PERGAMON

www.elsevier.nl/locate/poly

Polyhedron 19 (2000) 2473–2481

POLYHEDRON

Metal chelates of *N*-carbamoylmethyl-iminodiacetate(2 −) ion Part IV. Isostructural ternary mixed-ligand cobalt(II) and nickel(II) chelates with *N*-carbamoylmethyl-iminodiacetate(2 −) ion, imidazole and aqua ligands. Synthesis, molecular and crystal structures and properties of $[M(ADA)(Him)(H_2O)]\cdot 1.5H_2O$ (M = Co, Ni)

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Abstract

Stoichiometric reaction of $CoCO_3\cdot Co(OH)_2\cdot 2H_2O$, or $NiCO_3\cdot 2Ni(OH)_2\cdot 4H_2O$ with H_2ADA and imidazole (Him) in water yields crystalline samples of compounds aqua(imidazole)(*N*-carbamoylmethyl-iminodiacetato)metal(II), $[M(ADA)(Him)(H_2O)]\cdot 1.5H_2O$ (M = Co, compound **I**, dark pink; M = Ni, compound **II**, bluish). Single-crystal X-ray diffraction studies were carried out. Both complexes are isostructural (orthorhombic system, space group *Pna*2(1), $Z = 8$). These crystals consist of slightly asymmetrical octahedral coordination units linked in a tridimensional network stabilised by hydrogen bonds where all N–H bonds of ADA and Him and probably O–H bonds of water molecules are involved. The asymmetric unit has two independent but very similar complex molecules and three water ones. Coordination bond distances for **I** (average in Å): Co–N(amino) = 2.14(1), Co–O(carboxyl) = 2.06(1), Co–O(carboxyl) = 2.08(1) and Co–O(amide) = 2.15(1) with ADA, Co–N(Him) = 2.04(1), and Co–O(aqua) = 2.13(1). Coordination bond lengths for **II** (average in Å): Ni–N(amino) = 2.08(1), Ni–O(carboxyl) = 2.04(1), Ni–O(carboxyl) = 2.06(1) and Ni–O(amide) = 2.012(1) with ADA, Ni–N(Him) = 2.01(1), and Ni–O(aqua) = 2.12(1). The ADA ligand acts as a tripodal tetradentate chelating one. On the basis of the octahedral structures of $[Ni(ADA)(H_2O)_2]$, reported in the literature, and of the new compounds, it is concluded that there is a preference for the N(Him)donor atom to occupy the *trans*-position to the M–N(ADA) bond.

Keywords: *N*-carbamoylmethyl-iminodiacetic acid; *N*-(2-amidomethyl)-iminodiacetic acid; *N*-(2-acetamido)-iminodiacetic acid; Imidazole; Mixed-ligand complexes; Aqua(imidazole)(*N*-carbamoylmethyl-iminodiacetato)nickel(II) sesquihydrate; Aqua(imidazole)(*N*-carbamoylmethyl-iminodiacetato)cobalt(II) sesquihydrate; Molecular and crystal structures; Magnetic, spectral and thermal properties

N-carbamoylmethyl-iminodiacetic acid also named *N*-(2-acetamido)-iminodiacetic acid or *N*-(2-amidomethyl)-iminodiacetic acid [$H_2ADA{=}H_2NCOCH_2N(CH_2CO_2H)_2$)] is a well known chelating agent, also used in 'biological buffers' of pH 6.0–7.4 [1]. Metal(II) ion–ADA chelation in solution has been known for a long time (metal = Mg, Ca, Sr, Ba, Mn, Co, Ni, Cu, Zn, Cd, Hg, Pb) [2]. The results of this study agree with more recent ones [3–6] about the stoichiometry and stability of ADA complexes in solution [2] which show that 'primary amide' deprotonation reactions for ML_2 chelates of Co(II) or Zn(II) [3] can arise in alkaline solutions. In alkaline solutions, Cu(II) dechelation processes have also been claimed upon ADA amide deprotonation [7,8].

Several papers have appeared in recent years concerning the mixed-ligand complexes of a variety of

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0277-5387/00/$ - see front matter
PII: S0277-5387(00)00547-7

metal ions and ADA as primary ligand. Such compounds have salicylhydroxamate [9a], thiosemicarbazide [9b], dithiocarbazate [9b], aromatic acids [9c], amino acids [9d,e] or salicylic acid derivatives [9f] as secondary ligands. A certain number of such mixed-ligand metal complexes having ADA have been obtained in solid state and characterised by spectral and other physico-chemical methods. However structural studies in this context were noticeably limited to one aqua–*oxo*-ADA complex with vanadium(IV) [10] and the potassium salt of an *oxo*-peroxo-ADA-vanadium(V) complex [11,12]. In such compounds, ADA acts as a tripodal-tetradentate ligand.

