

Two intra-molecular inter-ligand C(aromatic)–H···O(carboxyl) interactions reinforce the formation of a single Cu(II)–N4(pza) bond in the molecular recognition between pyrazine-2-carboxamide (pza) and the (iminodiacetato)copper(II) chelate. Synthesis, molecular and crystal structure and properties of [Cu(IDA)(pza)(H₂O)] · H₂O

María Pilar Brandi-Blanco ^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 3 October 2002; accepted 24 October 2002

Abstract

Aqua(pyrazine-2-carboxamide)(iminodiacetato)copper(II) monohydrate, [Cu(IDA)(pza)(H₂O)] · H₂O, was synthesised and characterised by thermal, spectral, magnetic and X-ray diffraction methods. Its crystal structure was solved to a final *R*1 = 0.058. The Cu(II) atom exhibits a square base pyramidal coordination (type 4 + 1) with IDA ligand in *mer*-tridentate configuration [Cu–N(aliphatic) 1.986(7), Cu–O(carboxyl) 1.933(6) and 1.938(5) Å], the Cu–N4(pza) bond [1.984(7) Å] and Cu–O(apical aqua) bond [2.347(8) Å]. The N4-monodentate ligand role of pza is in contrast with that of the *N,O*-bidentate pza-Cu(II) chelation in [Cu(pza)₂(ClO₄)₂] or [Cu(acac)(pza)(ClO₄)] · H₂O. In the molecular recognition between Cu(II) chelate and pza the Cu–N4(pyridine-like) coordination mode is preferred because it enables the additional contribution of two weak intra-molecular inter-ligand C(aromatic)–H···O (IDA) interactions.

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

Keywords: Copper; Pyrazine-2-carboxamide; Iminodiacetate; Crystal structure; Molecular recognition; Hydrogen bond

1. Introduction

Because of the tridentate chelating role of the iminodiacetate(2-) ion (IDA) and the plasticity of the copper(II) coordination stereochemistry, an important research has been devoted to the structure of {[Cu(IDA)(H₂O)₂]_n} (compound 1) [1] and a variety of

mixed-ligand complexes of Cu(II), IDA-like and *N*-heterocyclic donor (auxiliary ligands). These ternary complexes are a source of inorganic structural correlations and bioinorganic model compounds for mono- or di-nuclear copper proteins. IDA exhibits a *fac*-NO + O(apical) conformation in compound 1 and in complexes such as [Cu(IDA)(2,2'-bipy)] · 6H₂O [2], Cu(II)(IDA)(2AMBzimH) [3], [Cu(NBzIDA)(HisNH₂)] [4] and [Cu(II)(IDA)(pyc)] · 2H₂O [5] (bipy = bipyridine, 2AMBzimH = 2-aminomethyl-benzimidazole, HisNH₂ = histamine, pyc = α -picolylamide and NBzIDA = *N*-benzyliminodiacetate(2-) ligand). These latter compounds

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

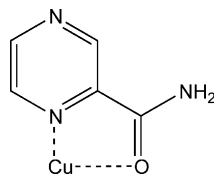
E-mail address: jniclos@ugr.es (J. Niclós-Gutiérrez).

have a Cu/IDA-like/*N*-heterocyclic donor molar ratio 1/1/2 or 1/1/1 + *D* where *D* is an aliphatic *N*-amino atom (for 2AMBzimH [3] and HisNH₂ [4]) or an *O*-amido atom (pyc [5]). In contrast, more than 20 known structures of compounds having an equimolar Cu/IDA-like/*N*-heterocyclic donor ratio (1/1/1) have IDA-like in *mer*-NO₂ chelating configuration. These cases include mono- and di-nuclear adenine Cu(II) derivatives [6] and the di-nuclear compound with bridging pirazine (pz) [(H₂O)₂(IDA)Cu(μ-pz)Cu(IDA)(H₂O)₂] · 2H₂O [7]. On this basis, we found it instructive to investigate the role of the pyrazine-2-carboxamide (so-called pyrazinamide, pza) as auxiliary ligand for the Cu(IDA) chelate because we could expect its *N,O*-bidentate chelation ('pyc-like mode', Scheme 1) or its N4-monodentate coordination ('pz-like mode', Scheme 2).

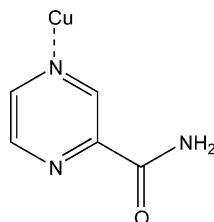
It is known that pza (an anti-tuberculosis drug) crystallises as four polymorphs [8] and plays a 'pyc-like role' in its mixed-ligand Cu(II) complexes with acetylacetonato [9] and/or perchlorato [10] ligands. Such pyc-like coordination is also known in three Cu(II)-pyrazine-2,3-dicarboxamide derivatives [11]. Interestingly pza binds to the Cu(I) atom by its N4 donor ('pz-like mode') [12] or as bridging ligand [13] (with 'pz-like and pyc-like coordinations').

