

# The unexpected tridentate role of the tripodal ligand *N*-(carbamoylmethyl)iminodiacetato(2<sup>−</sup>) (ADA) in a new mixed-ligand nickel(II) complex with 2,2′-bipyridine (bipy) as secondary ligand: structure of [Ni(ADA)(bipy)(H<sub>2</sub>O)]·4H<sub>2</sub>O

E. Bugella-Altamirano <sup>a</sup>, J.M. González-Pérez <sup>a</sup>, D. Choquesillo-Lazarte <sup>a</sup>,  
R. Carballo <sup>b</sup>, A. Castiñeiras <sup>c</sup>, J. Niclós-Gutiérrez <sup>a,\*</sup>

<sup>a</sup> Department of Inorganic Chemistry, Faculty of Pharmacy, University of Granada, Campus de Cartuja, s/n, E-18071 Granada, Spain

<sup>b</sup> Department of Inorganic Chemistry, Faculty of Sciences, University of Vigo, E-36200 Vigo, Spain

<sup>c</sup> Department of Inorganic Chemistry, Faculty of Pharmacy, University of Santiago de Compostela, E-15706 Santiago de Compostela, Spain

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## Abstract

The crystal structure of a new mixed-ligand nickel(II) complex of *N*-(carbamoylmethyl)iminodiacetato(2<sup>−</sup>) (ADA) and 2,2′-bipyridine (bipy), with formula [Ni(ADA)(bipy)(H<sub>2</sub>O)]·4H<sub>2</sub>O (compound 3), reveals an unexpected tridentate ADA ligand, with a free *N*-(2-amidomethyl) arm, in contrast with all other known structures of metal–ADA chelates which have ADA<sup>2−</sup> as tripodal–tetradentate ligand. This finding is explained on the basis of a structural comparison with the compounds of [Ni(ADA)(H<sub>2</sub>O)<sub>2</sub>] (1) and [Ni(ADA)(Him)(H<sub>2</sub>O)]·1.5H<sub>2</sub>O (2, Him = imidazole) which reveals significant changes in Ni–N(amino tertiary) and Ni–O(amide) bond lengths as well as in the ADA denticity and ligand conformation concerning the iminodiacetato(2<sup>−</sup>) moiety (IDA) in these Ni(II) chelates. The ADA-ligand conformation is *mer*-IDA + O(amide), *fac*-IDA + O(amide) or only *fac*-IDA-tridentate in 1, 2 or 3 respectively. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Ligand conformation; Denticity; Amide; Iminodiacetate; Bipyridine; Nickel complex

## 1. Introduction

Alkaline earth, transition and post-transition metal chelates of *N*-carbamoylmethyl-iminodiacetic acid [H<sub>2</sub>ADA = H<sub>2</sub>NCOCH<sub>2</sub>N(CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>] are well known in solution. The stability of these complexes has broad interest because of the useful application of this amid-amino diacid in biological buffer solutions. Structural data for ADA-metal complexes were surprisingly limited until few years ago to an oxo-peroxo-ADA-vanadium(V) complex [1] and an oxo-ADA-vanadium(IV) compound [2]. In addition, we have reported the structure of free acid H<sub>2</sub>ADA [2a,2b] and of the following ADA-metal ion derivatives: {[Cu(ADA)]·H<sub>2</sub>O}<sub>n</sub> [2b,2e], [Cu(HADA)<sub>2</sub>] [2c], [Cu(ADA)(Him)] [2d],

[Cu(ADA)(1PhHim)], [2e], [Cu(ADA)(5PhHim)]·H<sub>2</sub>O, [2e], [Cu(ADA)(1BzHim)]·H<sub>2</sub>O, [2e], [Cu(ADA)(dampu)]·dampu·5H<sub>2</sub>O, [2e], [Cu(ADA)(HisNH<sub>2</sub>)]·1.5H<sub>2</sub>O, [2e], [Cu(ADA)(2,2′bipy)]·3H<sub>2</sub>O, [2b,2e], [Ni(ADA)(H<sub>2</sub>O)<sub>2</sub>] (here after compound 1) [2a] and the iso-structural compounds [M(ADA)(Him)(H<sub>2</sub>O)]·1.5H<sub>2</sub>O [M = Co<sup>II</sup>, Ni<sup>II</sup> (compound 2)] [2f], where Him = imidazole, Ph = phenyl, Bz = benzyl, dampu = 2,6-diaminopurine, HisNH<sub>2</sub> = histamine and 2,2′-bipy = 2,2′-bipyridine.

