New copper(II) compound having protonated forms of ethylenediaminetetraacetate(4−) ion (EDTA) and adenine (AdeH): synthesis, crystal structure, molecular recognition and physical properties of (AdeH2)[Cu(HEDTA)(H2O)]·2H2O

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Abstract

The stoichiometric reaction of $Cu_2CO_3(OH)_2$, ethylenediaminetetraacetic acid ($H_4EDTA = C_2H_4(N(CH_2CO_2H)_2)_2$) and adenine (AdeH) in water yields crystalline samples of adeninium aqua-(ethylenediamine-N,N,N'-triacetato-N'-acetic)copper(II) dihydrate. The compound (AdeH2)[Cu(HEDTA)(H2O)]·2H2O was studied by TG analysis (with FT-IR study of the evolved gasses), IR, electronic and ESR spectra, magnetic susceptibility data, and single crystal X-ray diffraction methods (monoclinic system, space group $P2_1/c$ ($a = 7.053(1)$, $b = 42.540(5)$, $c = 7.798(1)$ Å, $\beta = 104.24(1)°$, $Z = 4$, and final $R_1 = 0.042$ for 5113 independent reflections). The asymmetric unit consists of a salt of adeninium(1+) and the aqua-copper(II) complex of $HEDTA^{3-}$ as chelating agent, and two crystallisation water molecules. The Cu(II) atom exhibits an elongated octahedral coordination (type $4+1+1$). The pentadentate $HEDTA^{3-}$ ligand has a typical E,G/R configuration and a free N-carboxymethyl arm. The uncoordinated $AdeH_2^+$ ion recognises the anion $[Cu(HEDTA)(H_2O)]^-$ through two rather linear N–H···O hydrogen bonds involving the protonated N1 heterocyclic atom and one H atom of the exocyclic-N6 amino group with two O atoms of the same $HEDTA^{3-}$ carboxylate group ($173(3)$ or $175(3)°$, and $2.64(1)$ or $2.80(1)$ Å, respectively). This ion pair recognises itself by a π,π-stacking between the six-membered aromatic rings of adjacent $AdeH_2^+$ ions which lay out slightly slipped ($\beta = \gamma = 10.1°$) and anti-parallel at 3.34 Å, thus forming aggregates $\{(AdeH_2)[Cu(HEDTA)(H_2O)]\}_2$. The remaining O–H (carboxy or water) and N–H (heterocyclic or exocyclic) polar bonds interact with O carboxylate or water atoms or N3 and N7 adeninium atoms building the crystal in an extensive 3D-hydrogen bonded network. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Copper(II) complex; Crystal structures; EDTA; Adeninium; Ion pair; Molecular recognition

1. Introduction

The interaction of nucleic acids or their constituents with metal ions has been a matter of extensive studies for more than the three past decades, because of their chemical and biological interest, covering structural, thermodynamic and kinetic works. In this broad context, certain recent studies have focused on metal complexes that can specifically recognise nucleobases [1]. We have interest in the structure of mixed-ligand copper(II) complexes having adenine (AdeH) as auxiliary ligand, because this N-rich nucleobase has proved to be a rather versatile metal-binding biomolecule. However, only a few structures have been reported for copper(II) with anionic adeninato (Ade⁻) [1–4], neutral AdeH [5–7] or cationic adeninium(1+) (AdeH2⁺) [8–10]. These are mono- [1,3,4,7,9,10], di- [2,5,6] or trinuclear [8] complexes which have the metal in various coordination polyhedrons (type 4, 4+1 or 4+2) where the nucleobase species is always linked to the copper(II)

