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Metal chelates of *N*-carbamoylmethyl-iminodiacetate(2 −) ion. Part III. Synthesis, XRD structures and properties of *N*-carbamoylmethyl-iminodiacetic acid (H_2ADA) and *cis*-diaqua(*N*-carbamoylmethyl-iminodiacetato)nickel(II), $[Ni(ADA)(H_2O)_2]$

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Abstract

N-(Carbamoylmethyl)iminodiacetic [$H_2ADA = H_2NCOCH_2N(CH_2CO_2H)_2$)] has been crystallised from water and characterised by X-ray crystallography (final value $R_1 = 0.051$). This compound exhibits a zwitterionic structure ($H_2ADA^{\pm}$) whose conformation is stabilised by an intra-molecular hydrogen bond interaction between the 'ammonium' hydrogen atom and the *O*-amide atom as acceptor one. All the other polar bonds give hydrogen bonds, which link adjacent zwitterions, one of them is a rather symmetrical and linear link (170(2)°). The appropriate stoichiometric reaction of nickel(II) hydroxycarbonate, $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$, and H_2ADA in water yields crystalline, green samples of *cis*-diaqua(*N*-carbamoylmethyl-iminodiacetato)nickel(II), $[Ni(ADA)(H_2O)_2]$ (**I**). Its single crystal X-ray diffraction study was also carried out (final $R_1 = 0.031$). The crystal of complex **I** consists of slightly asymmetrical, octahedral coordination units linked in a three-dimensional network stabilised by hydrogen bonds where the water molecules play the most relevant role. Coordination bond distances in **I** (Å): Ni(1)–N(1) = 2.072(2), Ni(1)–O(11) = 2.051(2), Ni(1)–O(21) = 2.045(2) and Ni(1)–O(31, amide) = 2.065(2) with ADA, and Ni(1)–O(1) = 2.000(2) and Ni(1)–O(2) = 2.106(2) with aqua ligands. ADA acts as tetradentate chelating ligand, which is in contrast with chelating and bridging functions for such ligand in the polymeric Cu(II) derivative, where the metal exhibits a square base pyramidal coordination (type 4 + 1). © 2000 Elsevier Science B.V. All rights reserved.

Keywords: *N*-(Carbamoylmethyl)iminodiacetic acid; *N*-(2-Amidomethyl)-iminodiacetic acid; *N*-(2-Acetamide)-iminodiacetic acid; *cis*-Diaqua(*N*-carbamoylmethyl-iminodiacetato)nickel(II); Molecular and crystal structure; Magnetic and spectral properties; Thermal stability

N-Carbamoylmethyl-iminodiacetic acid or *N*-(2-amidomethyl)iminodiacetic acid (also named *N*-(2-acetamide)iminodiacetic acid) [$H_2ADA = H_2NCOCH_2N(CH_2CO_2H)_2$)] is widely used in biological buffers of pH 6.0–7.4. Since many years, metal ion-ADA chelation in solution has been studied for a variety of divalent ions (M = Mg, Ca, Sr, Ba, Mn, Co, Ni, Cu, Zn, Cd, Hg, Pb) [1]. These initial results of Schwarzenbach et al. have been partially supported by more recent studies [2–5] about the stoichiometry and stability of ADA complexes in solution. These works also showed cases where the de-protonation reaction of the primary amide takes place for $M(ADA)_2$ chelates (M = Co or Zn) [2]. Cu(II) de-chelation has also been claimed upon ADA amide de-protonation [6,7]. In contrast, studies concerning ADA complexes in solid state are scarce ones. In fact, crystal structure determinations were limited to only two different *oxo*-ADA–vanadium compounds [8–10] both having ADA as a tripodal-tetradentate ligand. It is worth noting that the structure of the free acid H_2ADA has not been reported, in spite of being a commercially available and widely used

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chelating agent. In addition, studies on ADA–metal chelates in solid state seem a suggestive matter as a source of structural information of the chelating role of the ADA bivalent anion $[H_2NCOCH_2N(CH_2CO_2^-)_2]$ as well as of the way in which its 'primary amide' group could be involved in the chelation of different metal ions. In this sense and as a part of our program on mixed-ligand Cu(II) complexes [11] we have synthesised and reported very recently for the first time the structure of compounds poly-[(*N*-carbamoylmethyl-iminodiacetato)copper(II) monohydrate], $\{[Cu(ADA)]\cdot H_2O\}_n$ [13], (imidazole)(*N*-carbamoylmethyl-iminodiacetato)-copper(II), [Cu(ADA)(ImH)] [12] and (2,2′-bipyridine)-(*N*-carbamoylmethyl-iminodiacetato)copper(II) three-hydrate, $[Cu(ADA)(bipy)]\cdot 3H_2O$ [13]. Such XRD studies [12,13] are our precedent reports in this series and they revealed again that ADA acts as tripodal-tetradentate but with remarkable differences in its ligand roles as well as in the coordination polyhedron of Cu(II) atom. The aim of this work is to report the structure of H_2ADA itself and to extend our contribution on ADA chelates to other metal ions with the synthesis and study of the structure and properties of its nickel(II) derivative.

