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Structure and magnetism of catena-poly[copper(II)-μ-dichloro-L-lysine]hemihydrate: Copper chains with monochloride bridges

Ricardo C. Santana [a,*], Bruno N. Ferreira [a], José R. Sabino [a], Jesiel F. Carvalho [a], Octavio Peña [b], Rafael Calvo [c]

[a] Instituto de Física, Universidade Federal de Goiás, Campus Samambaia, CP 131, 74001-970 Goiânia (GO), Brazil
[b] UMR 6226 CNRS, Institut des Sciences Chimiques de Rennes, Université de Rennes 1, 35042 Rennes, France
[c] Facultad de Bioquímica y Ciencias Biológicas, Universidad Nacional del Litoral, and INTEC (CONICET-UNL), Güemes 3450, 3000 Santa Fe, Argentina

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ABSTRACT

We report the preparation and characterization by elemental analysis, infrared (IR), single crystal X-ray diffraction, magnetic measurements and electron paramagnetic resonance (EPR) of the new compound catena-poly[copper(II)-μ-dichloro-L-lysine]hemihydrate, with formula $C_6H_{14}Cl_2CuN_2O_2\cdot(H_2O)_{0.5}$, here after called [Cu(lys)Cl_2]. The compound crystallizes in the space group C2 with copper ions in a square pyramidal coordination, and the structure consists of zigzag chains along the ***b*** axis bridged by equatorial-apical chlorine bonds with Cu–Cu distance of 3.5414(4) Å, and a small Cu–Cl–Cu angle of 85.47(6)°. Magnetic susceptibility and isothermal magnetization curves reveals a weak antiferromagnetic interaction $2J = -0.30(2)$ cm^{-1} supported by the Cu–Cl–Cu bridge connecting Cu^{II} neighbors in the chains. EPR spectra at 34.0 GHz were obtained in powdered samples and in a single crystal with $\boldsymbol{B}_0$ in three orthogonal planes. Assuming an axially symmetric molecular ***g***-matrix, we obtained principal *g*-values $g_{//} = 2.2794(9)$ and $g_{\perp} = 2.0489(3)$ from the crystal *g*-matrix calculated using the observed angular variation of the EPR line position. The angular variation of the line width, largest along the chain direction, is attributed to dipolar couplings between Cu^{II} ions in the lattice. The magnetic and EPR results are discussed in terms of the exchange couplings.

1. Introduction

Metal-amino acid compounds are appropriate model systems of biomolecules to investigate the molecular and electronic structure of metal ions in protein-like structures [1] and the exchange interactions transmitted through the chemical paths connecting the unpaired spins [2]. As copper is an abundant bioelement providing active sites to several metalloenzymes and proteins [3–6], many efforts have been oriented to study copper amino acid complexes [7]. Also, several copper(II)-amino acid complexes have been shown to display a spin-chain behavior [8]. L-Lysine is one of three basic amino acids and has a positive charge on its side-chain at pH 7.0, favouring the formation of metal complexes [9].

Since the early work of Dunitz [10], compounds containing Cu^{II} motifs connected by one [11–20] or two [21–25] chloride bridges have been reported. In chain compounds one-chloride bridges may connect equatorial and apical positions, with Cu–Cl–Cu angles varying from 80 to 180°. Magnetic studies and magneto structural analyses in these compounds [11–20] have gained attention in the field of magnetism [26–28], and since the works of Willet et al. [29] and Hatfield et al. [30–32], efforts have been directed to relate the exchange coupling $2J$ ($\mathcal{H}_{ex}(i, i+1) = -2J_{i,i+1}\boldsymbol{S}_i\cdot\boldsymbol{S}_{i+1}$), as generally defined for chain compounds [33]), with the structural features such as Cu–Cl–Cu bond angles, and Cu···Cu and Cu–Cl distances describing the chloro-bridged Cu^{II} motifs [28,29,34].

In this work we have studied the new copper compound catena-poly[copper(II)-μ-dichloro-L-lysine]hemihydrate, here after called [Cu(lys)Cl_2], exhibiting chains of copper ions connected by chlorine bridges with an unusually small Cu–Cl–Cu bond angle. We synthesized the compound, solved the crystal structure, and performed magnetic and EPR studies, with the aim to investigate the electronic properties of the Cu molecules, and the magnetic interactions between neighbor Cu^{II} ions in the chains. The magneto structural correlations of the Cu–Cl–Cu equatorial-apical bond are discussed.

