Journal of Solid State Chemistry 196 (2012) 489–497

Contents lists available at SciVerse ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Crystal structure, spectroscopic, magnetic and electronic structure studies of a novel Cu(II) amino acid complex $[Cu(\text{L-arg})_2(H_2O)]_2(P_4O_{12})\cdot 8H_2O$

H. Hemissi [a,*], M. Nasri [b], S. Abid [a], S.S. Al-Deyab [c], E. Dhahri [b], E.K. Hlil [d], M. Rzaigui [a]

[a] *Laboratory of Materials Chemistry, Faculty of Sciences of Bizerte, 7021 Zarzouna-Bizerte, Tunisia*
[b] *Laboratoire de Physique Appliquée, Faculté des Sciences, B.P. 1171, 3000 Sfax, Université de Sfax, Tunisie*
[c] *Petrochemical Research Chair, College of Science, King Saud University, Riyadh, Saudi Arabia*
[d] *Institut Néel, CNRS—Université J. Fourier, BP 166, 38042 Grenoble, France*

ARTICLE INFO

Article history:
Received 23 March 2012
Received in revised form
23 June 2012
Accepted 2 July 2012
Available online 14 July 2012

Keywords:
L-arginine
Cyclotetraphosphate
Binuclear complex
Crystal structure
Magnetism
Electronic structure calculations

ABSTRACT

Single crystals of a novel copper (II) complex with the amino acid L-arginine (L-arg) and cyclotetraphosphate, $[Cu(\text{L-arg})_2(H_2O)]_2(P_4O_{12})\cdot 8H_2O$, were prepared in aqueous solution and were characterized by X-ray diffraction, spectroscopy (diffuse reflectance, UV–vis and IR) and thermal analysis. Magnetic measurements and electronic structure calculations were also performed. Crystal structure determination reveals that this compound has a nonsymmetrical atomic arrangement, containing mainly a binuclear $[Cu(\text{L-arg})_2(H_2O)]_2^{4+}$ cation and an uncoordinated cyclotetraphosphate counter-anion ($P_4O_{12}^{4-}$). The tetravalent cation contains two independent Cu(II) ions in two different chemical environments. This compound exhibits an antiferromagnetic (AFM) to paramagnetic (PM) phase transition at a temperature (T_N) lower than 2 K. The values of paramagnetic Curie–Weiss temperature (θ_{cw}) and the exchange parameter (J/K_B) emphasize the existence of an antiferromagnetic interaction between the neighboring copper ions.

1. Introduction

Transition metal complexes of amino acids or peptides have been attracted much attention owing to their remarkable physical and chemical properties [1–5], and currently they have interest in supramolecular chemistry and pharmacology. These relatively simple complexes could serve as model systems to enhance our understanding for the more complicated metalloproteins and biochemical processes as well as drug production [6,7]. In addition, the design and self-assembly of metal complexes of amino acids have recently much interest. Yamauchi et al. [8–12] reported a number of Cu(II) complexes of L-arginine ;$[Cu(\text{L-arg})_2]_m(X)\cdot nH_2O$ containing different counter-anions X^{m-} and they demonstrated that the self-organized structures are also controlled by selecting the counter-anion. After these results, this complex family has not known much advancement [13–16]. Particularly, only one Cu(II) complex of arginine containing monophosphate anions is reported [17]. To extend these previous studies on the Cu(II)–Arg–X systems, we have found that it is interesting to use condensed phosphates, in this system, which are strong coordinating counter - anion and potential hydrogen bond acceptors [18]. In this context, we have reported the synthesis and characterization of new binuclear Cu(II)–L-arginine complex of cyclotetraphosphate $[Cu(\text{L-arg})_2(H_2O)]_2(P_4O_{12})\cdot 8H_2O$. In addition, magnetic measurements and electronic structure calculations are presented as well.

2. Materials and methods

2.1. Preparartion of binuclear complex

The title compound was prepared by adding an aqueous solution (15 mL) of L-arginine (0.14 g, 0.82 mmol) to an aqueous solution (5 mL) of $CuCl_2\cdot H_2O$ (0.07 g, 0.41 mmol) with stirring at room temperature. An aqueous solution (10 mL) of $Na_4P_4O_{12}.4H_2O$ (0.10 g; 0.20 mmol), prepared according to the Ondik process [19], was added dropwise and the mixture was allowed to stirring for an additional 1 h. The resulted royal blue solution was allowed to stand over several days to give deep blue parallelepipeds. The PXRD pattern of synthesized product is in good agreement with the calculated pattern from the single crystal data, indicating the phase purity of the sample (Fig. 1).

2.2. Crystal structure determination

X-ray intensities were collected at room temperature using an Enraf- Nonius Mach3 diffractometer equipped with graphite-

---

[*] Corresponding author. Fax: +216 72 590 566.
E-mail address: hanene.hemissi@fsb.rnu.tn (H. Hemissi).

0022-4596/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jssc.2012.07.004

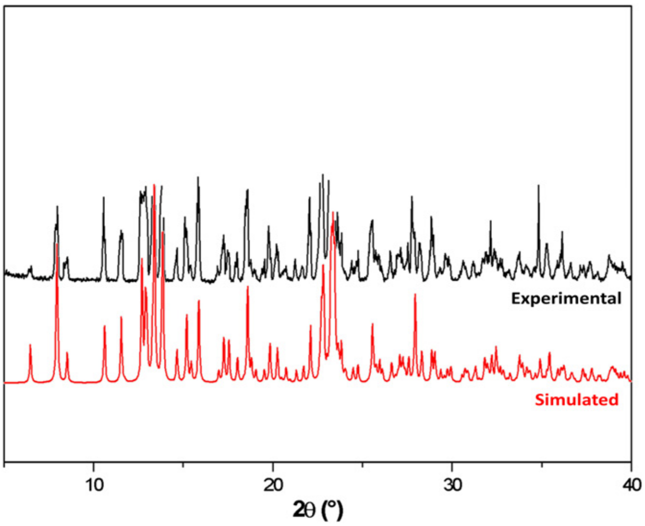

Fig. 1. Simulated and experimental powder X-ray diffraction patterns of $[Cu(L\text{-}arg)_2(H_2O)]_2(P_4O_{12})\cdot 8H_2O$.