1. Experimental

1.1. N-carbamoylmethyl-iminodiacetic acid (H_2ADA)

This compound was purchased from Aldrich. Crystals suitable for X-ray structure determination were obtained by re-crystallisation of the commercial available product in water. To this purpose, 500 mg of H_2ADA were dissolved in approximately 80 ml of doubly-distilled water, with stirring and heating (approximately 60°C) for 2 h. The resulting solution was left to cool and then filtered over a crystallisation dish. Evaporation at room temperature (r.t.) produces abundant and well-shaped crystals of this free acid, which were collected by filtration and air-dried.

1.2. Synthesis of cis-diaqua(N-carbamoylmethyl-iminodiacetato)nickel(II), $[Ni(ADA)(H_2O)_2]$, complex **I**

It was obtained by stoichiometric reaction of $NiCO_3\cdot 2Ni(OH)_2\cdot 4H_2O$ (250.9 mg, 0.66 mmol, Merck) and H_2ADA (380.3 mg, 2 mmol) in doubly-distilled water (100 ml) in a Kitasato flask, heating ($t < 50°C$) and stirring under reduced pressure (to remove the CO_2, by-product) for 1 h. Then the reacting mixture was heated and stirred 20 h at 60°C. The resulting clear and green solution was left to cool and then slowly filtered to remove an almost inappreciable amount of non-reacted NiO (insoluble by-product). After 3 weeks of slow evaporation at r.t. (remaining volume of 10–15 ml) the solution was filtered over a little crystallisation dish which was partially covered with a watch glass. That reduces the evaporation rate. After several days, well-shaped green crystals of complex **I** appeared, many of them were suitable for X-ray diffraction studies. For a few days, additional amounts of product were collected by the same way. If super-saturation of mother liquor arises, the addition of little volumes of water and ethanol and further slow evaporation of the solution induce again the crystallisation process. The product was collected by filtration, washed with a little of cool water and air-dried. It can be re-crystallised several times from water. Yield: variable but usually $< 55\%$. Calc. for complex **I** ($C_6H_{12}N_2NiO_7$): C, 25.48; H, 4.28; N, 9.90; Ni, 20.75. Found: C, 25.19; H, 4.36; N, 9.72; Ni, 20.7% (complexometry [14]).

1.3. X-ray data collection and reduction, structure solution and refinement

A colourless prismatic crystal of H_2ADA or a green plate crystal of $[Ni(ADA)(H_2O)_2]$ was mounted on a glass fibre and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range of $8.834 < \theta < 18.278$ or of $9.551 < \theta < 20.927$, respectively, in an Enraf Nonius MACH3 automatic diffractometer [15]. Data were collected at 293 K using Mo Kα radiation ($\lambda = 0.71073$ Å) and the ω-scan technique, and corrected for Lorentz and polarisation effects [16]. A semi-empirical absorption correction (ψ-scan) was made [17]. The structure was solved [18] by direct methods or by Paterson and Fourier methods, respectively, which revealed the position of all non-hydrogen atoms, and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [19]. All hydrogen atoms were located from difference Fourier maps and were refined isotropically. Atomic scattering factors were from the 'International Tables for X-ray Crystallography' [20]. Molecular graphics were prepared with the programs PLATON-97 or PLATON-98 [21] or ZORTEP [22]. A summary of the crystal data, experimental details and refinement results are listed in Table 1.

1.4. Physical measurements

Nickel(II) titration was carried out by standard EDTA complexometry [14]. For this purpose, a sample (534.9 mg) of compound **I** was placed in a precipitation device (250 ml) and mineralised with 2 N sulphuric acid (10 ml) and 10 N hydrogen peroxide (5 ml) solutions. The mineralisation process of the complex would be carried out covering the reaction device of the resulting green solution with a watch glass and then smoothly heating it a few minutes. Such reaction and the decomposition of H_2O_2 (in excess) lead to an acid solution of nickel(II) sulfate which was quantitatively diluted with doubly-distilled water into a volumetric flask (250 ml). Aliquots (25 ml) of this solution were diluted with approximately 100 ml of doubly-distilled water in the corresponding Erlenmeyer flasks. Each aliquot was added of buffer solution pH 10 (ammonia/ammonium chloride, 10 ml) and murexide (Merck, mixed at a 1:2000 ratio with potassium nitrate) as metal-indicator. Such mixtures were heated to approximately 60°C prior to initiate each titration with 10^{-2} M Na_2H_2EDTA (Merck) solution (standardised with a reference $ZnCl_2$ solution and eriochrome black T (Merck) as indicator [14]). Elemental analysis (C, H and N) were performed in the Scientific Instrumental Centre of the University of Granada as described earlier [11]. FTIR spectra were obtained by the KBr disc technique (with KBr Aldrich FTIR grade) on a Nicolet FTIR 20SXB or a Jasco FTIR 410 instrument. Thermogravimetric studies of both compounds (22–550°C) in air flow (100 ml min^{-1}) and the corresponding spectra of evolved gases were recorded using a Shimazu Thermobalance TGA-DTG-50H coupled with a FTIR Nicolet Magma 550 (and a mass spectrometer Fisons Thermolab). The electronic (reflectance) spectrum of **I** (175–3300 nm) was obtained in a Cary 5E spectrophotometer. The magnetic susceptibility of **I** was measured in the temperature range 80–300 K using a Manics DM magnetometer. The susceptometer was calibrated with mercury tetrakis(thiocyanato)cobaltate(II). Corrections for the diamagnetism (122×10^{-6} cm^3 mol^{-1}) were estimated from Pascal constants [23].