2. Experimental

2.1. Synthesis

2.1.1. Materials

The reagents and solvents were used as received without further purification and all experiments were carried out in open atmosphere. The L-lysine hydrochloride ($C_6H_{14}N_2O_2\cdot HCl$) and copper nitrate trihydrate ($Cu(NO_3)_2\cdot 3H_2O$) used for the synthesis were

* Corresponding author. Tel./fax: +55 62 3521 1014.
E-mail address: santana@if.ufg.br (R.C. Santana).

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2.1.2. [Cu(lys)Cl_2]

Crystals of [Cu(lys)Cl_2] were grown by precipitation from water or ethanol solutions of 1:1 molar ratios of L-lysine·HCl, and $Cu(NO_3)_2{\cdot}3H_2O$. The aqueous solution was prepared by mixing 55.75 g of L-lysine·HCl and 73.71 g of copper nitrate trihydrate in 50 ml of distilled water. The mixture was heated to about 50 °C while vigorously stirred, and after few minutes a clear and homogeneous solution with intense blue coloration was obtained. The solution was allowed to evaporate slowly at 24 °C and few crystals precipitated after 2 months. Alcoholic solutions were prepared by adding 0.500 g of L-lysine·HCl and 0.613 g of copper nitrate trihydrate to 500 ml of ethanol 99.5%, heated to 50 °C and stirred during about 5 h until the complete dissolution of the solutes; the alcohol was allowed to evaporate slowly at 24 °C, and after few days microcrystals were obtained from the clear bluish solution. L-lysine·HCl is highly soluble in water and the viscosity of the solution is large during the crystallization, making difficult the mass transport process and requiring long time for nucleation and growth. On the other hand, the solubility of the compound in ethanol is low, the solvent evaporation does not cause a significant increase in the solution viscosity, and crystals can be obtained after few days. The growth habit of the crystals obtained using both solvents are similar, they display an acicular morphology elongated along the ***b*** axis and well defined prismatic faces. The crystals grown from aqueous solution have dimensions up to about $2 \times 0.3 \times 0.2$ mm^3 while the dimensions of those from alcoholic solutions are few microns. X-ray diffraction measurements demonstrated that crystals grown from both solutions have the same crystal structure. *Anal.* Calc. for $C_6H_{14}Cl_2CuN_2O_2(H_2O)_{0.50}$: C, 24.9; H, 5.2; N, 9.7; Cu, 21.9. Found: C, 24.3; H, 4.6; N, 9.9; Cu, 22.0%.

2.2. Methods

Crystal composition was investigated by elemental analysis of CNH performed on a Perkin Elmer series II 2400 analyzer, and Cu^{II} content by optical emission spectroscopy on a Perkin Elmer 3000 DV. IR spectra were recorded on a Nicolet 510P FT-IR spectrophotometer using [Cu(lys)Cl_2] powder diluted in KBr pellets.

Magnetic measurements were performed with a Quantum Design Squid magnetometer MPMS XL5 using calibrated gelatine capsules as sample holders having a small diamagnetic contribution and containing 78.2 mg of powdered [Cu(lys)Cl_2]. The magnetic susceptibility was measured in the temperature (T) range between 2 and 280 K, under a magnetic field $B_0 = \mu_0 H = 0.1$ T (μ_0 is the permeability of the vacuum). A magnetization isotherm was measured at 2 K with B_0 between 0 and 5 T.