The structural research of ADA–metal chelates in solid state seems a useful tool because it can provide information about the chelating role of the divalent anion $H_2NCOCH_2N(CH_2CO_2^-)_2$. Particular interest focuses on the way in which its 'primary amide group' takes part in metal ion chelation. In this sense and as a part of our studies on mixed-ligand Cu(II) complexes having IDA or IDA-derivatives and *N*-heterocyclic ligands, we have synthesised for the first time the compound (imidazole)(*N*-carbamoylmethyl-iminodiacetato)-copper(II), [Cu(ADA)(ImH)] [13a]. In recent reports we reported the structures of compounds $\{[Cu(ADA)]\cdot H_2O\}_n$ and $[Cu(ADA)(bipy)]\cdot 3H_2O$ (bipy = 2,2′-bipyridine) [13b] and of the H_2ADA acid itself and the nickel derivative *cis*-$[Ni(ADA)(H_2O)_2]$ [13c]. Again, the XRS study of these complexes has revealed that ADA acts as a tripodal-tetradentate ligand. In the case of the octahedral Ni(II)–ADA chelate, the *cis*-coordination of both aqua ligands suggests several possibilities for substitution by other ligands which we consider in our research projects. For example, replacing only one water molecule by an imidazole (Him) in this latter complex, two different possibilities of linking Him ligand to the nickel(II) atom arise. These are in *cis*- or *trans*-position versus the metal–N(ADA) bond. The aim of the present work is to find an answer to this question. In this connection, we report the synthesis, crystal structure and properties of two new mixed-ligand complexes of nickel(II) or cobalt(II) having aqua, ADA and Him as choice ligand set.

1. Experimental

1.1. Synthesis of aqua(imidazole)(N-carbamoylmethyl-iminodiacetato)-metal(II) sesquihydrate for cobalt(II) and nickel(II)

$[M(ADA)(Him)(H_2O)]\cdot 1.5H_2O$, compounds **I** (Co) or **II** (Ni), were obtained by stoichiometric reaction between $CoCO_3\cdot Co(OH)_2\cdot 2H_2O$ (252.2 mg, 1 mmol, Merck, Co ≥ 47%) or $NiCO_3\cdot 2Ni(OH)_2\cdot 4H_2O$ (250.0 mg, 0.67 mmol, Merck, Ni ≥ 47%) and H_2ADA (380.3 mg, 2 mmol, Aldrich, 98%) in water (100 ml) in a Kitasato flask, heating ($t < 50$°C) and stirring under reduced pressure (to remove the CO_2 by-product) for 3 h. These mixtures were still stirred 24 h at ~60°C and then slowly filtered to remove an almost inappreciable amount of non-reacted CoO or NiO (insoluble by-products). The pH of the reacting mixtures was not controlled during the synthesis processes. The resulting pink or green solutions were left to cool and imidazole (136.2 mg, 2 mmol, Merck, >99%) was added with stirring, which produces colour intensification (Co) or a change to a bluish colour (Ni). After 3 weeks of slow evaporation at room temperature (the remaining volume being 10–15 ml) the solutions were filtered over a small crystallisation dish and covered with a watch glass to reduce the rate of evaporation. After several days, well-shaped dark pink or bluish crystals of complexes **I** or **II**, respectively, appeared, which were suitable for X-ray diffraction studies. Additional amounts of products were formed again and collected in the same way. If mother liquor super-saturation arises, the addition of small volumes of water and ethanol and slow evaporation as before can induce the crystallisation. These products were collected by filtration, washed with a little of cool water and carefully air-dried. They can be re-crystallised several times from water. Yield: variable but usually <60%. *Anal.* Calc. for compound $C_9H_{17}CoN_4O_{7.5}$ (**I**): C, 30.01; H, 4.76; N, 15.56; Co, 16.36. Found: C, 30.20; H, 4.95; N, 15.65; Co, 16.27%. *Anal.* Calc. for complex $C_9H_{17}N_4NiO_{7.5}$ (**II**): C, 30.03; H, 4.76; N, 15.57; Ni, 16.31. Found: C, 30.27; H, 4.64; N, 15.36; Ni, 16.24%.

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

A prismatic crystal of compound **I** (dark pink) or **II** (bluish) 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 $7.794 < \theta < 11.448$ or of $9.966 < \theta < 10.501$, respectively, in an Enraf Nonius MACH3 automatic diffractometer [14]. 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 [15]. A semi-empirical absorption correction (ψ scan) was made [16]. The structure was solved by direct methods [17] and subsequent difference Fourier maps and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [18]. All hydrogen atoms were located in their calculated positions (C–H 0.93–0.97 Å) and were refined using a rigid model. Hydrogen atoms of water were not located. The absolute configuration was established [19].

Atomic scattering factors were taken from the 'International Tables for X-ray Crystallography' [20]. Molecular graphics were prepared with the program PLATON-98 [21]. A summary of the crystal data, experimental details and refinement results are listed in Table 1.

1.3. Physical measurements

Cobalt(II) or Nickel(II) titration was carried out by standard EDTA complexometry using xilenol orange as metallochromic indicator [22a]. Alternative procedures using murexide indicator in weak alkaline solution (for Co and Ni) or alizarin complexone in weak acid solution (for Co) are available [22b]. For this purpose an accurately weighted sample (≥ 0.5 g) of each of the studied compounds was mineralised with 2 N sulphuric acid and hydrogen peroxide solutions in a precipitation vessel covered with a watch glass. The reaction and decomposition of H_2O_2 in excess were favoured by heating carefully and the resulting green solution of nickel(II) sulfate or pink solution of cobalt(II) sulfate was quantitatively diluted with doubly-distilled water into a 250 ml volumetric flask. Aliquots (25 ml) of these solutions were titrated as described elsewhere [13c,22]. Elemental analysis (C, H, N) were performed in the Scientific Instrumental Centre of the University of Granada as described earlier [13]. Infrared (IR) spectra were obtained by the KBr disc technique on a Nicolet FTIR 20SXB or a JASCO FTIR 410 instrument. TG (pyrolysis) of studied compounds and analysis of evolved gases were recorded (295–775 K) in air flow (100 ml min^{-1}) using a Shimazu Thermobalance TGA-DTG-50H coupled with an IR-FT Nicolet Magma 550 (and mass spectrometer Fisons Thermolab). Electronic (reflectance) spectra (175–3300 nm) were obtained in a Cary 5E spectrophotometer. The magnetic susceptibilities of **I** and **II** were 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 of ligands and metal atom (150×10^{-6} cm^3 mol^{-1} for both compounds) were estimated from Pascal constants [23,24].