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atom by the N(9) donor (as mono-dentate) [1,3,4,7,9,10] or in a μ-N(3),N(9) bridging mode (oligomers) [2,5,6,8]. Such coordination modes in non-substituted adenine species are understood on the basis that the N(9) donor atom is the most basic among its five nitrogen atoms, followed by N(1) [1]. Interestingly a single metal–N(3)–adenine coordination has been proved in the structure of [Ni(AdeH)(tren)Cl]Cl [11] and [Pd(thiacyclophane)(A-deH)]BF$_4$ [12]. A variety of structures concerning adeninium(1+) and adeniniun(2+) ions (for this latter, four inorganic salts [13–15]) are also known. Compounds which have AdeH$_2^+$ cation are a broad variety of salts with inorganic or organic counter-anions as well as adeninium(1+)–metal complexes of nickel(II) [16], copper(II) [8–10], zinc(II) [17–19] cadmium(II) [20] and silver(I) [21]. In the Cd(II) derivative the AdeH$_2^+$ ligand acts as a bridge, with an unexpected μ-N3,N7 coordination mode [20]. In Ag(I) complexes, AdeH$_2^+$ ion links the metal by N(9) atom [21], whereas in Ni(II) [16] and Zn(II) [17–19] derivatives the donor is unusually the N(7) atom. Keeping this in mind, as a part of the laboratory work for our students in Inorganic Aspects of Biological Processes [22], the following proposal was made: to carry out the reaction of AdeH and aqua(dihydrogen-ethylenediaminetetraacetato)copper(II), [Cu(H$_2$EDTA)(H$_2$O)], an acid-complex derivative of ethylenediaminetetraacetic acid (H$_4$EDTA) whose structure was reported by Stephens a long time ago [23]. In this octahedral complex the pentadentate H$_2$EDTA^{2-} ligand has one coordinated and one free acetic arms. We could expect that this acidic complex should react with neutral AdeH to give the AdeH$_2^+$ ion. This adeninium(1+) ion could or could not bind the copper(II) atom. In this latter case it probably replaces the aqua ligand, which in the parent complex is among the four closest donors. The best way to find definitive answers to these hypotheses is to perform the X-ray structure determination of the corresponding reaction product. In this connection, we have carried out the synthesis, structure and properties of the title compound.

2. Experimental

All chemicals were commercially available products of reagent grade and used without further purification.

2.1. Synthesis of title compound 1

Adeninium [aqua(ethylenediamine-*N,N,N′*-triace-tato-*N′*-acetic acid)copper(II) dihydrate} (1) (AdeH$_2$)[Cu(HEDTA)(H$_2$O)]·2H$_2$O, was obtained by reaction of Cu$_2$CO$_3$(OH)$_2$ (221 mg, 1 mmol, Probus or Aldrich) and H$_4$EDTA (588.5 mg, 2 mmol, Sigma) in water (100 ml) in a Kitasato flask, by heating (15 min, *t* < 50 °C) and

stirring under reduced pressure (to remove the CO$_2$, by-product). The resulting blue solution was stirred and heated at 60 °C during 30 min. After leaving it to cool to room temperature (r.t.), it was slowly filtered (without vacuum, to remove a very small amount of CuO) on an Erlenmeyer flask. Adenine (270 mg, 2 mmol) was added to this clear blue solution and stirred. No appreciable change of colour occurs in the solution, which was filtered without vacuum on crystallisation device. By slow evaporation of the clear solution at r.t. (1–2 weeks), crystals of compound 1 were observed. First poly-crystals were removed by filtration. The evaporation of the remaining solution (partially covered with a plastic film) gives many well-shaped crystals of the desired product suitable for X-ray diffraction studies. Several fractions of the product were collected by filtration, washed with cold water and air-dried. The blue compound is stable at r.t. without apparent water loss. It can be re-crystallised at r.t. from water. Yield: 980 mg (90%). C$_{15}$H$_{25}$CuN$_7$O$_{11}$: Calc.: H 4.64, C 33.18, N 18.06. Found: H 5.13, C 32.99, N, 18.19%. Calc. Cu 11.7. Found: Cu 17.6% (EDTA complexometry [24]). If the solution of compound 1 became microbiologically contaminated, ethanol should be added, the solution covered with a plastic film, filtered without vacuum 2 or more days after, and left to evaporate as before. Using a molar ratio Cu(II)/H$_4$EDTA/AdeH 1:1:2, a pale blue powder of the type Cu(EDTA)·(AdeH$_2$)$_2$·nH$_2$O is also obtained. However, no suitable crystals for X-ray diffraction studies of such compound have yet been obtained. The analytical data of this product is close to a 1:2 metal/ligand molar ratio, but at the present time it seems not consistent enough to a well-defined stoichiometry.