Table 1
Crystal data and structure refinement for H_2ADA and complex $[Ni(ADA)(H_2O)_2]$ (**I**)

	H_2ADA	Complex **I**
Empirical formula	$C_6H_{10}N_2O_5$	$C_6H_{12}N_2NiO_7$
Formula weight	190.16	282.89
Temperature (K)	293(2)	293(2)
Wave length (Å)	0.71073	0.71073
Crystal system, space group	monoclinic, $P2(1)/n$	monoclinic, $C2/c$
Unit cell dimensions		
a (Å)	8.426(1)	11.133(1)
b (Å)	11.334(1)	8.914(2)
c (Å)	8.991(2)	20.255(2)
β (°)	107.61(1)	104.66(1)
Volume (Å^3)	818.4(2)	1944.6(4)
Z, calculated density (Mg m^{-3})	4, 1.543	8, 1.932
Absorption coefficient (mm^{-1})	0.135	2.021
$F(000)$	400	1168
Crystal size (mm)	$0.35 \times 0.15 \times 0.15$	$0.35 \times 0.35 \times 0.15$
Theta range for data collection (°)	2.90–30.41	2.97–27.97
Index ranges	$0h12$, $-16k0$, $-12l12$	$-14h0$, $-11k0$, $-25l26$
Reflections collected/unique	2618/2471 [$R_{int} = 0.0393$]	2462/2349 [$R_{int} = 0.0222$]
Completeness	95.5% (to $2\theta = 30.41$)	47.1% (to $2\theta = 27.97$)
Absorption correction	Psi-scan	Psi-scan
Max. and min. transmission	0.961 and 0.906	0.976 and 0.770
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2471/0/158	2349/0/193
Goodness-of-fit on F^2	0.963	1.106
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.051$, $wR_2 = 0.098$	$R_1 = 0.031$, $wR_2 = 0.068$
R indices (all data)	$R_1 = 0.222$, $wR_2 = 0.132$	$R_1 = 0.061$, $wR_2 = 0.080$
Largest difference peak and hole (e Å^{-3})	0.242 and −0.272	0.359 and −0.500

2. Results and discussion

2.1. Structure and properties of N-(carbamoylmethyl)iminodiacetic acid (H_2ADA)

Bond lengths and angles between non-hydrogen atoms and hydrogen bond distances and angles of this compound are given in Table 2. The crystal consists of a hydrogen bonded network of molecules where all polar N–H and O–H bonds are involved as 'H-donor' in this interactions. The acid dissociation constants of H_2ADA=H_2L have pK_a values ($I = 0.1$ (KNO_3) and 25°C) of $pK_0 = 1.59 < pK_1 = 2.31 \ll pK_2 = 8.98$ for the dissociation of the species H_3L^+ (cationic), H_2L (neutral), and HL^- (anionic), respectively [2]. Consequently it should be assumed that its protonated species and, in particular, its neutral molecule will exist as a zwitterion in solution (such as $H_2ADA^{\pm}$ for the molecular species). Our structural results indicate that the molecule also exists as a dipolar ion in solid state, and it represents the asymmetric unit of the crystal.

Two structural features of this amino-polycarboxylic acid seem of major interest. Firstly, its conformation seems intra-stabilised by only one hydrogen bond which is made up by the ammoniun proton with the O(31) amide atom as 'acceptor'. In spite of that, the C(32)–O(31) bond distance (1.231(3) Å) is not lengthened compared to the averaged distance of the C=O(amide) bond in primary amides (1.24(1) Å) [24]. The distance (2.590(3) Å) and angle (113(2)°, close to the tetrahedral angle) of this intra-molecular hydrogen bond agree reasonably well with those reported for a variety of amino-polycarboxylic acids such as iminodiacetic acid and many others [25]. It is worth noting that the O-amide atom should be preferred to a negatively

Table 2
Selected bond lengths (Å) and angles (°) for H_2ADA with e.s.d. values in parentheses [a]

Non-hydrogen atoms

O(11)–C(12)	1.222(3)	C(31)–N(1)–C(21)	13.0(2)
O(12)–C(12)	1.272(3)	C(31)–N(1)–C(11)	11.7(2)
O(21)–C(22)	1.212(3)	C(21)–N(1)–C(11)	12.2(2)
O(22)–C(22)	1.297(3)	N(1)–C(11)–C(12)	12.1(2)
O(31)–C(32)	1.231(3)	O(11)–C(12)–O(12)	27.0(2)
N(1)–C(31)	1.491(3)	O(11)–C(12)–C(11)	16.9(2)
N(1)–C(21)	1.493(3)	O(12)–C(12)–C(11)	16.0(2)
N(1)–C(11)	1.497(3)	N(1)–C(21)–C(22)	13.2(2)
N(32)–C(32)	1.319(3)	O(21)–C(22)–O(22)	26.6(2)
C(11)–C(12)	1.516(3)	O(21)–C(22)–C(21)	19.3(2)
C(21)–C(22)	1.513(3)	O(22)–C(22)–C(21)	14.1(2)
C(31)–C(32)	1.511(3)	N(1)–C(31)–C(32)	07.3(2)
O(31)–C(32)–N(32)	124.4(2)		
O(31)–C(32)–C(31)	118.8(2)		
N(32)–C(32)–C(31)	116.7(2)		