2. Results and discussion

By reaction of Cu₂CO₃(OH)₂ (1 mmol), H₂IDA (2 mmol) and pza (2 mmol) in 150 ml of water, a blue solution was obtained. Its evaporation first produces light blue crystals of compound 1 (which were filtered off) and then dark blue crystals of the title compound 2 and white crystals of pza. These latter products can be separated to obtain a pure sample of 2 in a ~20% of yield. Analytical data were consistent with a formula type Cu(IDA)(pza)·2H₂O. The sample contains suitable crystals for the structure determination, which was



Scheme 1.



Scheme 2.

solved from 2705 unique reflections ($I > 2\sigma(I)$) by direct methods to a final value of $R1 = 0.058$ (triclinic system, space group *P*-1; $a = 7.219(1)$, $b = 9.710(1)$, $c = 10.545(1)$ Å; $\alpha = 107.47(1)$, $\beta = 90.70(1)$, $\gamma = 103.77(1)^\circ$, $Z = 2$, $T = 293(2)$ K, $D = 1.647$ mg m⁻³). The O2 atom of non coordinated water is disordered over two positions with occupancy factors of 0.58(4) and 0.42(4) for O2A and O2B, respectively. Compound 2 has a molecular structure (Fig. 1). The Cu(II) atom exhibits a square base pyramidal coordination (type 4 + 1) supplied by IDA in *mer*-NO₂ tridentate coordination, the N4(pza) donor and the apical O-aqua ligand. The tetragonality $T = 0.84$ is in accordance with the Cu–OW bond length and the distortion towards a bipyramidal coordination has a significant low value ($\tau = 3.3\%$). The rather planar amide group and the heterocycle ring of the pza define a dihedral angle of only 3.8(5)^o due to the intra-ligand hydrogen bonding interaction N4–H4B...N3 (2.34(1) Å, 106^o). Moreover, the heterocycle ring of pza ligand and the basal coordination plane P1 define a dihedral angle of only 10.5(4)^o. This latter angle has a remarkable structural significance because it enables two weak intra-molecular inter-ligand interactions of the type C(aromatic)–H...O (coordinated carboxyl) as Fig. 1 reveals. They are C31–H31...O21 (2.96(1) Å, 119^o) and C34–H34...O11 (3.00(1) Å, 117^o). It seems clear that both C(arom)–H...O interactions actively contribute to the internal geometry of the complex molecule. We can conclude that the Cu–IDA chelate and pza selectively recognise each other by the formation of the Cu–N4(pza) coordination bond and the referred C–H...O two hydrogen bonds. The crystal

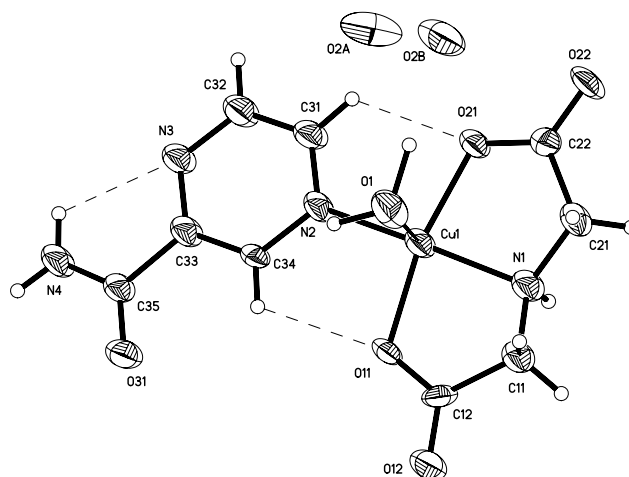


Fig. 1. Molecular structure of [Cu(IDA)(pza)(H₂O)] · H₂O showing the intra-ligand interaction N4–H...N3 in pza and the two C(aromatic)–H...O (carboxyl) intra-molecular inter-ligand interactions which reinforce the Cu–N(pza) bond, thus contributing to the Cu(IDA)-pza molecular recognition. Bond lengths (Å): Cu1–O21 = 1.933(6), Cu1–O11 = 1.938(5), Cu1–N2 = 1.984(7), Cu1–N1 = 1.986(7), Cu1–O1 = 2.347(8). Trans-coordination angles (°): O21–Cu1–O11 = 168.1(2), N2–Cu1–N1 = 166.2(3).