2.2. Crystal structure determination

A blue prismatic crystal of (AdeH)[Cu(HEDTA)-(H$_2$O)]·2H$_2$O was mounted on a glass fibre and used for data collection. Crystal data were collected at 291(2) K, using a Bruker SMART CCD 1000 diffractometer. Graphite monochromated Mo Kα radiation (λ = 0.71073 Å) was used throughout. The data were processed with SAINT [25] and corrected for absorption using SADABS (transmission factors: 0.9189–0.6729) [26]. The structure was solved by direct methods using the program SHELXS-97 [27] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97 [28]. Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were located unambiguously from difference Fourier maps and refined isotropically. Atomic scattering factors from 'International Tables for X-ray Crystallography' [29]. Molecular graphics were obtained with the program PLATON [30]. A summary of the crystal data, experimental details and refinement results are listed in Table 1.

Table 1
Crystal data and structure refinement for compound **1**

Empirical formula	$C_{15}H_{25}CuN_7O_{11}$
Formula weight	542.96
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	7.053(1)
b (Å)	42.540(5)
c (Å)	7.4978(1)
β (°)	104.24(1)
Volume (Å^3)	2180.5(2)
Z	4
Calculated density (Mg m^{-3})	1.654
Absorption coefficient (mm^{-1})	1.075
$F(000)$	1124
Crystal size (mm)	$0.40 \times 0.14 \times 0.08$
θ range for data collection (°)	1.91–28.01
Index ranges	$-9 < h < 9$, $-56 < k < 55$, $-8 < l < 9$
Reflections collected/unique	13576/5113 [$R_{int} = 0.0509$]
Completeness to $\theta = 28.02°$	95.9%
Absorption correction	SADABS
Max and min transmission	0.9189 and 0.6729
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5113/0/407
Goodness-of-fit on F^2	0.910
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.042$, $wR_2 = 0.064$
R indices (all data)	$R_1 = 0.087$, $wR_2 = 0.072$
Largest difference peak and hole (e Å^{-3})	0.394 and -0.394

2.3. Physical measurements

Elemental analysis was performed on a Fisons–Carlo Erba EA 1108 microanalyser (C, H, N) or by standard EDTA complexometry (Cu). The infrared spectrum was obtained by the KBr disc technique on a JASCO FT-IR 410 instrument. TG analysis (pyrolysis) of the studied compound (295–875 K) in air flown (100 ml min^{-1}) and corresponding IR spectra of evolved gasses were recorded using a Shimazu Thermobalance TGA-DTG-50H coupled with an FT-IR Nicolet Magna 550. Electronic (reflectance) spectrum (175–3300 nm) was obtained in a Varian Cary-5E spectrophotometer. RSE spectrum of a polycrystalline sample was recorded without magnetic dilution in a spectrophotometer Bruker ESP 300E (X band) at r.t. Magnetic susceptibility was measured at the temperature range 80–300 K using a Manics DM magnetometer. The susceptometer was calibrated with mercury tetrakis(thiocyanato)cobaltato(II). Corrections for the diamagnetism (-271.47×10^{-6} cm^3 mol^{-1}) were estimated from Pascal's constants [31]. Experimental susceptibilities were also corrected for the temperature-independent paramagnetism (60×10^{-6} cm^3 mol^{-1}).