Hydrogen bonds

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
N(1)–H(1)···O(31)	0.93(3)	2.09(3)	2.590(3)	113(2)
O(12)–H(12) ···O(22) # 1	1.25(4)	1.23(4)	2.477(2)	170(2)
N(32)–H(32A) ···O(11) # 2	0.89(3)	2.12(3)	2.970(3)	161(3)
N(32)–H(32B) ···O(21) # 3	0.89(4)	2.18(4)	3.062(3)	170(3)

[a] Symmetry transformations used to generate equivalent atoms: i: # 1 = $-x+1/2$, $y+1/2$, $-z+3/2$; ii: # 2 = $-x+1/2$, $y-1/2$, $-z+5/2$; iii: # 3 = $x-1$, y, z.

charged *O*-carboxylate atom. This is not the case for other *N*-substituted-iminodiacetic acids having a suitable 'acceptor' atom in the *N*-side chain. In such compounds the ammonium hydrogen atom forms a hydrogen bond with the 'acceptor' atom of the *N*-side chain as well as with one ('bifurcated' cases [25–27]) or with two ('trifurcated cases' [25,28]) *O*-carboxylate atoms of the acetate arms. Secondly, carboxylic and carboxylate groups from pairs of adjacent dipolar ions $H_2ADA^{\pm}$ (related by the symmetry code # 1 = i: $-x+1/2$, $y+1/2$, $-z+3/2$) are linked by a rather short, symmetrical and nearly linear hydrogen bond O(12) – H(12)···O(22^i) with an overall distance of 2.477(2) Å and angle of 170(2)° (see Fig. 1 and Table 2). This unique hydrogen bond is consistent with the rather similar ratio of carbon–oxygen bond distances (Å) in the two linked 'carboxyl' groups, C(12)–O(12)/C(12)–O(11) (1.272(3)/1.222(3)) = 1.041 and C(22)–O(22)/C(22)–O(21) (1.297(3)/1.212(3)) = 1.070. Indeed it is on the basis of the small difference in such ratios that the acid hydrogen atom could be formally assigned to the O(12) atom. In other words, the consideration of a carboxylic –C(12)O(11)O(12)H(12) group and a carboxylate –C(22)O(21)O(22)$^-$ one to the zwitterion H_2ADA in the crystal (as depicted in Fig. 1) is in some ways a practical approach or a simplification.

With necessary caution, we can attempt to correlate our crystal structure results with the high pK_a value of the studied amino-amide acid derivative. With this aim, it is instructive to consider that H_2ADA acid is the result of replacing the secondary amino hydrogen atom from the iminodiacetic acid ($H_2IDA{=}HN(CH_2CO_2H)_2$) by the *N*-(2-amidomethyl) or *N*-(carbamoylmethyl) arm. It is generally assumed that this latter neutral group ($-CH_2CONH_2$) displays a moderate electron withdrawing effect ($-I$) [24] but in fact it should be operative in the hydrogen bonding intra-stabilisation, as our structural results have stated. These two effects will act in an opposite sense and the final state should depend on the balance within them. Several sets of acidity (pK_a) or protonation constants are available for H_2IDA acid or IDA(2 –) ion, respectively, for a ionic strength of $I = 0.1$ M (KNO_3) and 25°C [29]. For example, a complete set of pK_a dissociation constant values, p$K_0 = 1.80$, p$K_1 = 2.58$ and p$K_2 = 9.27$, for the three dissociation steps of the cationic species (H_3IDA^+) of iminodiacetic acid is available [30]. Consequently, it can be seen that the three pK_a values of H_2ADA are approximately 0.2–0.3 pK_a units lower than the corresponding values of H_2IDA.

Concerning the vibrational properties, the relative simplicity of groups in H_2ADA molecule allow us the following tentative assignations of bands (wave-numbers in cm^{-1}) in its IR spectrum [31]: ν(OH) of carboxylic group at 3400–3384, $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ of primary amide group at 3320 and 3250, ν_{as} and ν_s of CH_2 at 3014 and 2990, and 3295, ν(C=O) of carboxylic group at approximately 1730 (shoulder), $\nu_{as}(COO^-)$ overlapped with ν(C=O) of primary amide group (also called 'amide I' band) at 1700, and $\delta(NH_2)$ of this latter group (so-called 'amide II' band) at 1681, $\delta(CH_2)$ at 1442, and $\nu_s(COO^-)$ at 1366. In this connection it is interesting to keep in mind that certain assignations concerning the amide primary group are only the best approximations. These are the cases of 'amide I and II' bands. The former is not due to a pure C=O stretching mode but is appreciably coupled with a C–N stretch and to some extent with the $-NH_2$ band [31a]. There is more controversy over the amide II band, but it is generally accepted that it is mainly due to the scissoring mode of the $-NH_2$ amide group. A band at 3050 cm^{-1} is assigned to a combination mode $\delta(NH_2$, amide) + $\nu_s(COO^-$, carboxylate group) (1681 + 1366 = 3047). Concerning the zwitterionic form of this compound, an interesting finding is a series of weak bands observed in the region of 2880–2000 cm^{-1} (in our case at 2860, 2825 and 2730 cm^{-1}, among others). They are frequently observed in the IR spectrum of amino-polycarboxylic acids hydrochlorides. The band at 2730 can be related with the stretching mode of the ammonium group $-N^{+}-H$ [31b,32]. In this connection, it should be noted that the asymmetric stretching mode of the carboxylate group (expected in the range 1600–1560 cm^{-1}) is moved to higher frequencies and overlapped in a broad band near 1700 cm^{-1}. Both effects are consistent with the unique symmetrical and nearly linear hydrogen bond linking the carboxylic and carboxylate group. The TG analysis with FTIR spectra of evolved gases of an anhydrous sample (7.053 mg) in air flow shows two overall pyrolytic steps (207–335 and 335–500°C) with production of H_2O, CO_2, CO, NH_3, NO and NO_2. The decomposition starts with the production of H_2O, CO_2 and traces of CO suggesting that it corresponds to the decarboxylation of two hydrogen bonded *N*-carboxymethyl arms (207–215°C).

