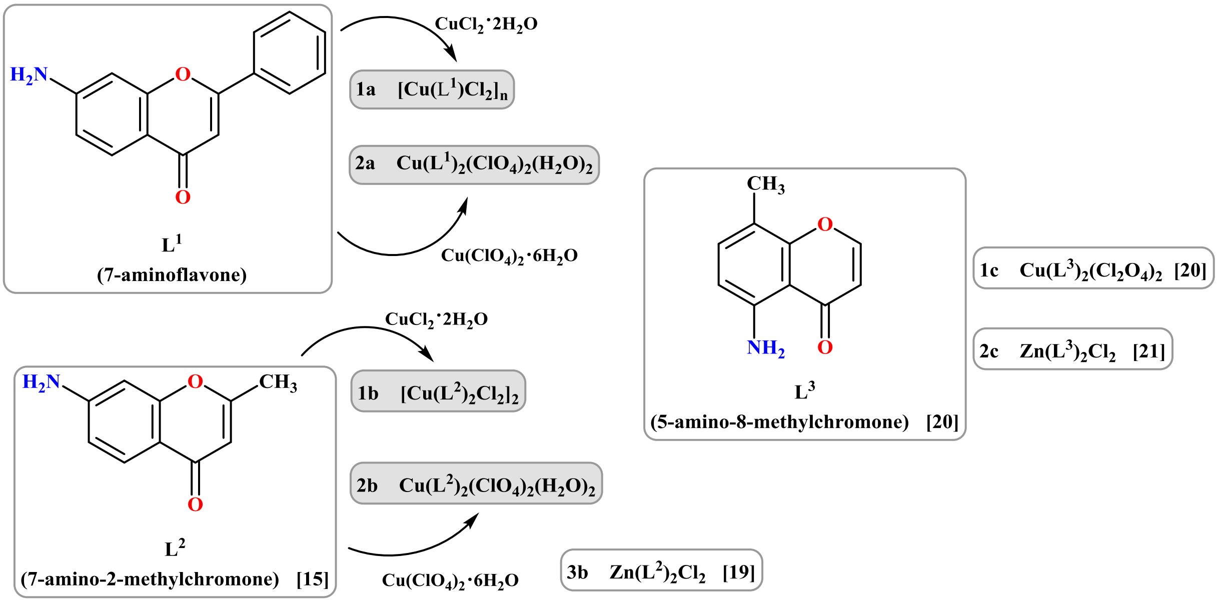

Fig. 1. Ligands and complexes described in this work in comparison to 5-amino-8-methylchromone. General synthesis of complexes **1a**,**b** and **2a**,**b**.