Table 1
Crystal data and structure refinement for complex [Co(ADA)(Him(H_2O)]·1.5H_2O (**I**) and complex [Ni(ADA)(Him)(H_2O)]·1.5H_2O (**II**)

	Compound **I**	Compound **II**
Empirical formula	$C_9H_{17}CoN_4O_{7.5}$	$C_9H_{17}N_4NiO_{7.5}$
Formula weight	360.19	359.95
Temperature (K)	293(2)	293(2)
Wave length (Å)	0.71073	0.71073
Crystal system, space group	orthorhombic, *Pna*2(1) (no. 33)	orthorhombic, *Pna*2(1) (no. 33)
Unit cell dimensions		
a (Å)	15.364(2)	15.191(4)
b (Å)	7.120(2)	7.093(2)
c (Å)	27.699(10)	26.517(5)
α, β, γ (°)	90	90
Volume (Å^3)	2818.4(2)	2857.6(11)
Z, D_{calc} (Mg m^{-3})	8, 1.629	8, 1.664
Absorption coefficient (mm^{-1})	1.217	1.401
F(000)	1472	1480
Crystal size (mm)	$0.25 \times 0.20 \times 0.15$	$0.25 \times 0.15 \times 0.10$
Theta range for data collection (°)	2.65–26.20	2.68–28.45
Index ranges	$0h19$, $-8k0$, $-33l0$	$-20h0$, $-9k0$, $-35l0$
Reflections collected/unique	2991/2991 [$R_{int} = 0.0393$]	3681/3681 [$R_{int} = 0.0000$]
Completeness	99.7% (to $2\theta = 26.20$)	99.9% (to $2\theta = 28.45$)
Absorption correction	Psi-scan	Psi-scan
Max. and min. transmission	0.961 and 0.902	0.918 and 0.934
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2991/1/358	3681/0/358
Goodness-of-fit on F^2	0.978	0.918
Final R indices [I > $2\sigma(I)$]	$R_1 = 0.063$, $wR_2 = 0.124$	$R_1 = 0.054$, $wR_2 = 0.092$
R indices (all data)	$R_1 = 0.290$, $wR_2 = 0.174$	$R_1 = 0.313$, $wR_2 = 0.133$
Absolute structure parameter	0.00	0.00
Largest difference peak and hole (e Å^{-3})	0.905 and −1.028	0.664 and −1.2100

2. Results and discussion

2.1. Molecular and crystal structure of aqua(N-carbamoylmethyl-iminodiacetato)metal(II) sesquihydrate with cobalt(II) or nickel(II) ions

Selected bond lengths and angles between non-hydrogen atoms and hydrogen bonding data of compounds **I** and **II** are given in Tables 2 and 3, respectively. From the data shown in Tables 1–3, it follows that both compounds are isostructural. Consequently, they could be discussed at the same time. The crystal of these compounds consist of complex units [M(ADA)(Him)(H_2O)] (hereafter M = Co or Ni) and non-bonded to the metal water molecules linked in a tridimensional hydrogen bonding network involving all polar N–H bonds of the ADA amide group and Him ligand, and probably O–H bonds of water molecules (see Tables 2 and 3). The asymmetric unit of the crystal of such compounds contains twice the formula (see Fig. 1 for nickel(II) derivative). Thus, each asymmetric unit contains two non-equivalent complex molecules from a crystallographic point of view and three non-coordinated water molecules. However, these complex

Table 2
Selected bond lengths (Å) and angles (°) for complex $[Co(ADA)(Him(H_2O)]\cdot 1.5H_2O$ (**I**) (e.s.d. values in parenthesis)

