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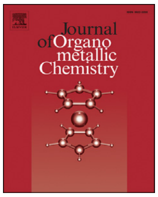

0D and 1D copper(II) coordination polymers based on 2-methyl-1H-imidazole: Structural, vibrational and magnetic characterizations

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ABSTRACT

Bis(2-methyl-1H-imidazolium)tetrachlorocuprate(II), monomer **1**, and 2-methyl-1H-imidazoliumaquatrichlorocuprate(II), polymer **2**, were synthesized and their crystal structures were determined. N/C—H···Cl hydrogen bonds stabilize the monomeric structure of the tetrachlorocuprate(II) anion together with the steric demand of the relatively large 2-methylimidazolium ions in the crystal lattice of **1**. Conversely, in **2**, O—H···Cl hydrogen bonds reduce the electron density on the chloride ions in such a way the electron repulsions decrease and coordination spheres with more ligands develop. Obviously, water may be a successful competitor for ligand sites in **2** as well. In **2**, The square-pyramidal structural parts $[CuCl_3(H_2O)]^-$ condense into polymeric chains of $-CuCl_2(H_2O)$-μ-Cl$-CuCl_2(H_2O)$-μ-Cl$-CuCl_2(H_2O)-$. In both complexes, aromatic amines linked through π···π interactions, are intercalated between the inorganic layers to provide a new structure topology that gathers between supramolecular and lamellar aspects. Magnetic measurements indicate the presence of weak antiferromagnetic interactions in compound **2**.

1. Introduction

The structural properties of chlorocuprates continue to be of interest because of their wide variety of stereochemical features and unexpected oligomeric species [1], as well as their significance for the elucidation of magnetostructural correlations [2,3] and the study of phase transitions [4–6]. One of the consequences of the Jahn–Teller theorem in the stereochemistry of copper(II) has been termed the "plasticity effect" [7], as a result of which copper(II) forms compounds of coordination number varying from 4 to 6, with many kinds of irregular coordination geometries. The geometry of the coordination polyhedron around copper(II) is also influenced by several subtleligand factors, such as ligand constraints and steric hindrance. Hydrated chlorocuprates, due to the possibility of their forming hydrogen bonds, are more complicated structurally than chlorocuprates. Among the hydrated chlorocuprates(II), many types of monomeric and polymeric species, such as $[CuCl_2(H_2O)_2]$ [8,9], $[CuCl(H_2O)]^+$ [10,3], $[CuCl_4(H_2O)]^{2-}$ [11], $[Cu_2Cl_5(H_2O)]^-$ [12,13] and $[Cu_3Cl_8(H_2O)_2]^{2-}$ [14] species, have been reported in recent decades. Complexes of imidazole derivatives with transition metal ions have attracted much attention because of their biological and pharmacological activities, such as antiviral and antimicrobial [15,16], antifungal and antimycotic [17], antihistaminic and antiallergic [18], anthelminthic [19] antitumoural and anti-metastatic properties [20–26]. 2-Methylimidazole, a compound widely used as a chemical intermediate (the manufacture of pharmaceuticals, photographic and photothermographic chemicals, dyes and pigments, agricultural chemicals and rubber), has been detected in cigarette smoke, as a result of pyrolysis. It is also an undesirable by-product in food and forage colored with caramel, such as beer, colas, caramel-colored syrups and soy sauce [27–29]. Thus in order to improve the knowledge in this kind of compounds we report herein the structural, spectroscopic and thermal characterization of both the anhydrous yellow phase $(C_4H_7N_2)_2[CuCl_4]$**(1)** and the hydrated green phase $(C_4H_7N_2)[CuCl_3(H_2O)]$**(2)**. The role of water molecule in stabilizing the structure through hydrogen bonding is explored. Compound **2**, having the shortest Cu···Cu distance, will also be magnetically investigated.

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2. Experimental section

2.1. Materials

All the employed chemicals (Copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$), Hydrochloric acid (HCl; 37%) and 2-methyl-1H-imidazole ($C_4H_6N_2$)) were commercial products (Sigma–Aldrich), which were used without further purification.

2.2. Synthesis

The compounds $(C_4H_7N_2)_2[CuCl_4]$ and $(C_4H_7N_2)[CuCl_3(H_2O)]$ are obtained by slow evaporation at room temperature. $CuCl_2 \cdot 2H_2O$ (1 g) was dissolved in a minimum volume of water. To this solution was mixed 2 g of 2-methyl-1H-imidazole ($C_4H_6N_2$) dissolved in 5 ml of 10 (M) HCl. The clear solution was stirred for 10 min until the complete dissolution and allowed to stand at room temperature. After a few days, yellow crystals of **1** having the form of rods suitable for X-ray diffraction were obtained. According to previous works [30,31], we can note that the concentration of HCl in the reaction medium plays an important role in the synthesis of compounds **1** or **2**. In fact, The green needle shaped crystals of **2** are readily obtained when using a dilute aqueous HCl solution (2 g ($C_4H_6N_2$), 1 g ($CuCl_2 \cdot 2H_2O$) in 10 ml of 6 (M) HCl).

