

A structural evidence for the preferential coordination of the primary amide group versus the unionised carboxyl group: synthesis, molecular and crystal structure, and properties of $[\text{Cu}(\text{HADA})_2]$, a new copper(II) bis-chelate ($\text{H}_2\text{ADA} = N$ -(2-carbamoylmethyl)iminodiacetic acid)

Elena Bugella-Altamirano^a, Josefa María González-Pérez^a, Duane Choquesillo-Lazarte^a, Rosa Carballo^b, Alfonso Castiñeiras^c, Juan Niclós-Gutiérrez^{a,*}

^a Department of Inorganic Chemistry, Faculty of Pharmacy, University of Granada, Granada E-18071, Spain

^b Department of Inorganic Chemistry, Faculty of Sciences, University of Vigo, Vigo E-36200, Spain

^c Department of Inorganic Chemistry, Faculty of Pharmacy, University of Santiago de Compostela, Santiago de Compostela E-15706, Spain

Received 16 September 2002; accepted 8 October 2002

Abstract

Bis(*N*-carboxymethyl-*N*-(2-carbamoylmethyl)glycinato)copper(II) has been synthesised by reaction of $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ and *N*-(2-carbamoylmethyl)-iminodiacetic acid (H_2ADA) in water. The new compound $[\text{Cu}(\text{HADA})_2]$ (1) has been characterised by thermal, spectral, magnetic and X-ray diffraction methods. Its crystal structure was solved to a final value of $R1 = 0.036$. The crystal consists in a 3D hydrogen bonded network builds up by centro-symmetric molecules where the Cu(II) atom exhibits an elongated octahedral coordination. The ligand HADA^- adopts a *fac*-NO+O(apical amido) tridentate chelating conformation [$\text{Cu1-N1}(\text{amino}) = 2.063(2)$, $\text{Cu1-O31}(\text{carboxylato}) = 1.917(2)$, $\text{Cu1-O11}(\text{amido}) = 2.380(2)$ Å] and has a free *N*-carboxymethyl arm. A structural comparison between 1 and bis(*N,N*-bis(carboxymethyl)glycinato)copper(II) dihydrate (compound 2) reveals that the amide primary group is preferred to the unionised carboxyl group to form a Cu(II)-N, O-glycinamide-like chelate ring instead of a Cu(II)-N, O-glycine-like one.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Amide; Copper(II); *N*-(2-carbamoylmethyl)iminodiacetic acid; Acid bis-chelate; Crystal structure

1. Introduction

Since a long time ago it is known that Cu(II) [1–4] or Ni(II) [1,3] atoms are able to give sparingly soluble acid bis-chelates with the diprotonated form H_2NTA^- of nitrilotriacetic acid (H_3NTA) which have the general formula $\text{M}(\text{H}_2\text{NTA})_2 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Ni}, \text{Cu}$). These and other transition or post-transition divalent metal ions also form acid chelates $\text{M}(\text{HNTA}) \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Pb}, \text{Hg}$) [1]. After a preliminary determination

of the space group and unit cell parameters for $[\text{Cu}(\text{H}_2\text{NTA})_2] \cdot 2\text{H}_2\text{O}$ [2] (hereafter compound 2) its molecular and crystal structure was firstly reported by our group [3] and later by others [4]. Compound 2 consists in a hydrogen bonded 3D network. The Cu(II) atom exhibits an octahedral copper(II) coordination, supplied by the two tridentate H_2NTA^- ligands which have a *fac*-NO+O(apical carboxyl) conformation and a free *N*-carboxymethyl arm. In addition, the crystal of $[\text{Cu}(\text{H}_2\text{NTA})\text{Cl}] \cdot 2(\text{melamine}) \cdot 2\text{H}_2\text{O}$ [5] revealed a square based pyramidal Cu(II) coordination supplied by a chloro ligand and once more the H_2NTA^- ligand with a *fac*-NO+O tridentate conformation and a free *N*-carboxymethyl arm. As a part of our program [6] on

* Corresponding author. Tel.: +34-958-243-855; fax: +34-958-246-219.