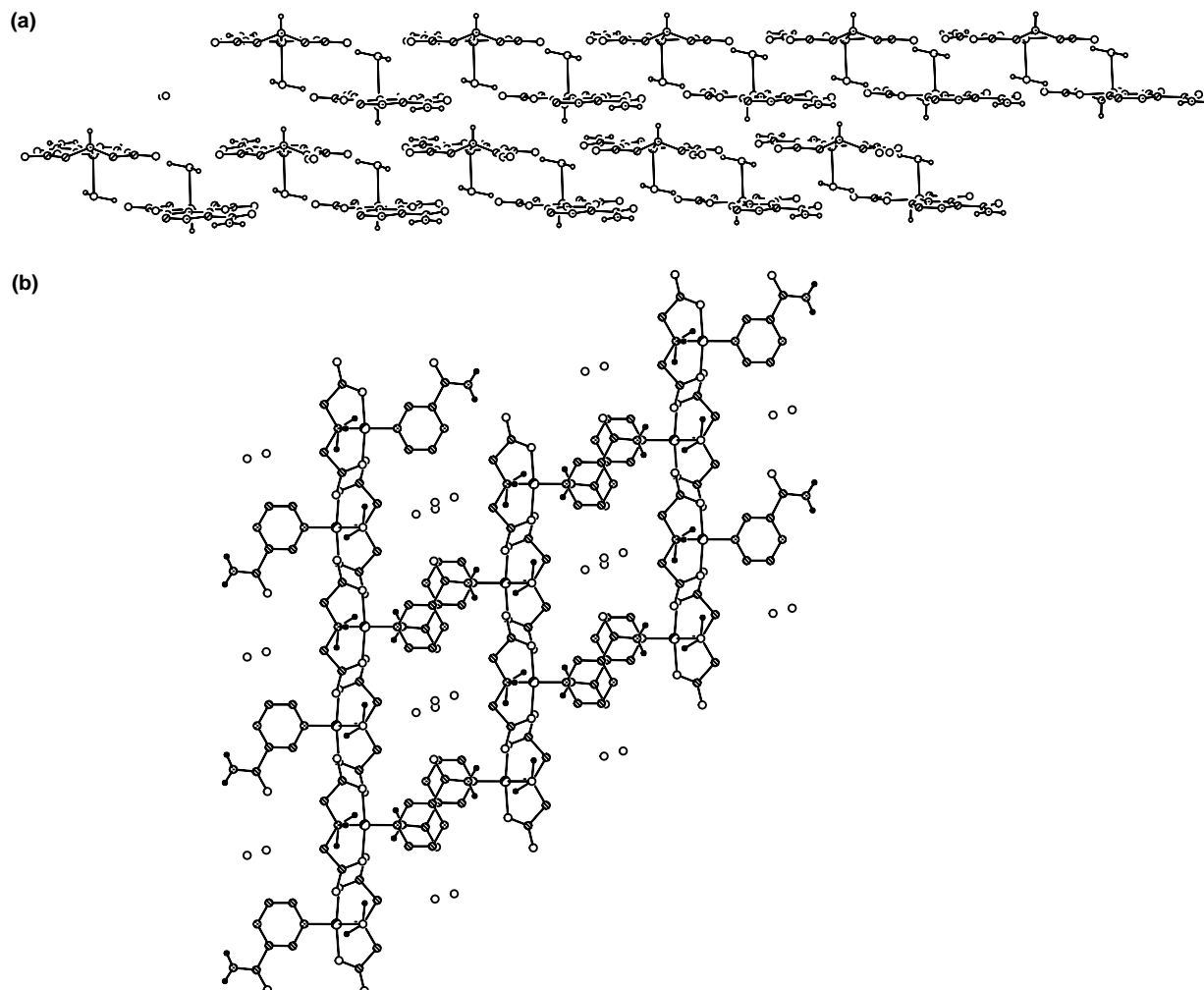


Fig. 2. Crystal packing of [Cu(IDA)(pza)(H₂O)] · H₂O. (a) Fragments of two 2D framework with the apical aqua ligands inside. (b) Disordered non-coordinated water molecules inside the channels formed by superimposed 2D frameworks.

consists in bi-layers of hydrogen bonded molecules connected inside by O–H···O (carboxyl) bridging interactions between aqua ligands of one layer and O(IDA) acceptors (O12 and O22) from the other. The pza ligand lies at the external faces forming N–H···O (carboxyl) bond with O12 and O22 IDA acceptors of the same layer. The faces of such 2D framework (Fig. 2(a)) have N–H(IDA) groups oriented towards two O-acceptors from adjacent ones forming weak bifurcated interactions (N1–H1···O12 + N1–H1···O22; 3.15 Å, 134(2)°). The remarkable weakness of these latter interactions is due to the implication of the non-coordinated O(IDA) acceptors [O12 and O22] in three H-bonding interactions. These 2D frameworks superimpose in the crystal forming channels where non-coordinated water molecules lie disordered as referred to above (Fig. 2(b)). No π , π -stacking interactions are operative because closest parallel pza-rings ($\alpha = 0.00^\circ$), which fall at an appropriate inter-planar distance (3.33 Å), are too much slipped ($\beta = \gamma = 33.7^\circ$). Additional

information about the synthesis, thermal stability and spectral (electronic, FT-IR) and magnetic (ESR spectrum, magnetic susceptibility at 80–300 K) properties could be obtained from the authors. Crystallographic data of [Cu(IDA)(pza)(H₂O)] · H₂O have been deposited with the Cambridge Crystallographic Data Centre CCDC 194230.