3. Results and discussion

3.1. Cu(II) coordination, conformation of ligands and crystal packing in compound **1**

Bond lengths and angles of the copper(II) coordination in the complex [Cu(HEDTA)(H$_2$O)]$^-$ of compound **1** are listed in Table 2. Structural data of the adeninium(1+) ion are given in Table 3. Hydrogen bonding data of the studied crystal are showed in Table 4. The studied compound consists of a salt of the complex anion [Cu(HEDTA)(H$_2$O)]$^-$ and the adeninium(1+) cation with two non-bonded to the metal water molecules (Fig. 1). The copper(II) atom exhibits a distorted octahedral coordination supplied by a penta-dentate HEDTA^{3-} anion and one aqua ligand. This coordination polyhedron is of the general type $4+1$ and closely related to those reported for the parent complex [Cu(H$_2$EDTA)(H$_2$O)] [23] (hereafter compound **2**) and the bimetallic derivative Ag[Cu(HEDTA)(H$_2$O)]·H$_2$O [32] (hereafter compound **3**). The metal falls at 0.083(1) Å from the mean plane P-1 [O1,O11,O15,N12] of the four closest donor atoms (0.075(1) and 0.13(1) Å in compounds **2** and **3**, respectively). In the three compounds which we are considering now, the partially protonated EDTA ligand acts as pentadentate giving a Cu(II)–ethylendiamine-like ring (E ring) and three Cu(II)–glycinato-like rings (one of them is a Cu(II)–glycine-like ring in compound **2**). Two of these three rings are so-called R rings (nearly perpendicular to the plane P-2 [Cu1,N11,N12]), and the

Table 2
Bond lengths (Å) and angles (°) for copper(II) coordination in compound **1**

Bond lengths	
Cu(1)–O(15)	1.941(1)
Cu(1)–O(11)	1.953(1)
Cu(1)–O(1)	1.954(1)
Cu(1)–N(12)	2.066(1)
Cu(1)–N(11)	2.373(1)
Cu(1)–O(17)	2.405(1)
Bond angles	
O(15)–Cu(1)–O(11)	176.64(1)
O(15)–Cu(1)–O(1)	89.06(1)
O(11)–Cu(1)–O(1)	92.51(1)
O(15)–Cu(1)–N(12)	85.69(1)
O(11)–Cu(1)–N(12)	93.48(1)
O(1)–Cu(1)–N(12)	166.28(1)
O(15)–Cu(1)–N(11)	97.48(1)
O(11)–Cu(1)–N(11)	79.19(1)
O(1)–Cu(1)–N(11)	110.65(1)
N(12)–Cu(1)–N(11)	82.64(1)
O(15)–Cu(1)–O(17)	91.35(1)
O(11)–Cu(1)–O(17)	91.49(1)
O(1)–Cu(1)–O(17)	94.29(1)
N(12)–Cu(1)–O(17)	73.20(1)
N(11)–Cu(1)–O(17)	153.57(1)

Table 3
Bond lengths (Å) and angles (°) for adeninium(1+) ion in compound **1**

Bond lengths	
N(21)–C(21)	1.313(1)
N(22)–C(22)	1.341(1)
N(22)–C(21)	1.375(1)
N(23)–C(22)	1.308(1)
N(23)–C(23)	1.350(1)
N(24)–C(25)	1.313(1)
N(24)–C(24)	1.377(1)
N(25)–C(25)	1.353(1)
N(25)–C(23)	1.355(1)
C(21)–C(24)	1.384(1)
C(23)–C(24)	1.390(1)
Bond angles	
C(22)–N(22)–C(21)	123.40(1)
C(22)–N(23)–C(23)	111.43(1)
C(25)–N(24)–C(24)	102.54(1)
C(25)–N(25)–C(23)	106.25(1)
N(21)–C(21)–N(22)	119.44(1)
N(21)–C(21)–C(24)	126.74(1)
N(22)–C(21)–C(24)	113.83(1)
N(23)–C(22)–N(22)	125.88(1)
N(23)–C(23)–N(25)	127.34(1)
N(23)–C(23)–C(24)	127.46(1)
N(25)–C(23)–C(24)	105.18(1)
N(24)–C(24)–C(21)	130.65(1)
N(24)–C(24)–C(23)	111.31(1)
C(21)–C(24)–C(23)	118.00(1)
N(24)–C(25)–N(25)	114.73(1)