EPR measurements were performed at 300 K in an ESP-300 Bruker spectrometer working at 34.0 GHz (Q-band), with a standard Bruker ER5101Q cylindrical cavity operating with 100 kHz magnetic field modulation, and a rotating magnet. The sample orientation was attained by gluing the *ab* growth face to a cleavage face of a KBr single crystal cubic holder defining a system ***xyz*** of orthogonal axes, with ***x*** ≡ ***a***, ***y*** ≡ ***b***, ***z*** ≡ ***c**** (***c**** = ***a*** × ***b***). This sample holder was mounted on top of a rexolite pedestal inside of the microwave cavity, and the spectra were recorded at 5° orientation intervals of the external magnetic field, in ranges of 180° of the *ab*, *bc** and *ac** planes, at 300 K. The magnetic field at the position of the sample was calibrated using DPPH ($g = 2.0036$) as field marker. Positions and peak-to-peak line widths (ΔB_{PP}) of the resonance were obtained by least-squares fitting of the spectra to Lorentzian derivative line shapes. The positions of the ***b*** axis in the *ab* and *bc** planes were determined within 1° from the symmetry properties of the angular variation of the *g*-value.

2.3. Crystallographic data collection and structure refinements

A needle shaped single crystal of [Cu(lys)Cl_2] was mounted on an Enraf–Nonius KappaCCD diffractometer [35] using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Diffraction data were acquired in φ–ω scan mode using the Bruker–Nonius COLLECT package [36] and the raw data processing was carried out with HKL Denzo–Scalepack [37]. Absorption correction was conducted using the indexed crystal faces and Gaussian quadrature methods [38]. The structure was solved using direct methods with SHELXS-97 [39] and the refinements were performed by full-matrix least squares on F^2 with SHELXL-97 [40]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were positioned geometrically and refined with riding constraints to their parent atoms. The water molecule hydrogen atom H31 was located in the density map and fixed. Art-work representations were prepared using ORTEP-3 [41] and MERCURY [42] from the suite of programs WINGX [43]. Details of the crystallographic and refinement data are given in Table 1.

3. Experimental results

3.1. Spectroscopic results of [Cu(lys)Cl_2]

The IR spectrum, not shown here for brevity, is consistent with the structural results. The NH_2 wagging mode was observed at 1585 cm^{-1} as a sharp shoulder of the intense −COO asymmetric stretching mode band at 1628 cm^{-1}, confirming the complex formation and the covalent bonding to copper. Characteristic stretching modes of the NH_2 group appear at ∼3294, ∼3242 and ∼3134 cm^{-1}. A band at 603 cm^{-1} is attributed to asymmetric vibration of Cu–N [44,45]. Other observed infrared bands are, 1504 cm^{-1} $-NH_3^+$ symmetric deformation, 1406 cm^{-1} $-CH_2$ scissor, 2935 cm^{-1} −C−H asymmetric stretching, 542 cm^{-1} $-COO^-$ wagging, 753 cm^{-1} $-COO^-$ scissor, 801 cm^{-1} $-CH_2$ rocking, 1341 cm^{-1} CH_2 twist [46].

Table 1
Crystal data and structure refinement for [Cu(lys)Cl_2].

Empirical formula	$C_6H_{14}Cl_2CuN_2O_2{\cdot}(H_2O)_{0.5}$
Formula weight	289.65
Temperature	298(2) (K)
Wavelength	0.71073 (Å)
Crystal system	monoclinic
Space group	C2 (N° 5)
Unit cell dimensions	
$a = 20.8260(11)$ (Å)	$\alpha = 90.0(1)$ (°)
$b = 5.8170(2)$ (Å)	$\beta = 104.831(3)$ (°)
$c = 9.4980(5)$ (Å)	$\gamma = 90.0(1)$ (°)
V	1112.30(9) (Å^3)
Z	4
D_{calc}	1.73 (Mg/m^3)
Absorption coefficient	2.422 (mm^{-1})
$F(000)$	592
Crystal size (mm), colour	$0.35 \times 0.05 \times 0.05$, blue
Index ranges	$-25 \leqslant h \leqslant 26$, $-5 \leqslant k \leqslant 7$, $-12 \leqslant l \leqslant 12$
Reflections collected	6995
Independent reflections (R_{int})	2368 (0.045)
Max. and min. transmission	0.904 and 0.685
Refinement method	full matrix least squares on F^2
Data/restraints/parameters	2366/9/138
Goodness-of-fit (GOF) on F^2	1.04
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.042$, $wR_2 = 0.1037$
R indices (all data)	$R_1 = 0.0656$, $wR_2 = 0.117$
Absolute structure parameter	−0.026(19)
Extinction coefficient	0.025(3)
Largest difference peak and hole	0.57 and −0.77 (e Å^{-3})