Cobalt(II) coordination			
Co(1)–N(12)	2.047(14)	Co(2)–N(22)	2.0311
Co(1)–O(11)	2.074(12)	Co(2)–O(21)	2.0446
Co(1)–O(13)	2.084(11)	Co(2)–O(23)	2.0659
Co(1)–O(1)	2.121(12)	Co(2)–N(21)	2.1016
Co(1)–O(15)	2.165(12)	Co(2)–O(2)	2.1349
Co(1)–N(11)	2.178(12)	Co(2)–O(25)	2.1438
Co(1)–Co(1)^{ii}	7.012(1)	Co(2)–Co(2)^{ii}	7.012(1)
Co(1)–Co(1)^{iv}	7.012(1)	Co(2)–Co(2)^{iv}	7.012(1)
N(12)–Co(1)–O(11)	105.1(5)	N(22)–Co(2)–O(21)	100.4
N(12)–Co(1)–O(13)	95.4(5)	N(22)–Co(2)–O(23)	93.2
O(11)–Co(1)–O(13)	91.1(5)	O(21)–Co(2)–O(23)	92.6
N(12)–Co(1)–O(1)	92.0(5)	N(22)–Co(2)–N(21)	175.7
O(11)–Co(1)–O(1)	87.0(5)	O(21)–Co(2)–N(21)	83.0
O(13)–Co(1)–O(1)	172.6(4)	O(23)–Co(2)–N(21)	84.0
N(12)–Co(1)–O(15)	98.6(5)	N(22)–Co(2)–O(2)	90.9
O(11)–Co(1)–O(15)	156.1(4)	O(21)–Co(2)–O(2)	89.8
O(13)–Co(1)–O(15)	89.4(5)	O(23)–Co(2)–O(2)	174.8
O(1)–Co(1)–O(15)	89.5(5)	N(21)–Co(2)–O(2)	91.8
N(12)–Co(1)–N(11)	174.8(6)	N(22)–Co(2)–O(25)	98.1
O(11)–Co(1)–N(11)	79.2(5)	O(21)–Co(2)–O(25)	161.3
O(13)–Co(1)–N(11)	81.6(5)	O(23)–Co(2)–O(25)	88.8
O(1)–Co(1)–N(11)	91.1(5)	N(21)–Co(2)–O(25)	78.7
O(15)–Co(1)–N(11)	77.2(5)	O(2)–Co(2)–O(25)	87.4

Hydrogen bonds [a]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
N(13)–H(13)···O(14) # 1	0.86	1.91	2.74(2)	160.1
N(16)–H(16A)···O(25)	0.86	2.20	3.01(2)	157.4
N(16)–H(16B)···O(13) # 2	0.86	2.10	2.94(2)	166.7
N(23)–H(23)···O(24) # 3	0.86	1.83	2.66(4)	160.7
N(26)–H(26A)···O(15)	0.86	2.27	3.07(2)	155.1
N(26)–H(26B)···O(23) # 4	0.86	2.06	2.90(2)	165.7

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

molecules are very similar from a chemical point of view. In both compounds the octahedral coordination polyhedron of the metal(II) atom is built up by means of the atom N(amino), two O(carboxyl) ones and the O(amide) donor of the tetradentate ADA^{2-} ion as well as the N(pyridine-like) atom of the Him ligand plus the O(aqua) donor of the coordinated water molecule. As regards the cobalt(II) derivative, it is widely recognised that such a $3d^7$ transition divalent metal ion adopts two major stereochemistries, distorted octahedral and tetrahedral [25]. In this connection, the ligand polarisability plays a discriminating role. Less polarisable or hard donors (as most O donor and N(amine) ones) favour octahedral structures in pink to violet cobalt(II) coordination compounds [25]. The reported case falls in this group and consequently its stereochemistry will be considered normal. On the other hand, the octahedral coordination of nickel(II) atom in compound **II** should be expected because it has been recently reported for $[Ni(ADA)(H_2O)_2]$ [13c] and it is the most frequent stereochemistry for this $3d^8$ divalent transition metal ion [25]. In contrast, it is worth noting that the structure of an analogous mixed-ligand Co(II)–ADA–H_2O complex remains unknown and all attempts to obtain X-ray quality crystals of this compound in our laboratories have been unsuccessful. Because the effective ionic radii of octahedral Ni(II) (0.72 Å [26]) and Co(II) (0.745 Å, high spin [25]) are very similar, there is no comment to add about the isostructural feature in the studied compounds. Otherwise the M(II) coordination polyhedron and the internal geometry of the ADA ligand have usual bonds and angles compared with related compounds. That includes known metal–ADA complexes [8–10,12,13], cobalt(II)–IDA chelates [27] or nickel(II)–IDA ones [28] as well as a variety of mixed-ligand complexes of cobalt(II) [29] or nickel(II) [30] having from one to four Him ligands.

The metal chelation of the tripodal ADA ligand in **I** and **II** represents the formation of two nearly coplanar M–glycinate-like rings and one M–glycinamide-like one sharing the M–N(amino) bond. One of the M–glycinate-like rings falls nearly coplanar to the plane [M, N(Him), O(aqua)] (hereafter so-called G ring). This chelate ring is less distorted (deviations from its mean ring plane ranging 0.00–0.08 Å) than the other two ones. Moreover such a G ring exhibits a slightly puckered configuration (both carbon atoms displaced at opposite side of its plane N–M–O) in complex units of Co(1) and Ni(1) atoms, and a slightly asymmetrical envelope configuration (both carbon atoms at the same side of its N–M–O plane) in complex units of Co(2) and Ni(2) atoms [30]. The remaining M–glycinate-like ring and the M–glycinamide-like one are nearly coplanar to each other (angle between mean planes of 14.4 ± 1.7°). These rings fall not coplanar/ nearly perpendicular to the plane [M, N(Him), O(aqua)] (and then, hereafter will be so-called R and R′ rings, respectively). All R and R′ chelate rings in the studied compounds (max. deviations of the atoms from its mean ring plane ≤ 0.28 Å) are significantly more distorted than the corresponding G one (max. deviations of the atoms from its mean ring plane ≤ 0.08 Å). In addition, these rings adopt invariably an asymmetrical envelope configuration (with both carbon atoms at the same side of its N–M–O plane) rather common in metal-amino acid chelates and closely related compounds [31].