Table 4
Bond distances (Å) and angles (°) for the hydrogen bonds in the crystal of compound **1**

D–H···A	d(D–H)	d(H···A)	d(D···A)	< (DHA)
O(3)–H(30B)···O(11)	0.791(3)	2.058(3)	2.847(1)	175.0(3)
O(3)–H(30A)···O(16)[i]	0.784(2)	1.992(2)	2.767(1)	169.8(2)
O(2)–H(20B)···O(3)[ii]	0.621(1)	2.114(2)	2.726(1)	169.2(2)
O(2)–H(20A)···N(24)[iii]	0.837(3)	2.020(3)	2.849(1)	170.4(3)
N(25)–H(25A)···O(2)[iv]	0.783(2)	1.889(2)	2.673(1)	178.4(2)
N(22)–H(22A)···O(17)	0.847(2)	1.795(2)	2.638(1)	172.9(1)
N(21)–H(21B)···N(23)[v]	0.824(1)	2.417(2)	3.118(1)	143.4(1)
N(21)–H(21A)···O(18)	0.986(3)	1.821(3)	2.804(1)	174.6(2)
O(13)–H(13)···O(12)[vi]	0.816(3)	1.822(3)	2.638(1)	177.8(3)
O(1)–H(10B)···O(16)[vii]	0.759(2)	1.918(3)	2.663(1)	166.8(2)
O(1)–H(10A)···O(18)[viii]	0.837(1)	1.848(2)	2.657(1)	162.4(1)

Symmetry codes: i = $x+1$, y, $z+1$; ii = x, y, $z-1$; iii = $-x+1$, $-y$, $-z+1$; iv = $-x$, $-y$, $-z+1$; v = $x+1$, y, z; vi = $x-1$, $-y+1/2$, $z-1/2$; vii = x, y, $z+1$; viii = $x-1$, y, z.

other, is a G ring (nearly coplanar to P-2) [32,33]. The G ring is more strained than the R ones [34], as the corresponding bond angles on the metal atom reveal (73.2° for the G ring, and 79.2 and 85.6° for R1 and R2 rings involving the O(18), O(15) and O(11) donor atoms, respectively). The free carboxymethyl arm in the three compounds could be considered as an 'opened G ring'.
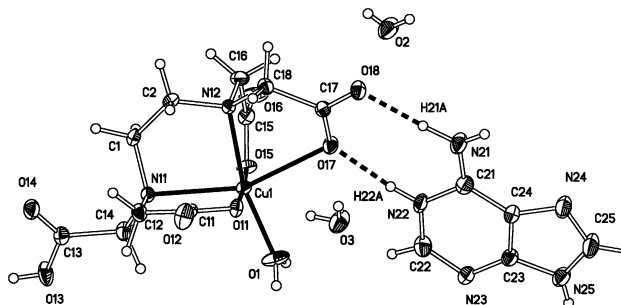

Fig. 1. Asymmetric unit in the crystal of (AdeH$_2$)[Cu(HEDTA)(H$_2$O)]·2H$_2$O (compound **1**) with the numbering scheme. The two rather linear hydrogen bonds involved in the cation–anion recognition are depicted as dashed links.

Among the three methylene groups linked to the same N atom, those of the E and G rings fall to the same side of the plane P-2, and that of the R ring, to the opposite side [33]. The partially protonated EDTA ligand exhibits in **1** a E,G/R conformation, as in all mononuclear octahedral metal–EDTA chelates [33]. The E ring is puckered. The G and R1 rings have unsymmetrical envelope conformations whereas the R2 ring adopts a less common puckered form [35].