E-mail address: jniclos@ugr.es (J. Niclós-Gutiérrez).

metal chelates of *N*-carbamoylmethyl-iminodiacetic acid, $\text{H}_2\text{ADA} = \text{H}_2\text{NCOCH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$, we succeeded in preparing a new complex of formula $[\text{Cu}(\text{HADA})_2]$ (compound 1). This compound focuses a noticeable interest because its expectable similarities with compound 2 and also by the fact that other aminotricarboxylic acids (H_3L) (such as nitrilotripropionic acid, *N*-(2-carboxyethyl)iminodiacetic acid and various *C*-substituted-nitrilotriacetic acids) have probed to be inappropriate for the preparation of $\text{Cu}(\text{H}_2\text{L})_2 \cdot n\text{H}_2\text{O}$ derivatives. Indeed, it is also known that the iminodiacetic acid (H_2IDA) as well as various *N*-benzyl-, *C*-alkyl-, *C*-phenyl- or *N,C*-(1,3-propylene)-substituted iminodiacetic acids (H_2Z) have also failed in our attempts to isolate acid bis-chelates of the type $\text{Cu}(\text{HZ})_2 \cdot n\text{H}_2\text{O}$.

2. Results and discussion

The stoichiometric reaction of $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ and H_2ADA in water yields crystalline samples of $[\text{Cu}(\text{HADA})_2]$ (1). However, in order to avoid the precipitation of this sparingly soluble in water product, it was found advantage in the reaction of $\text{Cu}_2\text{CO}_3(\text{OH})_2$ (0.5 mmol), H_2ADA (1.1 mmol) in 120 ml of water, with stirring, heating and under vacuum to remove the CO_2 (by-product) followed by the addition of a solution H_2ADA (1 mmol) in 50 ml of water. To this mixture water was added to the complete solution (total volume ~ 200 ml). The sky-blue crystals of the desired product appeared after no more than one day and were collected in successive fractions to a yield of 375–400 mg (~ 85 –90%). It could be washed with water and air-dried. Compound 1 gave many single crystals, but a considerable number of experiments were carried out until crystals of suitable size for X-ray diffraction studies were obtained. Analytical data were consistent with the above-referred formula. The crystal was studied on an Enraf–Nonius CAD4 diffractometer using $\text{CuK}\alpha$ radiation. Its structure was solved by Patterson and Fourier methods (1682 unique reflections ($I > 2\sigma(I)$) for 160 parameters) and refined by a full-matrix least-squares procedure to a final value of $R1 = 0.036$. Relevant crystal data: monoclinic system, space group $\text{P}2_1/c$; $a = 9.324(1)$, $b = 12.175(1)$, $c = 7.715(1)$ Å; $\beta = 112.74(1)^\circ$, $Z = 2$, $T = 293(2)$ K, $D = 1.817$ mg m^{-3} .

The compound consists in centrosymmetric and elongated octahedral molecules where two HADA^- anions act as *N*-carbamoylmethyl-glycinato-like ligands in a *fac*-NO+O(apical amido) tridentate configuration, also having a free *N*-carboxymethyl arm (Fig. 1). The coordination bond lengths are: $\text{Cu1-N1}(\text{amino}) = 2.063(2)$, $\text{Cu1-O31}(\text{ionised carboxyl}) = 1.917(2)$, $\text{Cu1-O11}(\text{amido}) = 2.380(2)$. The tetragonality is $T = 0.84$. The crystal is a 3D H-bonded network where $-\text{COO}(22)$