On the other hand, the Him ligand is, as expected, planar within 0.03(1) Å. The metal ion is out of the Him plane at a distance ranging from only 0.008(1) Å for Ni(1) up to 0.130(1) Å for Ni(2) (being of 0.050(1) and 0.076(1) Å for Co(1) and Co(2) cases, respectively). The Him plane is slightly twisted ($<10°$) versus the mean plane defined by its N(pyridine-like) donor atom and the three ADA donors involved in the R and R′ chelate rings. This fact means that the heterocyclic

Table 3
Selected bond lengths (Å) and angles (°) for complex [Ni(ADA)(Him)(H_2O)]·1.5H_2O (**II**) (e.s.d. values in parenthesis)

Nickel(II) coordination			
Ni(1)–N(12)	2.013(9)	Ni(2)–O(21)	2.0317
Ni(1)–O(11)	2.054(8)	Ni(2)–O(23)	2.0481
Ni(1)–O(13)	2.065(8)	Ni(2)–N(21)	2.0849
Ni(1)–N(11)	2.076(10)	Ni(2)–O(2)	2.1177
Ni(1)–O(15)	2.101(8)	Ni(2)–O(25)	2.1317
Ni(1)–O(1)	2.112(9)	Ni(2)–N(22)	2.0155
Ni(1)–Ni(1)^{ii}	7.093(1)	Ni(2)–Ni(2)^{ii}	7.093(1)
Ni–1)–Ni(1)^{iv}	7.093(1)	Ni(2)–Ni(2)^{iv}	7.093(1)
N(12)–Ni(1)–O(11)	99.6(4)	N(22)–Ni(2)–O(21)	100.3
N(12)–Ni(1)–O(13)	94.4(4)	N(22)–Ni(2)–O(23)	92.8
O(11)–Ni(1)–O(13)	88.8(4)	O(21)–Ni(2)–O(23)	92.6
N(12)–Ni(1)–N(11)	177.3(4)	N(22)–Ni(2)–N(21)	175.7
O(11)–Ni(1)–N(11)	82.4(4)	O(21)–Ni(2)–N(21)	83.1
O(13)–Ni(1)–N(11)	83.8(4)	O(23)–Ni(2)–N(21)	84.4
N(12)–Ni(1)–O(15)	99.0(4)	N(22)–Ni(2)–O(2)	91.2
O(11)–Ni(1)–O(15)	161.3(3)	O(21)–Ni(2)–O(2)	89.9
O(13)–Ni(1)–O(15)	91.2(4)	O(23)–Ni(2)–O(2)	174.8
N(11)–Ni(1)–O(15)	79.0(4)	N(21)–Ni(2)–O(2)	91.4
N(12)–Ni(1)–O(1)	91.2(4)	N(22)–Ni(2)–O(25)	98.2
O(11)–Ni(1)–O(1)	87.7(4)	O(21)–Ni(2)–O(25)	161.4
O(13)–Ni(1)–O(1)	173.9(3)	O(23)–Ni(2)–O(25)	88.9
N(11)–Ni(1)–O(1)	90.7(4)	N(21)–Ni(2)–O(25)	78.6
O(15)–Ni(1)–O(1)	90.5(4)	O(2)–Ni(2)–O(25)	87.3

Hydrogen bonds [a]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
N(13)–H(13)···O(14) # 1	0.86	1.89	2.73(2)	164.0
N(16)–H(16A)···O(25)	0.86	2.24	3.04(2)	155.4
N(16)–H(16B)···O(13) # 2	0.86	2.09	2.93(2)	167.9
N(23)–H(23)···O(24) # 3	0.86	1.88	2.71(2)	160.9
N(26)–H(26A)···O(15)	0.86	2.25	3.04(2)	151.9
N(26)–H(26B)···O(23) # 4	0.86	2.05	2.90(2)	166.3

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

ligand falls nearly perpendicular to the other two sets of roughly coplanar four donor atoms. An interesting structural correlation follows the structures of compounds **I** and **II**. That is, the preference of Him ligand for the *trans*-position to the N(ADA) donor one. Such correlation can not be inferred either from the structure of the complex [Cu(ADA)(Him)] [13a] because of its five-coordinated stereochemistry or from the structure of the closely related octahedral complex in the compound bis(imidazole)(nitrilopropionamide-diacetato)-nickel(II) monohydrate [30k] because of the presence of two Him ligands together with a tetradentate nitrilopropionamide-diacetate(2 −) ion.

It seems instructive to carry out a comparison of averaged coordination bond distances and *trans*-angles in [Ni(ADA)(H_2O)$_2$] [13c] and compounds **I** and **II** (Table 4). The following insights arise: (1) It should be noted the remarkable similarity of the average value for all six metal–ligand bond lengths. Such similarity is obviously higher for the two closely related nickel(II) compounds (with and without the Him ligand instead of an aqua one). (2) In these three compounds, the coordination bonds to four donor atoms of the tripodal ligand ADA are noticeably similar in length to each other (being more significant for [Ni(ADA)(H_2O)$_2$]). (3) In both new compounds the longest bond is that of M–O(amide). That is not observed for the diaqua–ADA–nickel(II) complex. (4) *Trans*-angles involving a M–O(aqua) bond or the M–N(Him) bond are nearly close to 180° (ranging from 173.7° to 179.3°) but the remaining *trans*-angle O(carboxyl)–M–O(amide) with both donors from ADA chelating ligand is significantly below this angle (in the range of 156–164°). These data reveal that the main source of the moderate but irregular distortion at the M(II) coordination polyhedron in the studied compounds arises from the chelate ring