On the other hand, assuming that the N–H bond in neutral AdeH corresponds to the most basic N9 atom (formula 1) and was reported for the crystal structure of the free base [36]), the protonation of the adenine is made in the called N1 atom (formula 2). Indeed, such N1 protonation has been reported for the crystal structure of the adenine hydrochloride *hemi*-hydrate [37] and all known structures involving the adeninium(1+) cation. The N1 protonation is consistent with the C(21)–N(22)–C(22) bond angle (123.4(3)°) which is larger than that of the free base by 4.7°. A similar difference (5°) corresponds to the Ni(II)-bounded adeninium in [Ni(NTA)(AdeH$_2$)(H$_2$O)]·2.5H$_2$O [16]. The adeninium(1+) cation is planar within ±0.025(1) Å.

In contrast to all other known Cu(II)–adeninium derivatives [8–10], which have coordinated adenium(1+) ligand, compound **1** consists, as referred above, of a salt. This means that the complex **2** reacts with AdeH to give the anion [Cu(HEDTA)(H$_2$O)]$^-$ which seems unable to recognise the cation AdeH$_2^+$ by means of a complexation process (for example, by a substitution reaction of aqua by the adeninium(1+) ligand). In contrast, Aoki et al. [16] have proved that the octahedral anion diaqua(nitrilotriacetate)nickel(II) recognises selectively the adeninium(1+) ion forming the neutral complex adeninium-aqua(nitrilotriacetato)nickel(II) (described as [Ni(NTA)(H$_2$O)(AdeH$_2$)]$_2$·5H$_2$O in the crystalline state [16]) where the unusual Ni–N7(AdeH$_2^+$) bond is reinforced by an intra-molecular

bond between an exocyclic N–H bond and one or two O-carboxylate atoms of the NTA ligand. Remarking that complexes $[Ni(NTA)(H_2O)_2]^-$ and $[Cu(HEDTA)(H_2O)]^-$ are both octahedral anions, we suggest that the difficulty of the latter in accepting the adeninium(1+) ion as a 'secondary' ligand arises from steric constraints favouring the recognition by the formation of an ion pair stabilised by inter-ionic hydrogen bonds. Consistently, the data of Table 4 reveal that, among others, there are two rather linear hydrogen bonds [the 'onium' $N(22)^+$–$H(22A)\cdots O(17)$ and exo-cyclic $N(21)$–$H(21A)\cdots O(18)$ interactions] where the adeninium(1+) ion acts twice as H-donor for the two O atoms of the same carboxylate group of the $HEDTA^-$ (Figs. 1 and 2). A detailed analysis [38] of the short aromatic ring–ring interactions (with centroid–centroid distances < 6.0 Å and its angles with the normal to the stacked ring planes, β and $\gamma < 60°$) reveals that such ion pairs recognise themselves to form aggregates $\{(AdeH_2)[Cu(HEDTA)(H_2O)]\}_2$ by a π,π-ring stacking interaction (Fig. 2). In the present case, for symmetry reasons, such interaction is displayed by the parallel six-membered rings of two adjacent $AdeH_2^+$ ions (symmetry code #5 = $-x$, $-y$, $1-z$). With a centroid–centroid vector of 3.39 Å and slipping angles (between the centroid–centroid vector and the normal to each stacked plane) $\beta = \gamma = 10.1°$, the inter-planar distance is 3.34 Å. Such stacking is rather close to, but not strictly, a 'face-to-face' interaction. In addition of the two referred inter-ionic hydrogen bonds, the remaining polar bonds (O–H from the $HEDTA^{3-}$ carboxyl group or water molecules and heterocyclic and exocyclic N–H of $AdeH_2^+$ ion) interact with carboxylate or water O atoms or adeninium N3 and N7 atoms (see Table 4). These hydrogen bonds involve nine different asymmetric units building the crystal as an extensive 3D network. The shortest hydrogen-bridges (2.638–2.672(4) Å) are those involving the aqua ligand, the free carboxylic group of $HEDTA^{3-}$ and both heterocyclic N–H bonds of $AdeH_2^+$ ion.