Acknowledgements

Financial support (Research Projects BQU2002-04523-C02 and BQU2002-03543) from the MCYT (Spain) and Ph. Doctoral grant to DChL from AEIC (MAE, Spain) are gratefully acknowledged.

References

- [1] M.J. Román-Alpiste, J.D. Martín-Ramos, A. Castiñeiras-Campos, E. Bugella-Altamirano, A.G. Sicilia-Zafra, J.M. González-Pérez, J. Nicolás-Gutiérrez, *Polyhedron* 18 (1999) 3341.

- [2] (a) G. Nardin, L. Randaccio, R.P. Bonomo, E. Rizzareli, J. Chem. Soc., Dalton Trans. (1980) 369;
(b) A. Castiñeiras, M.E. Abarca, I. de la Cueva, J.M. González, J. Niclós, J. Coord. Chem. 30 (1993) 273.
- [3] I.S. de la Cueva, A.G. Sicilia, J.M. González, E. Bugella, A. Castiñeiras, J. Niclós, React. Funct. Polym. 36 (1998) 221.
- [4] E. Bugella-Altamirano, J.M. González-Pérez, A.G. Sicilia-Zafra, A. Castiñeiras-Campos, J. Niclós-Gutiérrez, XI Spanish-Italian Congress on Thermodynamics of Metal Complexes, Valencia, Spain, 1998, Report P18.
- [5] E. Bugella-Altamirano, J.M. González-Pérez, D. Choquesillo-Lazarte, J. Niclós-Gutiérrez, A. Castiñeiras-Campos, Z. Anorg. Allg. Chem. 625 (2000) 930.
- [6] (a) E. Bugella-Altamirano, D. Choquesillo-Lazarte, J.M. González-Pérez, M.J. Sánchez-Moreno, R. Marín-Sánchez, J.D. Martín-Ramos, B. Covelo, R. Carballo, A. Castiñeiras, J. Niclós-Gutiérrez, Inorg. Chim. Acta 339 (2002) 160;
(b) M.J. Sánchez-Moreno, D. Choquesillo-Lazarte, J.M. González-Pérez, R. Carballo, A. Castiñeiras, J. Niclós-Gutiérrez, Inorg. Chem. Commun. 5 (2002) 800.
- [7] (a) Xu Duanjun, Cheng Chaorong, Xu Yuanzhi, Zhou Kangjing, Jiegou Xuaxue 6 (1987) 39;
(b) Xu Yuanzhi, Cheng Chaorong, Xu Duanjun, Chen Deyu, Huaxue Wuli Xuebao 2 (1989) 450.
- [8] (a) Y. Takaki, Y. Sasada, T. Watanabe, Acta Crystallogr. 13 (1960) 693;
(b) R.K. Tiwari, N. Deo, T.P. Singh, J. Sci. Res. Bhopal, India 2 (1980) 161;
(c) R.K. Tiwari, T.C. Patel, T.P. Singh, Indian J. Phys. Sect. A 56 (1982) 413;
(d) G. Ro, H. Sorum, Acta Crystallogr., Sect. B 28 (1972) 991.
- [9] Z. Jin Zhong, N. Matsumoto, H. Okawa, S. Kida, Mem. Fac. Sci. Kyushu U., Ser. C. 17 (1990) 221.
- [10] M. Sekizaki, Acta Crystallogr., Sect. B 29 (1973) 327.
- [11] (a) C.L. Klein, E.D. Stevens, C.J. O'Connor, R.J. Majeste, L.M. Trefonas, Inorg. Chim. Acta 70 (1983) 151;
(b) M. Mondal, S. Ray, Acta Crystallogr., Sect. B 33 (1977) 2297;
(c) M. Sekizaki, Bull. Chem. Soc. Jpn. 54 (1981) 1461.
- [12] (a) M.A.S. Goher, F.A. Mautner, J. Chem. Soc., Dalton Trans. (1999) 1535;
(b) M.A.S. Goher, F.A. Mautner, Polyhedron 19 (2000) 601.
- [13] M. Munakata, L.P. Wu, T. Kuroda-Sowa, M. Maekawa, K. Moriwaki, S. Kitagawa, Inorg. Chem. 36 (1997) 5416.