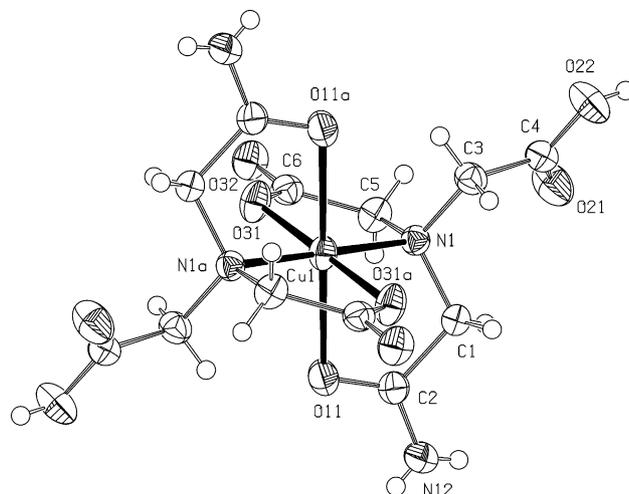


Fig. 1. Molecular structure of $[\text{Cu}(\text{HADA})_2]$.

$\text{H}(22) \cdots \text{O}(32^i)$, $-\text{CON}(12)-\text{H}(12\text{A}) \cdots \text{O}(32^{ii})$ and $-\text{CON}(12) - \text{H}(12\text{B}) \cdots \text{O}(11^{iii})$ interactions are operative (symmetry codes $i = -x, y - 1/2, -z + 1/2$, $ii = x, y, z - 1$ and $iii = x, -y + 1/2, z - 1/2$). It should be noted that the primary amide group acts as O-acceptor and as double N–H donor in these intermolecular links. This active amide role involves amide \cdots carboxylate and amide \cdots amide bridges in the crystal packing. In addition, there are unionised carboxyl \cdots carboxylate bridges, as in Fig. 2 could be appreciate. A structural comparison of compounds 1 ($[\text{Cu}(\text{HADA})_2]$) and 2 ($[\text{Cu}(\text{H}_2\text{NTA})_2] \cdot 2\text{H}_2\text{O}$) seems instructive. In both of them, all polar bonds (O–H or N–H) are involved in the crystal building forming hydrogen bonds. Moreover, the structure of 1 strongly suggests that the amide primary group is preferred to the unionised carboxyl group to form a $\text{Cu}(\text{II})-\text{N}$, O-glycinamide-like chelate ring instead of a $\text{Cu}(\text{II})-\text{N}$, O-glycine-like one. This finding can be rationalised on the basis of the different electron withdrawing effect of the groups $-\text{NH}_2 < -\text{OH}$ on the carbonyl moiety of the functional groups $-\text{CONH}_2$ and $-\text{COOH}$, respectively. Consequently, in compound 1 we should appreciate the coordinating trend of three different but related groups $-\text{COOH}(\text{free}) < -\text{CONH}_2$ (occupying apical sites) $< -\text{COO}^-$ (among the four closest donors). Curiously, the $-\text{C}(\text{NH}_2)\text{O}-\text{Cu}$ bond length in 1 is longer than its related $-\text{C}(\text{OH})\text{O}-\text{Cu}$ bond distance in 2 (2.321(2) Å). This apparent anomaly is explained by the fact that the $-\text{C}(\text{NH}_2)\text{O}-\text{Cu}$ group acts twice as donor whereas the $-\text{C}(\text{OH})\text{O}-\text{Cu}$ acts once as H-donor in hydrogen bonding formation. Compound 1 has an interesting FT-IR spectrum (wave-numbers in cm^{-1}) where bands due to the following modes could be identified: $\nu_{\text{as}}(\text{NH}_2)$ 3315, $\nu_{\text{s}}(\text{NH}_2)$ 3246, $\nu(\text{C}=\text{O})$ 1651 and $\delta(\text{NH}_2) \sim 1620$ –1625 (shoulder) of $-\text{CONH}_2$ chromophores; $\nu(\text{O}-\text{H})$ as a broad absorption in 3800–2300, $\nu(\text{C}=\text{O})$ 1732, $\nu(\text{C}-\text{O}) + \delta(\text{O}-\text{H})$ 1405 and $\delta(\text{O}-\text{H})$ 1214 of H-bonded $-\text{COOH}$