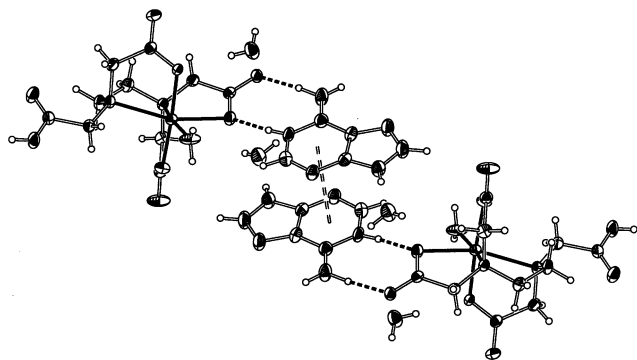Fig. 2. Formation of aggregates $\{(AdeH_2)[Cu(HEDTA)(H_2O)]\}_2$ by anti-parallel π,π-stacking interaction between adeninium(1+) cations in the crystal of $(AdeH_2)[Cu(HEDTA)(H_2O)]\cdot 2H_2O$.

The structural results reported here offer a definitive answer to the main question of the aim of the present work. In this context, we can also consider that hypoxanthine (6-hydroxopurine) is unable to bind directly to the Ni–NTA chelate, because it has not the possibility to form an appropriate inter-ligand hydrogen bond, whereas the hypoxanthinato(1−) ion acts as a bridging ligand in $[\{Cu(tren)\}_2(\mu\text{-hypoxanthina-to})](ClO_4)_3$ (tren = tris(2-aminoethyl)amine) [1] because each tren ligand forms an inter-ligand hydrogen bond with the bridging base. In addition, the Ni–NTA chelate is unable to coordinate the cytosinium(1+) ion because of the protonation of the 'N3' donor, but three inter-ligand hydrogen bonds are used in the inter-ionic recognition process in the salt (cytosinium)$[Ni(NTA)(H_2O)_2]\cdot 2H_2O$ [16]. This latter compound resembles the compound **1** in the out-spherical attachment of the protonated base to the metal chelate. However, it should be noted that the cytosynium(1+) ion has not an available N-heterocyclic donor, whereas the N-heterocyclic coordination of the adeninium(1+) ion to the copper(II) [8–10] and other metal ions [11,12] is well known.