2.3. Single-crystal data collection and structure determination

Small crystals of the two compounds **1** and **2** were glued to a glass fiber mounted on a four-circle Nonius KappaCCD area-detector diffractometer with graphite monochromatized Mo Kα radiation, using an Oxford Cryosystems cooler. Data collection, absorption corrections frame scaling and unit cell parameters refinements were carried out with CrysAlisCCD and CrysAlisRED [32]. The structures analyses were carried out with the monoclinic symmetry, space groups C2/c and $P2_1/c$, for **1** and **2**, respectively, according to the automated search for space group available in Wingx [33]. Structures of **1** and **2** were solved with direct methods using SHELXS-97 [34], and refined by a full-matrix least squares technique with SHELXL-97 [34] with anisotropic thermal parameters for all non H-atoms. The aqua H atoms were located in a difference map and refined with O–H distance restraints of 0.85(2) Å and H–H restraints of 1.39(2) Å so that the H–O–H angle fitted to the ideal value of a water molecule. H atoms bonded to C and N atoms were positioned geometrically and allowed to ride on their parent atoms, with C–H = 0.95 Å and N–H = 0.88 Å. The drawings were made with DIAMOND program [35]. The main crystallographic data and refinement parameters are presented in Table 1.

2.4. Infrared spectroscopy

All IR measurements were investigated using a Perkin Elmer 1600FT spectrometer. Samples were diluted with spectroscopic KBr and pressed into a pellet. Scans were run over the range 400–4000 cm^{-1}.

2.5. Thermal analyses

TGA-DTA measurements of **1** and **2** were performed on raw powders with a TGA/DTA 'SETSYS Evolution' (Pt crucibles, Al_2O_3 as a reference) under air flow (100 ml/min). The thermograms were collected on 10.5 mg samples in the RT-650 °C range (heating rate of 5 °C/min).

2.6. Magnetic studies

DC magnetic measurements were carried out for powder samples placed in a gel capsule, using the MPMS5-XL SQUID magnetometer.

3. Results and discussion

3.1. Infrared spectra

In both IR spectra (Fig. 1a and b, for **1** and **2** respectively), the presence of 2-methylimidazolium was checked, indeed, it is known that the narrow bands at 3153.7 and 3150.90 cm^{-1}, for **1** and **2** respectively, correspond to the ν_{C-H} stretching modes of the 2-methylimidazolium ring [36]. The vibrational bands from 1002 to 1438 cm^{-1} can be assigned to the ring stretching frequency of the 2-methylimidazolium cation [37]. The $\nu_{C=N}$ mode can be found at 1438 cm^{-1}. The bands remaining in the 686–859 cm^{-1} region can be associated with the deformations of the imidazole ring. The IR spectrum of the complex **2** shows a strong and broad band extending over the frequency range 2000–3600 cm^{-1}. The band in this region is attributed to the stretching vibrations, ν_{O-H}, of the hydroxyl groups in the water molecules. The essential features of the bands in this region indicate the presence of hydrogen bond involving the uncoordinated N–H groups of the 2-methylimidazolium cation and aqua H, with Cl atoms.

3.2. Crystal structure

3.2.1. Crystal structure of $(C_4H_7N_2)_2[CuCl_4]$*(**1**)*

The asymmetric unit of $(C_4H_7N_2)_2[CuCl_4]$ consists of one cation and one half-anion, bisected by a twofold rotation axis of the C2/c space group through the metal center: Cu (Wyckoff site: **4e**) (Fig. 2). The Cu–Cl distances range from 2.245 (11) to 2.255 (11) Å and Cl–Cu–Cl angles vary from 97.10 (6) to 134.16 (4)° (Table 2), these values fall in the range reported previously for compounds containing Cu–Cl anions [38]. To determine the geometry around copper ion, the tao parameter (τ_4), which was introduced by Addison, Reedijk and coworkers in 1984 [39], can be helpful. This uses an empirical method based on bond angles to give a percentage of distortion to the ideal extremes, which are tetrahedral and square planar geometries. Calculated τ_4 parameter for **1** is 0.46 which demonstrate that the $[CuCl_4]^{2-}$ anion exhibits an intermediate geometry between regular tetrahedral (T_d) and square planar (D_{4h}) which might be expected since the copper (II) is d^9 and therefore possess an unpaired electron which can cause distortion according to the Jahn–Teller effect. Bond lengths and angles within the 2-methylimidazolium cation are comparable to the values observed in other homologous derivates [36,40]. The crystal packing shows that the isolated molecules form organic–inorganic layers parallels to the (a, c) plane and alternate along the c axis with no significant inter-and intra-stack Cl⋯Cl interactions (shortest being 4.605 (2) Å) with the separation distance between Cu centers being 7.495 (2) Å. These layers are stabilized and interconnected significantly through extensive C/N–H⋯Cl hydrogen bonding between the inorganic and organic moieties and π⋯π stacking interactions between the aromatic rings of the amine molecules themselves (Fig. 3). Indeed, the C⋯Cl distances vary from 3.473 (2) to 3.566 (3) Å, while the N⋯Cl distances vary from 3.090 (3) to 3.232 (5) Å. The centroid–centroid distance and dihedral angle between the aromatic rings are 3.36 Å and 0.00°, respectively, displaying typical π⋯π stacking interactions. These values are almost comparable to the corresponding values for intramolecular π⋯π interactions, showing that π⋯π contacts may further stabilize the structure. Then, both C/N–H⋯Cl and π⋯π stacking