2.2. Structure and properties of cis-diaqua(N-carbamoylmethyl-iminodiacetato)nickel(II)

Selected bond lengths and angles between non-hydrogen atoms and hydrogen bond distances and angles of this compound are given in Table 3. Complex **I** consist of molecular units $[Ni(ADA)(H_2O)_2]$ (see Fig. 2). Each molecule represents the asymmetric unit of the crystal, and eight molecules compose the unit cell. The crystal is built up by means of a three-dimensional hydrogen bonding network involving all polar bonds, from the $-NH_2$ amide group of the ADA ligand and O–H bonds of aqua ones (Table 3). The atoms N(1), O(11), O(21) and O(31, amide) of the tetradentate ADA^{2-} ion and the atoms O(1) and O(2) of coordinated water molecules define an octahedral surrounding to the nickel(II) atom. That is recognised as the most common geometry for nickel(II) coordination compounds [33] as it is observed in a host of nickel(II) complexes with an extremely wide range of mono- and polydentate ligands. The four donor atoms of the tripodal ligand ADA are similar in length (average 2.058(2) Å) whereas the two *cis*-Ni–O(water) bonds (2.000(2) and 2.102(2) Å) are the shortest and the longest ones. Additionally the *trans*-angles involving such Ni–O(water) bonds (175.6 and 179.3(1)°) are close to 180°, but the *trans*-angle O–Ni–O with donors of chelating ADA is significantly the closest (163.8(1)°). As a consequence, both ADA and aqua ligands are responsible in some way for the moderate but irregular distortion of the Ni(II) coordination polyhedron. Otherwise the internal geometry of the Ni(II) coordination and ADA ligand have usual values compared to related compounds. This includes the ADA ligand in known metal–ADA complexes [8–10,12,13], several Ni–IDA chelates [34] and a variety of compounds involving Ni(II)–O(amide) bonds [35]. These latter compounds include diaqua-tetrakis(acetamide)nickel(II) [35a], bis-(iminodiacetamide)nickel(II) diperchlorate [35d] and bis-(imidazole) (nitrilopropionamidediacetato) nickel(II) monohydrate [35g].

The tripodal chelating role of ADA represents the formation of two nearly coplanar Ni–glycinate-like rings and a third Ni–glycinamide-like one, all three sharing the Ni–N(1, amino) bond. The mean planes of both Ni–glycinate-like rings (P(2) and P(3) involving