Unless in the ‘acid’ bis-chelate [Cu(HADA)<sub>2</sub>] with two *tri*-dentate, partially protonated HADA(1<sup>−</sup>) ligands having a ‘free’ (non-complexed) *N*-carboxymethyl arm, all other ADA-metal derivatives of known structure contains the *tetra*-dentate tripodal ligand ADA(2<sup>−</sup>). In the iso-structural octahedral compounds [M(ADA)(Him)(H<sub>2</sub>O)]·1.5H<sub>2</sub>O (M = Co<sup>II</sup>, Ni<sup>II</sup>, [2f]) the Him ligand is selectively linked to the metal in *trans* to the

\* Corresponding author; Tel.: +34-958-243-855; fax: +34-958-246 219.  
E-mail address: jniclos@ugr.es (J. Niclós-Gutiérrez).

M–N(ADA) bond, thus following the trend of Him to occupy the *trans* position to the Cu–N(IDA or IDA-derivative) bond (IDA = iminodiacetato(2–) ligand). Such structural correlation seems to be operative in [Cu(CEIDA)(Him)] [3a] but it cannot be afforded from the structure of [Ni(CEIDA)(Him)<sub>2</sub>] · H<sub>2</sub>O [3b] because the tetra-dentate role of CEIDA = *N*-(2-carbamoyl-ethyl)iminodiacetato(2–) ligand [H<sub>2</sub>NCOCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>CO<sub>2</sub><sup>–</sup>)<sub>2</sub>] and two Him molecules completes the octahedral coordination of the Nickel(II) atom. As a part of our structural studies on mixed-ligand metal-complexes, we report now the structure of [Ni(ADA)(bipy)(H<sub>2</sub>O)] · 4H<sub>2</sub>O.

## 2. Results and discussion

By stoichiometric reaction of Ni<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub> · 4H<sub>2</sub>O (2 mmol, Merck), H<sub>2</sub>ADA (6 mmol, Aldrich) and 2,2'-bipy (6 mmol, Aldrich) in water (100 ml), filtration and evaporation at room temperature, we have obtained the titled compound in a good yield (2.5 g, 84.5%; C<sub>16</sub>H<sub>26</sub>N<sub>4</sub>NiO<sub>10</sub>, formula weight 493.12). The compound crystallises in the monoclinic system, space group P2<sub>1</sub>/n, *a* = 9.010(2), *b* = 18.741(3), *c* = 12.710(2) Å, β = 93.07(1)°, *Z* = 4, *T* = 293(2) K; solved by direct methods from 4984 unique reflections [*I* > (2σ(*I*))] for 280 parameters, and refined to final R1 = 0.059, wR2 = 0.128 and GOF 0.907 indices. The asymmetric unit is shown in the Fig. 1.

This structure represents a slightly distorted octahedral coordination. Two surprising features arise from the comparison between the structure reported here (see Fig. 1) and those of all other metal chelates of ADA [1,2a,2b] (unless that of the 'acid' bis-chelate [2c]) and also those of CEIDA [3]. Firstly, the unexpected 'tridentate' chelating role of ADA ligand, as an iminodiacetato(2–) ligand and with the *N*-carbamoylmethyl arm non-complexed to the Nickel(II) atom. And second, the fact that the *N,N'*-bidentate heterocyclic ligand 2,2'-bipy chelates the Nickel(II) atom, but without the occupancy of the *trans* position to the Ni–N(ADA) bond of the Ni(ADA)-like moiety in the new compound. This latter observation results particularly remarkable on the basis of the octahedral coordination usually exhibited by

the Ni(II) with aminopolycarboxylates and closely related ligands, as indeed it is referred in all Ni(II) complexes of IDA, ADA and CEIDA with known structure. There are no π,π-stacking interactions between bipy ligands and the crystal is built by a H-bonding network which produces a 2D assembly of complex molecules connected by non coordinated water.