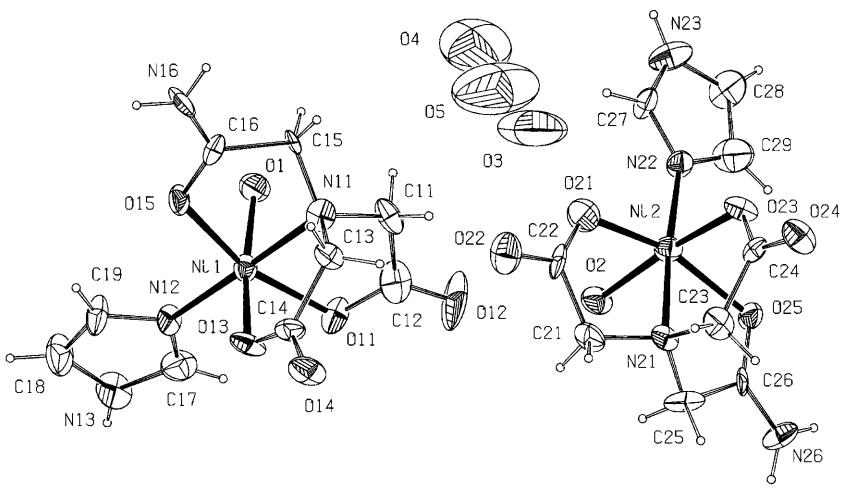

Fig. 1. Asymmetric unit in the crystal of compound [Ni(ADA)(Him)(H_2O)]·1.5H_2O (**II**).

Table 4
Structural relationships in mixed-ligand complexes $[Ni(ADA)(H_2O)_2]$ [13c] and $[M(ADA)(Him)(H_2O)]\cdot 1.5H_2O$ (M = Ni in **II**, Co in **I**): bond lengths (Å) and *trans*-angles (°)

Bond	$[Ni(ADA)(H_2O)_2]$	Compound **II** [a]	Compound **I** [a]
Bond lengths			
M–O(carboxyl, ADA)	2.051(2)	2.043	2.042
M–O(carboxyl, ADA)	2.045(2)	2.056	2.075
M–O(amide, ADA)	2.065(2)	2.116	2.154
M–N(amide, ADA)	2.072(2)	2.081	2.133
M–O(aqua) or N(Him)	2.000(2)	2.014	2.078
M–O(aqua)	2.106(2)	2.115	2.128
Average M–L bond	2.057	2.071	2.102
Bond angles			
N(amino)–M–O(aqua) or N(Him)	175.6	176.5	175.3
O(carboxyl)–M–O(aqua)	179.3	174.4	173.7
O(carboxyl)–M–O(amide)	163.8	161.4	158.7

[a] Average values for the two crystallographic independent complex units.