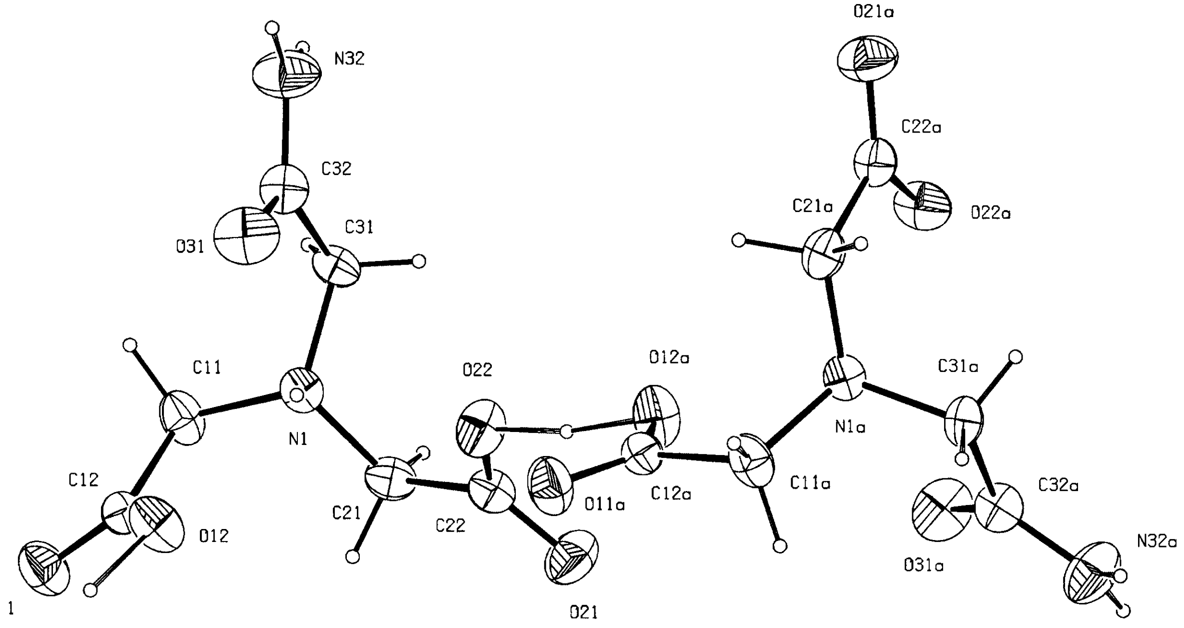

Fig. 1. Structure of the acid *N*-(carbamoylmethyl)iminodiacetic acid (H_2ADA) showing the symmetrical and nearly linear inter-molecular hydrogen bond between two adjacent zwitterions. Symmetry code $a = \#1 = \text{i}$: $-x+1/2$, $y+1/2$, $-z+5/2$.

Table 3
Selected bond lengths (Å) and angles (°) for [Ni(ADA)(H_2O)$_2$] (**I**) with e.s.d. values in parentheses [a]

Nickel(II) environment			
Ni(1)–O(1)	2.000(2)	O(1)–Ni(1)–O(21)	95.8(1)
Ni(1)–O(21)	2.045(2)	O(1)–Ni(1)–O(11)	92.1(1)
Ni(1)–O(11)	2.051(2)	O(21)–Ni(1)–O(11)	92.2(1)
Ni(1)–O(31)	2.065(2)	O(1)–Ni(1)–O(31)	99.9(1)
Ni(1)–N(1)	2.072(2)	O(21)–Ni(1)–O(31)	163.8(1)
Ni(1)–O(2)	2.106(2)	O(11)–Ni(1)–O(31)	90.7(1)
Ni–Ni^{vi}	5.192(1)	O(1)–Ni(1)–N(1)	175.5(1)
Ni–Ni^{iv}=Ni–Ni^{vii}	6.869(1)	O(21)–Ni(1)–N(1)	82.3(1)
		O(11)–Ni(1)–N(1)	84.0(1)
		O(31)–Ni(1)–N(1)	82.1(1)
		O(1)–Ni(1)–O(2)	88.4(1)
		O(21)–Ni(1)–O(2)	87.1(1)
		O(11)–Ni(1)–O(2)	179.3(1)
		O(31)–Ni(1)–O(2)	89.8(1)
		N(1)–Ni(1)–O(2)	95.5(1)
ADA aqua ligands			
O(11)–C(11)	1.247(3)	C(12)–N(1)–C(22)	111.8(2)
O(21)–C(21)	1.276(3)	C(12)–N(1)–C(32)	111.7(2)
O(22)–C(21)	1.237(3)	C(22)–N(1)–C(32)	113.9(2)
O(31)–C(31)	1.279(4)	O(11)–C(11)–N(11)	122.9(3)
O(32)–C(31)	1.245(3)	O(11)–C(11)–C(12)	121.9(2)
N(1)–C(12)	1.477(4)	N(11)–C(11)–C(12)	115.2(3)
N(1)–C(22)	1.482(4)	N(1)–C(12)–C(11)	112.9(2)
N(1)–C(32)	1.483(4)	O(22)–C(21)–O(21)	125.1(2)
N(11)–C(11)	1.320(4)	O(22)–C(21)–C(22)	117.5(2)
C(11)–C(12)	1.510(4)	O(21)–C(21)–C(22)	117.3(2)
C(21)–C(22)	1.533(4)	N(1)–C(22)–C(21)	112.1(2)
C(31)–C(32)	1.528(4)	O(32)–C(31)–O(31)	124.8(3)
		O(32)–C(31)–C(32)	117.2(3)
		O(31)–C(31)–C(32)	117.9(2)
		N(1)–C(32)–C(31)	112.0(2)
O(1)–H(1A)	0.76(3)	H(1A)–O(1)–H(1B)	116(3)
O(1)–H(1B)	0.74(4)		
O(2)–H(2A)	0.87(4)	H(2A)–O(2)–H(2B)	105(3)
O(2)–H(2B)	0.82(4)		

Hydrogen bonds

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
O(1)–H(1A) ···O(22) # 1	0.76(3)	1.88(3)	2.637(3)	169(3)
O(1)–H(1B) ···O(32) # 2	0.74(4)	2.04(4)	2.757(3)	163(4)
O(2)–H(2A) ···O(31) # 2	0.87(4)	1.89(4)	2.756(3)	170(4)
O(2)–H(2B) ···O(32) # 3	0.82(4)	2.02(4)	2.832(3)	174(3)
N(11)–H(11A) ···O(21) # 4	0.84(4)	2.09(4)	2.910(4)	163(4)
N(11)–H(11B) ···O(11) # 5	0.80(4)	2.55(4)	3.060(3)	123(3)

[a] Symmetry transformations used to generate equivalent atoms: i: # 1 = $x-1/2$, $y+1/2$, z; ii: # 2 = $-x$, $-y$, $-z$; iii: # 3 = $x+1/2$, $y+1/2$, z; iv: # 4 = $-x+1/2$, $y-1/2$, $-z+1/2$; v: # 5 = $-x$, y, $-z+1/2$; vi: # 6 = $1-x$, $1-y$, $1-z$; vii: # 4 = $1/2-x$, $1/2+y-$, $1/2-z$.