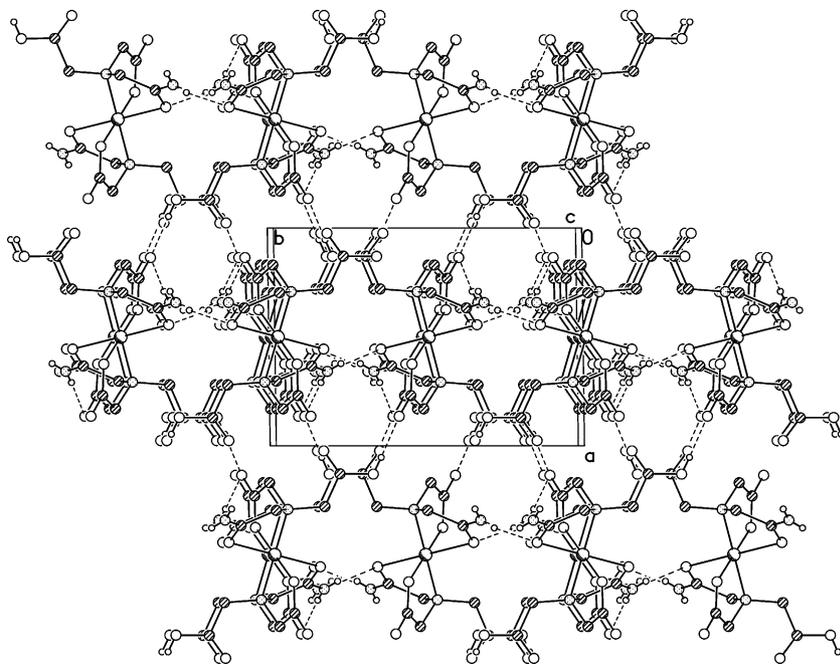


Fig. 2. Crystal packing of $[\text{Cu}(\text{HADA})_2]$.

groups; $\nu_{\text{as}}(\text{COO})$ 1592 and $\nu_{\text{s}}(\text{COO})$ overlapped in the band at 1405 for ionised carboxyl groups. Additional information about the synthesis, thermal stability and spectral (electronic, FT-IR) and magnetic (ESR spectrum, susceptibility data at 80–300 K) properties could be obtained from the authors. Crystallographic data of $[\text{Cu}(\text{HADA})_2]$ have been deposited with the Cambridge Crystallographic Data Centre CCDC 194231.

Acknowledgements

Financial support (research projects BQU2002-04523-C02 and BQU2002-03543) from FEDER (EEC) and MCYT (Spain) and Ph. Doctoral grants to EBA

from MECD (Spain) and DChL from AEIC (MAE, Spain) are gratefully acknowledged.

References

- [1] F.J.M. Rajabalee, *J. Inorg. Nucl. Chem.* 36 (1974) 557.
- [2] S.H. Whitlow, *Inorg. Chem.* 12 (1973) 2286.
- [3] Nguyen-Huy Dung, B. Viossat, A. Busnot, J.M. González-Pérez, S. González-García, *J. Nioclós-Gutiérrez, Inorg. Chem.* 27 (1988) 1227.
- [4] F. Ben Amor, N. Bourguiba, A. Driss, T. Jouini, *Acta Crystallogr., Sect. C* 54 (1998) 197.
- [5] Yugen Zhang, Li Jianmin, M. Nishiura, T. Imamoto, *Chem. Lett.* (1999) 543.
- [6] E. Bugella-Altamirano, J.M. González-Pérez, D. Choquesillo-Lazarte, R. Carballo, A. Castiñeiras, J. Nioclós-Gutiérrez, *Inorg. Chem. Commun.* 5 (2002) 727, and references therein.