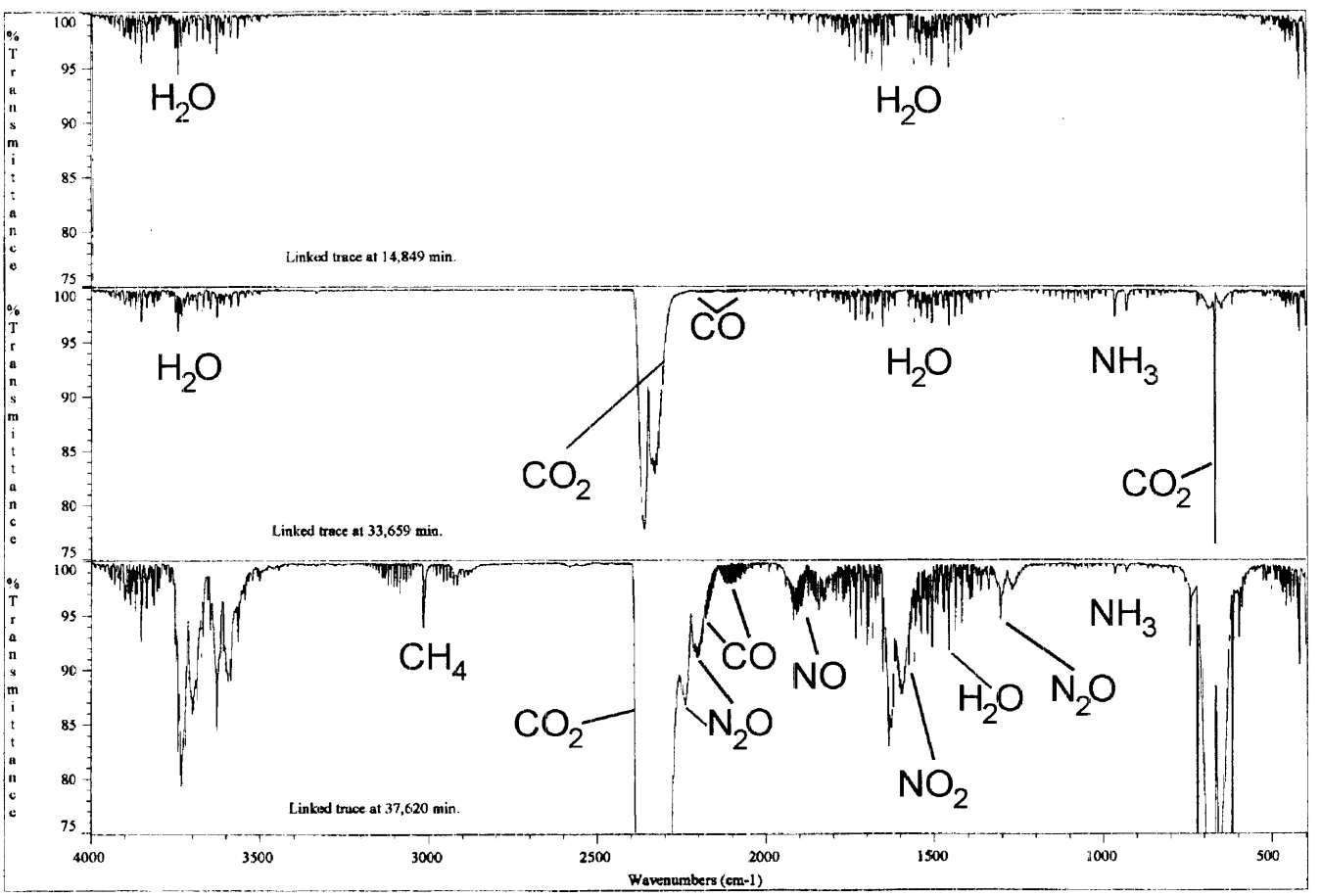

Fig. 2. Selected FTIR spectra from three steeps of the thermo-gravimetric analysis for compound **I**. (a) Spectrum at $t = 14.849$ min from first step showing only bands of water in first steep. (b) Spectrum at $t = 33.659$ min from second step with bands of water, CO_2, CO (traces) and ammonia. (c) Spectrum at $t = 37.620$ min from the beginning of third step showing bands of water, CO_2, CH_4, N_2O, NO and NO_2.

constraints in the tripodal ADA ligand. In this connection, it is worth noting that just the most distorted set of four nearly coplanar donor atoms in compounds **I** and **II** is that of the four oxygen ones (three from ADA, one from aqua). Indeed these four oxygen atoms define a folded square with a mean plane P[4(O)] from which both *trans*-pairs of oxygen donor atoms are displaced similarly but in opposite sense ($\pm 0.13(2)$ Å),

whereas the atoms of the other two sets of roughly coplanar four-donor ones deviates $<0.06(2)$ Å from its corresponding mean plane. The metal atom is also largely moved (0.20–0.29(2) Å) out of such P[4(O)] plane towards the Him ligand (whereas the deviation of the metal atom from the other two referred mean planes is $<0.04(2)$ Å).

2.2. Properties of aqua(N-carbamoylmethyl-iminodiacetato)metal(II) sesquihydrate for cobalt(II) and nickel(II)

The TG analysis in air-flow (with FTIR spectra of evolved gases) of compounds **I** and **II** are similar and show three steps. The first step (85–187°C for **I** and 135–235°C for **II**) corresponds to the loss of non-coordinated water, as it is supported by FTIR spectra (Fig. 2(a)). The other two steps corresponds to the overlapped pyrolysis of organic ligands (Fig. 2(b,c)) to give probably Co_2O_3 or $NiO{\cdot}Ni(NO_3)_2$ at 425°C. The weight loss and evolved gases in the second step (187–335°C, Fig. 2(b) for compound **I**) correspond to the loss of coordinated water plus the 2-amidomethyl arm of ADA, the organic ligand which begins the oxidative pyrolysis.

Since the isostructural relationship of compounds **I** and **II**, their IR spectra are extremely similar. They allow the identification of the main characteristic absorption bands (wave-numbers in cm^{-1}) expected for aqua and ADA ligands [32]: A very broad band (3800–2500) including ν(OH) of water, $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ of primary amide group at 3330 and 3141(3128), ν(C=O) of primary amide group ('amide I' band) at 1675, $\delta(H_2O)$, $\delta(NH_2)$ ('amide II' band) and $\nu_{as}(COO^-)$ overlapped at 1610 (1611), δ(N–H) of Him at 1542, and $\nu_s(COO^-)$ at 1403. Difference $\Delta(COO) = 207 \pm 1$ cm^{-1} in accordance with the expected ionic nature of the M(II)–O(carboxylato) bonds.

Electronic spectra of compounds **I** and **II** are typical of Co(II) (ground state $^4T_{1g}(F)$) and Ni(II) (ground state $^3A_{2g}(F)$) octahedral complexes, respectively. The spectrum of **I** shows bands at $\nu_1 = 8420$, $\nu_2 = 16\,100$ (shoulder) and $\nu_3 = 19\,350$ cm^{-1}, which fall between those of the hexaaqua-ion and the $[Co(NH_3)_6]^{2+}$ ion [25]). The spectrum of **II** shows bands $\nu_1 = 9930$ (shoulder at $\sim 14\,500$), $\nu_2 = 16\,420$ and $\nu_3 = 25\,975$ cm^{-1}. It can be assumed that $\nu_1 = 10$ Dq $= \Delta_o$, and a value of 856 cm^{-1} is obtained for the Racah parameter B', 83% of the B parameter in the free ion. Δ_o and B' in **II** are higher than those of *cis*-diaqua(*N*-carbamoylmethyl-iminodiacetato)nickel(II) [13c] as expected for the substitution of one aqua ligand by Him.