It is also instructive to compare the different role of aqua ligand in compounds [Ni(ADA)(Him)(H<sub>2</sub>O)] · 1.5H<sub>2</sub>O [2f] and [Ni(ADA)(bipy)(H<sub>2</sub>O)] · 4H<sub>2</sub>O. In the former the Him ligand prefers such coordination site and the aqua ligand is in *trans* versus one of the two O(carboxyl) donor atom, but in the latter, the aqua ligand is in the *trans*-site to the Ni–N(ADA tridentate) bond. In order to explain the unexpected tridentate role of ADA in the studied complex, a comparison of Ni–ADA donor bond lengths is made in Table 1. It can appreciate that the increasing substitution of aqua ligands in [Ni(ADA)(H<sub>2</sub>O)<sub>2</sub>] (compound 1) by one or

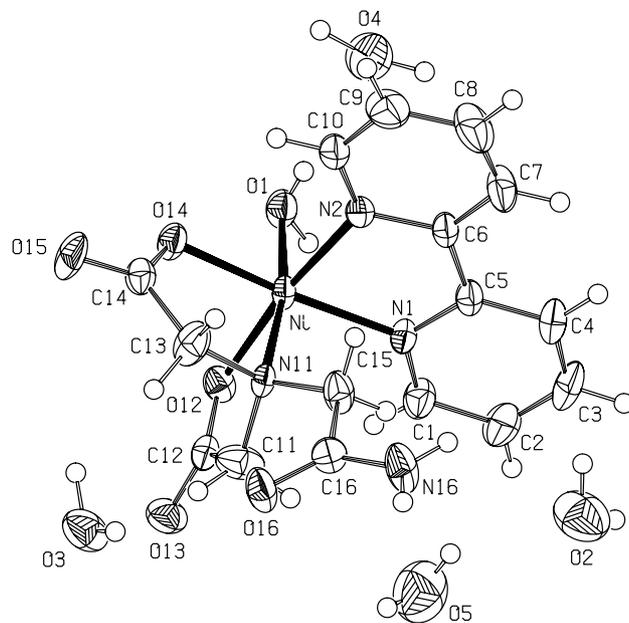


Fig. 1. Asymmetric unit of [Ni(ADA)(bipy)(H<sub>2</sub>O)] · 4H<sub>2</sub>O (compound 3). Coordination bond lengths (Å): Ni–N(11) 2.168(3), Ni–O(12) 2.041(3), Ni–O(14) 2.040(3) with ADA, Ni–N(1) 2.067(3) and Ni–N(2) 2.061(3) with bipy and Ni–O(1) 2.085(2) with aqua ligand. *Trans*-coordination angles are N(11)–Ni–O(1) 170.3°, N(2)–Ni–O(12) 172.5° and N(1)–Ni–O(14) 174.0°.

Table 1  
Coordination bond lengths (Å) in Ni(II)–ADA compounds

Compound →	1 [2a]	2 (average) [2f]	3 (this work)
Ni–N(amino)	2.072(2) <	< 2.081 <	< 2.168(3)
Ni–O(carboxyl)	2.045(2)	2.043	2.040(3)
Ni–O(carboxyl)	2.051(2)	2.056	2.042(3)
Ni–O(amido)	2.065(2) <	< 2.116 <	< Non existent!
Ni–O(aqua)	2.000(2)	2.115	2.085(2)
Ni–O(aqua)	2.106(2)	–	–
Ni–N(Him or bipy)	–	2.014	2.061(3)
Ni–N(bipy)	–	–	2.067(3)