O(11) and O(21) atoms, respectively) define a dihedral angle of 81.1°. The mean plane P(4) of Ni–glycinamide-like ring defines dihedral angles of 80.5° and 18.5° with P(2) and P(3) planes, respectively. The most distorted chelate ring is that involving the O(11) atom, with maximum deviations of −0.034 and 0.029 Å for O(11) and C(11) atoms, respectively, from the mean plane P(2) of the five atoms forming such a ring. These three chelate rings exhibit slightly distorted asymmetric-envelope conformation, rather common for α-amino-acidato and α-aminopolycarboxylato ligands in its metal ion chelates (with both carbon atoms lying on the same side of the plane defined by its corresponding atoms Ni, N and O of each ring) [36]. In this respect, the greatest unequal deviations correspond to C(21) (0.44 Å) and C(22) (0.69 Å) from the plane of Ni(1)N(1)(21) atoms.

The IR spectrum of complex **I** permits the identification of bands from main characteristic absorption modes expected for aqua and ADA ligands. The following tentative assignations can be made (wave-numbers in cm^{-1}) in its IR spectrum: ν(OH) of the aqua ligand at 3436 and 3364, $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ of the primary amide group at approximately 3300 (as a shoulder of the second ν(OH) band) and 3160, $\nu_{as}(CH_2)$ at 2992 and 2973, $\nu_s(CH_2)$ at 2931 and 3910, ν(C=O) of the primary amide group (also called 'amide I' band) at 1667, $\delta(H_2O)$ at 1627, $\delta(NH_2)$ of this latter group (also called 'amide II' band) overlapped with $\nu_{as}(COO^-)$ at 1603 and 1587, $\delta(CH_2)$ at 1471 and 1433, and $\nu_s(COO^-)$ at 1391. The difference $\Delta(COO) = \nu_{as}(COO) - \nu_s(COO) = 196$ cm^{-1} is in accordance with the expected mainly ionic nature of the Ni(II)–O(carboxylato) bonds. Obviously, in this spectrum the ν_{as}(C=O) of carboxylic group (as a shoulder at approximately 1730 cm^{-1} in the ligand spectrum) is now missing. The two bands of the primary amide group have lower frequencies in the complex spectrum than in that of the H_2ADA. Such displacements should be regarded with care because, as mentioned above, the bands 'amide I and II' are not pure C=O stretching and scissoring –NH_2 amides, respectively [28a]. The TG analysis (with FTIR spectra of evolved gases) of an anhydrous sample of complex **I** (7.221 mg) in air flow shows two rather separate steps (165–275 and 275–400°C). The first step corresponds to the water loss (exp. 13.329%, calc. for $2H_2O$ 12.737%). The second one is that of the ADA pyrolysis with production of H_2O, CO_2, CO (traces), N_2O and NH_3, and NO_2. The ADA decomposition starts slowly with production of H_2O, CO_2 and traces of N_2O suggesting that it corresponds to the *N*-carbamoylmethyl arm of the ligand. But such process shows a very sharp weight loss near to 378°C with overlapped production of the referred gasses. The dehydration and ADA pyrolysis leaves a residue of crude NiO (exp. 27.023%, calc. for pure NiO 26.410%). The electronic spectrum shows bands $\nu_1 = 9560$ (shoulder at approximately 14250), $\nu_2 = 16077$ and $\nu_3 = 25445$ cm^{-1}

due to the electronic transitions ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}$ (with a shoulder for ${}^3A_{2g}(F) \rightarrow {}^1E_g$), ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$. This spectrum is typical of an octahedral Ni(II) surrounding [33]. Since it can be assumed that $\nu_1 = 10\ \mathrm{Dq} = \Delta_o$, a value of 856 $\mathrm{cm^{-1}}$ is obtained for the Racah parameter B', that is 83% of the B parameter in the free ion. These data are in accordance with the predominant ionic nature of the Ni(II) atom in the complex **I**. The values of Δ_o and B' in this compound are higher than those of hexaaquanickel(II) (8500 and 945 $\mathrm{cm^{-1}}$, respectively) as expected for the substitution of four aqua ligands with the ADA one. Indeed the Δ_o values yield the following series of complexes: $[Ni(H_2O)_6]^{2+} < [Ni(ADA)(H_2O)_2] < [Ni(NH_3)_6]^{2+}$ ($\Delta_o = 10750\ \mathrm{cm^{-1}}$) $< [Ni(en)_3]^{2+}$ ($\Delta_o = 11200\ \mathrm{cm^{-1}}$) [33]. These spectral data support the placement of ADA ligand between aqua and ammonia or ethylendiamine in the nephelauxetic series. A plot of $1/\chi$ data versus T (K) ($T = 80$–298 K) is linear (with a statistical r^2 factor of 0.9993) according to a Curie–Weiss behavior, $\chi_{\mathrm{mol}} = C/(T - \theta)$ (Fig. 3). The Curie constant is $C = 1.10$ $\mathrm{K{\cdot}emu{\cdot}mol^{-1}}$ and a Weiss constant of $\theta = 5.58$. The experimental value of μ_{eff} for Ni(II) atom in the studied complex **I** is 2.97 BM, in accordance with the molecular and crystal structure here reported where the shortest inter-metallic Ni–Ni$^{\mathrm{vi}}$ distances is 5.193(1) Å (symmetry code vi: $\#6 = 1 - x, 1 - y, 1 - z$). This value lies within the range of typical experimental ones (2.8–3.5 BM) in mononuclear octahedral Ni(II) complexes with a ${}^3A_{2g}$ ground state [37]. It is slightly higher than the spin-only one ($\mu_{\mathrm{eff}} = g[S(S+1)]^{1/2} = 2.83$) suggesting that there is a small orbital angular moment contribution to the effective magnetic moment of the nickel(II) atom.