Table 1
Crystal data, intensity collection parameters and refinement results for $[Cu(L\text{-}arg)_2(H_2O)]_2(P_4O_{12})\cdot 8H_2O$.

Empirical formula	$C_{24}H_{60}Cu_2N_{16}O_{10}\cdot P_4O_{12}\cdot 8(H_2O)$
Formula weight (g mol^{-1})	1319.97
Crystal system/space group	Triclinic/P1
a (Å)	8.439 (2)
b (Å)	11.715 (2)
c (Å)	14.505 (2)
α (deg.)	107.902 (1)
β (deg.)	97.751 (1)
γ (deg.)	92.412 (2)
Volume (Å^3)	1346.8 (4)
Z	1
Density (calc.) (g cm^{-3})	1.627
$F(000)$	690
θ-Range for data collection (deg.)	2.1–27.0
Index ranges	$-13\leq h\leq 13$, $-18\leq k\leq 18$, $-23\leq l\leq 23$
Reflections collected	12,685
Independent reflections	11,972 [$R_{int}=0.0001$]
Observed reflections [$I>2\sigma(I)$]	5424
Data/restraints/parameters	11,972/37/745
Goodness-of-fit on F^2	0.94
Final R indices [$I>2\sigma(I)$]	$R1=0.0657$; $wR2=0.0887$
R indices (all data)	$R1=0.2160$; $wR2=0.1171$
Largest diff. peak and hole (e Å^{-3})	0.54 and -0.44
Flack parameter	-0.03 (2)

monochromatic Ag$K\alpha$ radiation ($\lambda=0.56087$ Å). The structure was solved by heavy-atom methods using the program DIRDIF [20] in the WinGX package [21]. The model was refined by full-matrix least-squares on F^2 with the program SHELXL-97 [22]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms of the organic ligand were positioned geometrically and were treated as riding on their parent atoms (N, C), with N–H=0.86, C–H=0.93 Å and with $U_{iso}(H)=1.2U_{eq}(C, N)$. Those of water molecules were located from difference Fourier maps and were refined with distance restraints of O–H=0.85 Å and H···H=1.38 Å. The experimental parameters used for the X-ray diffraction data collection as well as the strategy followed for the crystal structure determination and its final results are gathered in Table 1.

2.3. Spectral measurements

UV–vis diffuse reflectance was performed on a Perkin Elmer spectrophotometer type instrument Lambda-45 coupled to an integration sphere type RSA-PE-20 in the range of 400–850 nm with a speed of 960 nm min^{-1} and an aperture of 4 nm. The electronic absorption spectrum was obtained for aqueous solution of the complex ($c=10^{-3}$ M) with a "Perkin-Elmer UV–vis spectrometer Lambda-11" in the range of 400–800 nm, using 10 mm quartz cell. The IR spectrum was recorded in a range of 450–4000 cm^{-1} with a "Spectrum 1000 Perkin-Elmer" spectrophotometer using a sample dispersed in a spectroscopically pure KBr pellet.

2.4. Thermal analysis

Thermal analysis was performed using "multimodule 92 Setaram analyzer" operating from room temperature up to 325 °C at an average heating rate of 5 °C min^{-1}.

2.5. Magnetic measurements

Magnetic measurements were obtained in the temperature range [2–100 K], with an external magnetic field varying from 0.05 to 5 T, using a BS_2 magnetometer developed in Louis Néel Laboratory of Grenoble.

2.6. Electronic structure calculations

The FLAPW method [23] has been used to perform DFT calculations using the local density approximation with wave functions as a basis. The Kohn–Sham equation and energy functional were evaluated consistently using the Full Potential Linearized Augmented Plane Wave (FLAPW) method. In this method, the space was divided into the interstitial and the nonoverlapping muffin tin spheres centered on the atomic site. The employed basis function inside each atomic sphere was a linear expansion of the radial solution of a spherically potential multiplied by spherical harmonics. In the interstitial region, the wave function was taken as an expansion of plane waves and no shape approximation for the potential was introduced in this region which is consistent with the full potential method. The core electrons were described by atomic wave functions which were solved relativistically using the current spherical part; the valence electrons were also treated relativistically in our case. The FLAPW calculations were performed with the crystal structure parameters obtained from our X-ray measurements. Spin polarized potential as well as the antiferromagnetic state was considered.

3. Results and discussion

3.1. Crystal structure description

The asymmetric unit consists of two independent Cu(II) ions, four L-arginine ligands in their zwitter-ionic forms, as well as one cyclotetraphosphate counter-anion and 10 water molecules (Fig. 2). The coordination spheres of the two Cu(II) ions are in the *cis*-equatorial planes formed by two nitrogen atoms and two oxygen atoms of the amino acid groups from a pair of L-arginine molecules acting as bidentate ligands. In both N_2O_2 groups, $N_2O_2(1)$ and $N_2O_2(2)$, around Cu(1) and Cu(2), respectively, the four coordinating atoms are co-planar with the mean deviations from the least-square planes of ± 0.0480 and ± 0.0732 Å. The two metal atoms Cu(1) and Cu(2) are deviated from these planes by $-0.0993(1)$ and 0.1031(1) Å, respectively. These planes are twisted