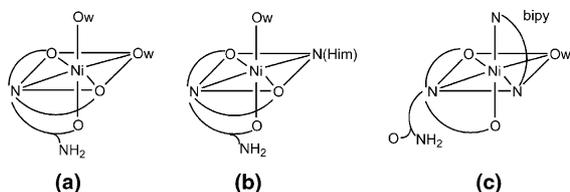


Fig. 2. Different ADA<sup>2-</sup> conformation modes in Nickel(II) complexes. (a) *mer*-IDA-like + O(amido) as in compound 1, (b) *fac*-IDA-like + O(amido) in compound 2 and (c) *fac*-IDA-like for compound 3.

two *N*-heterocyclic donor atoms, as in [Ni(ADA)((Him)H<sub>2</sub>O)] · 1.5H<sub>2</sub>O (2) and [Ni(ADA)(bipy)] · 4H<sub>2</sub>O (3), respectively produces a significant lengthening of the Ni–N(amino) and Ni–O(amido) coordination bonds. These trends could be responsible of two major structural effects: (1) The lack of a preference to link one *N*-heterocyclic (bipy) donor in the *trans*-site to the lengthened Cu–N(amino) bond. (2) The lengthening of the Ni–O(amido) bond to such an extent that it is not formed in compound 3. These changes also imply modifications in the ADA conformation which can be referred as *mer*-IDA-like + O(amido), *fac*-IDA-like + O(amido) and *fac*-IDA-like in compounds 1 [1], 2 [2f] and 3, respectively (see Fig. 2). Indeed the dihedral angle between mean planes of Ni-glycinato chelate rings ( $\phi$ ) are 16.3°, 83.3° (average) and 83.2° for compounds 1, 2 and 3, respectively.

Crystallographic data for the structural analysis of compound 3, [Ni(ADA)(bipy)(H<sub>2</sub>O)] · 4H<sub>2</sub>O has been deposited with the Cambridge Crystallographic Data Centre CCDC 18823. Available analytical data, thermogravimetric data (with FT-IR identification of evolved gases), FT-infra-red and electronic (reflectance) spectra and (80–300 K) magnetic properties are likely consistent with the molecular and/or crystal structure reported here. Details of the structural study and physicochemi-

cal properties of compound 3 are available from the authors upon request.

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### References

- [1] (a) M. Sivák, J. Tyršlová, S. Pavelčík, J. Marek, *Polyhedron* 15 (1996) 1062; (b) G.J. Colpas, B.H. Hamstra, J.W. Kampf, V.L. Pecoraro, *J. Am. Chem. Soc.* 118 (1996) 3469.
- [2] (a) E. Bugella Altamirano, J.M. González Pérez, A.G. Sicilia Zafra, J. Niclós Gutiérrez, A. Castiñeiras Campos, *Polyhedron* 19 (2000) 2463; (b) E. Bugella Altamirano, A. Castiñeiras Campos, J.M. González Pérez, A.G. Sicilia Zafra, J. Niclós Gutiérrez, ISMEC'99, S. Martino al Cimino (Viterbo, Italia), 1999, Report C 17; (c) A. Castiñeiras Campos, E. Bugella Altamirano, D. Choquesillo Lazarte, J.M. González Pérez, and J. Niclós Gutiérrez, SIMEC'2000, Valencia (Spain), 2000, Report P12; (d) E. Bugella Altamirano, J.M. González Pérez, A.G. Sicilia Zafra, J. Niclós Gutiérrez, A. Castiñeiras Campos, *Polyhedron* 18 (1999) 3333; (e) E. Bugella Altamirano, J.M. González Pérez, D. Choquesillo-Lazarte, R. Carballo, A. Castiñeiras Campos, J. Niclós Gutiérrez, submitted for publication (2002); (f) E. Bugella Altamirano, J.M. González Pérez, A.G. Sicilia Zafra, J. Niclós Gutiérrez, A. Castiñeiras Campos, *Polyhedron* 19 (2000) 2473.
- [3] (a) A.S. Antsyshkina, G.G. Sadikov, A.L. Poznyak, V.S. Sergienko, *Russ. J. Inorg. Chem.* 43 (2) (1998) 187; (b) L.M. Shkol'nikova, K.D. Suyarov, A.A. Masyuk, A.L. Poznyak, N.M. Dyatlova, *Koord. Khim.* 16 (1990) 1096.