3. Concluding remarks

The nickel(II) atom exhibits an octahedral coordination in the molecule of complex **I**, which represents a common feature for this metal(II) ion. However, that differs from the square base pyramidal coordination reported for the corresponding copper(II) derivative which has a polymeric structure [12]. In addition, it is worth noting that two *cis*-aqua ligands in the nickel(II) complex gives the possibility for further studies of mixed-ligand complexes of such a metal ion, ADA, and a variety of mono- and bi-dentate ligands. At present, we continue working to evaluate these possibilities [38] on the basis of our present results and keeping in mind the structure of bis(imidazole)(nitrilopropionamidediacetato)nickel(II) monohydrate [35g] reported some years ago.

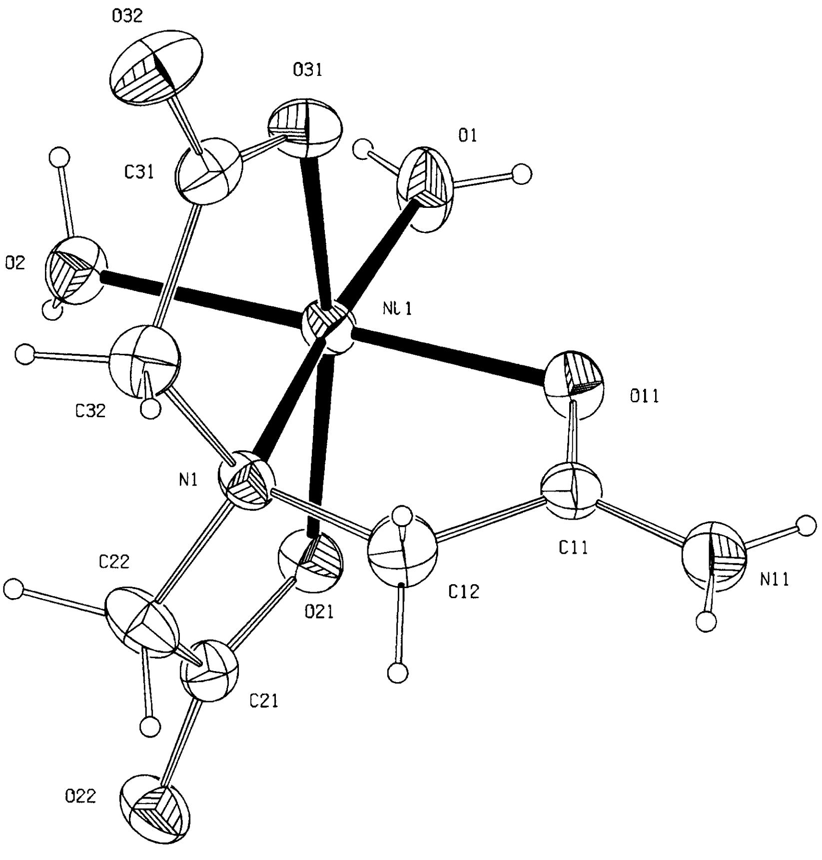

Fig. 2. Asymmetric unit in the crystal of compound $[Ni(ADA)(H_2O)_2]$ (**I**).

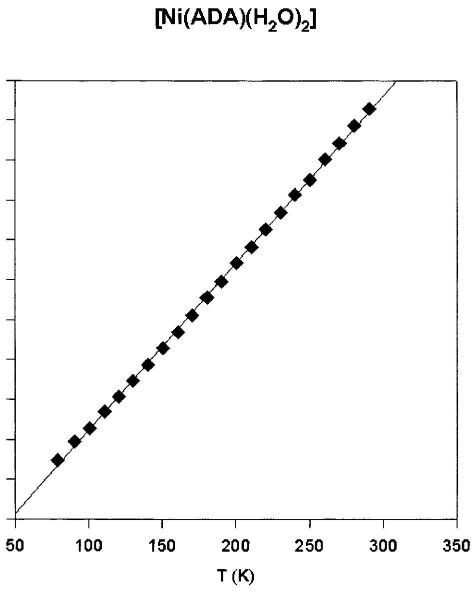

Fig. 3. Thermal variation of $\chi_M T$ for complex **I** (◆). The solid line corresponds to the best theoretical fit (see text).

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 134789 for H_2ADA and CCDC No. 134790 for $[Ni(ADA)(H_2O)_2]$ (**I**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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