For both compounds studied, a plot of $1/\chi$ data versus T (K) ($T = 80$–290 K) is linear (with a statistical factor r^2 of 0.9997) according to a Curie–Weiss behaviour, $\chi_{mol} = C/(T-\theta)$, (see Fig. 3(a) for cobalt(II) case). The experimental value of the effective magnetic moment (μ_{eff}) for the metal(II) atom is 5.10 or 3.22 BM for **I** or **II**, respectively, within the corresponding ranges for mononuclear high-spin octahedral cobalt(II) [25] or in octahedral nickel(II) [26], in agreement with the structures reported, where the shortest inter-metallic distances are >7 Å.). The μ_{eff} value for the cobalt(II) complex largely exceeds the spin-only value [24] suggesting that there is an appreciable contribution of orbital angular momentum [25]. That can be attributed to its T ground term resulting in temperature-dependent orbital contributions to the magnetic moment. Accordingly, experimental values of μ_{eff} fall of with decreasing temperature (Fig. 3(b)).

3. Concluding remarks

Compounds **I** and **II** have octahedral stereochemistry for cobalt(II) and nickel(II) atoms, respectively, a rather common coordination for these metal(II) ions in moderate ligand fields. Such stereochemistry has been also observed in *cis*-diaqua(*N*-carbamoylmethyl-iminodiacetato)-nickel(II) [13c], the 'parent' complex of

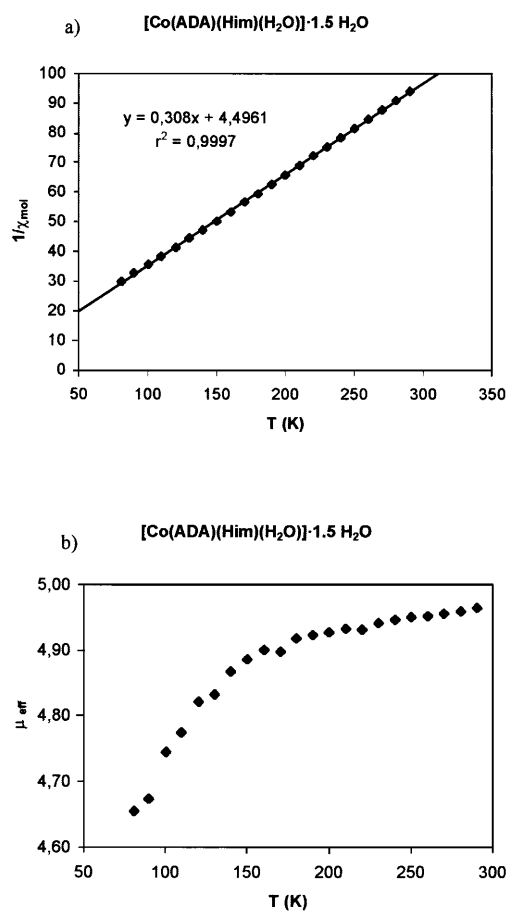

Fig. 3. Magnetic properties of compound **I**. (a) A plot of $1/\chi_{mol} = f(T)$: (◆, experimental; solid straight line represents the best theoretical fit to the linear form of the Curie–Weiss law). (b) Dependence of the effective magnetic moment versus the temperature.

compound **II**. This is in contrast to the distorted square-base pyramidal coordination found in the corresponding copper(II) derivatives, $\{[Cu(ADA)]\cdot H_2O\}_n$ (which has a polymeric structure [13b]) and [Cu(ADA)(Him)] [13a].

On the basis of the octahedral Ni(II) coordination in the above referred chelates, new structural relationships can be inferred [13c]. This study reveals that imidazole comes in the complex $[Ni(ADA)(H_2O)_2]$ replacing the aqua ligand just in *trans* to the bond Ni(II)–N(amino) with ADA. This ligand substitution reaction does not seem to cause significant changes in bond lengths and angles around the Ni(II) atom. In compounds **I** and **II**, one aqua ligand remains linked to the metal atom. That could permit further ligand substitution reactions. This possibility promotes new studies on mixed-ligand metal complexes with ADA and a variety of mono- and bi-dentate ligands.

The structure of the aqua–ADA–cobalt(II) complex remains unknown. Efforts will be made to cover this lack of information. On the other hand, at this moment, all known structures show ADA as an effective tripodal tetradentate ligand [11–13]. This feature suggests a remarkable ligand flexibility, but additional studies for metal ions with different crystallo-chemical properties will be required.

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 134849 for compound $[Co(ADA)(Him(H_2O)]\cdot 1.5H_2O$ (**I**) and CCDC no. 134848 for compound $[Ni(ADA)(Him)(H_2O)]\cdot 1.5H_2O$ (**II**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

This paper is devoted to the memory of Prof. Sergio Cabani (University of Pisa, Italy) recently deceased. He encouraged many contributions on thermodynamics and kinetics of metal complexes. We are grateful to the Dirección General de Enseñanza Superior e Investigación Científica, MEC, Spain, for financial support (Project PB-98-0605-C03-03). A.C. thanks the Xunta de Galicia for the financial support (Project XUGA20309B97). A research grant to E.B.A. from Ministerio de Educación y Cultura is gratefully acknowledged.

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