3.2. Properties of compound 1

The TG/DTG analysis of compound **1** (5.834 mg, 20 °C min^{-1}, in air flown) reveals its thermal decomposition in four steps. Selected FT-IR spectra of the evolved gasses are shown in Fig. 3. The first one (115–180 °C, maximum rate of weight loss at 151 °C, experimental weight loss 6.980% > calculated for $2H_2O$ 6.636%) is due to the loss on non-coordinated water, and lead to a starting actual 'TG-formula' $(AdeH_2)[Cu(HEDTA)(H_2O)]\cdot 2.1H_2O$ (FW 544.747; calculated weight loss 6.945% for $2H_2O$, in good agreement with the experimental value 6.980%). The second step (180–310 °C, weight loss of 36.582%) corresponds reasonably to the estimated loss (35.453%) of the aqua ligand and the pyrolysis of the free carboxymethyl arm ($-CH_2COOH$) and two acetate arms ($-CH_2COO^-$) from $HEDTA^{3-}$ ligand. Consistently, only water loss is observed during the first step, whereas FT-IR spectra during the second step show bands of H_2O, CO_2 and CO. The third step (310–440 °C) produces H_2O, CO_2, N_2O, and lower amounts of NH_3 and CO, whereas the last step (440–480 °C) gives H_2O, CO_2, N_2O, NO and a little CH_4 and NH_3. These steps correspond to the overlapped pyrolysis of the $HEDTA^{3-}$ residue and $AdeH_2^+$ ligand, giving a residue of CuO (experimental 14.651% and calculated 14.602% for the TG-formula). It seems rather improbable that the adeninium(1+) ion pyrolyses at so higher temperatures (> 300 °C) and perhaps adeninate(1−) is formed before this process occurs.
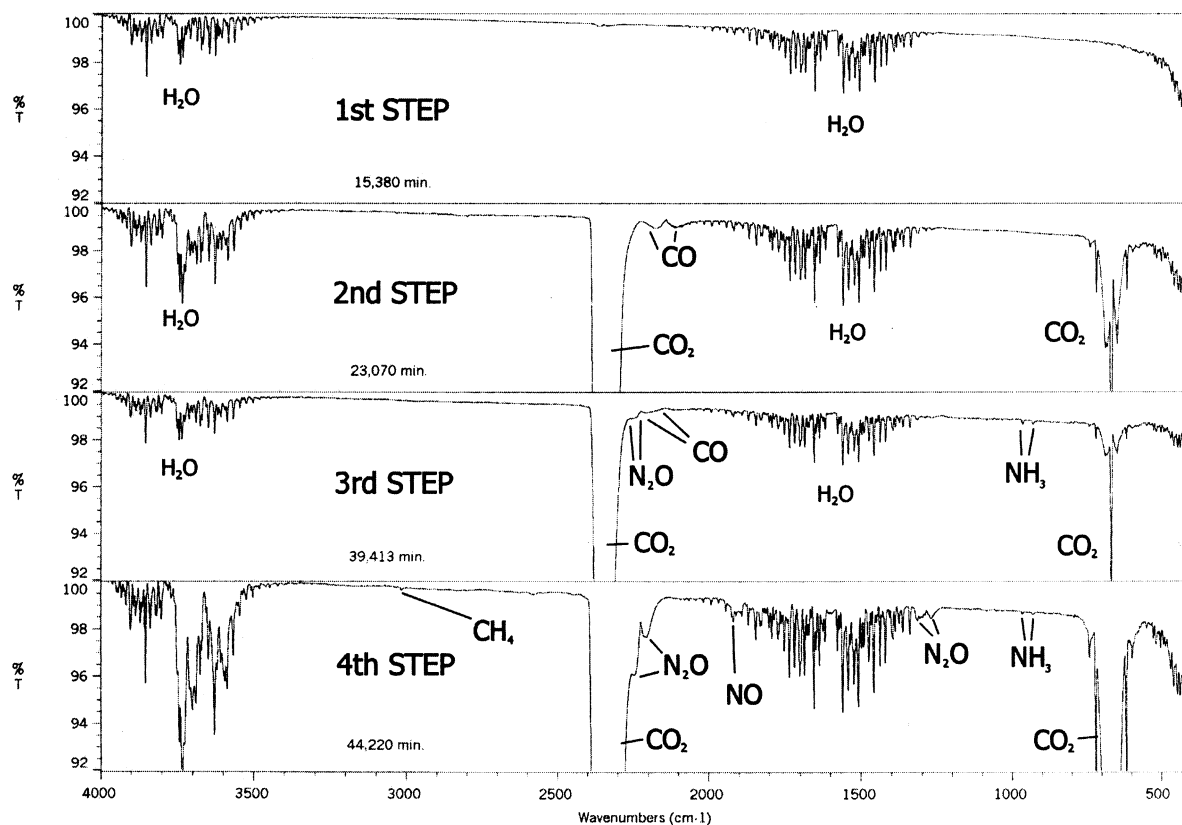
Fig. 3. Selected FT-IR spectra for identification of evolved gasses in the four steps of decomposition and pyrolysis of $(AdeH_2)[Cu(HEDTA)(H_2O)]\cdot 2H_2O$.

The IR spectrum has many peaks and bands expected for contributions of water and/or aqua, $HEDTA^{3-}$ and $AdeH_2^+$ ligands. Tentative assignments (in cm^{-1}) are as follows: $\nu_{as}(H_2O)$, 3440; $\nu_s(H_2O)+\nu_{as}(NH_2)$, 3356; $\nu_s(NH_2)$, 3242; the N^+-H chromophore gives a typical series of peaks in the range 2800–2250 [39] (six peaks in this case), including one at 2760 of $\nu(N^+-H)$; $\nu(C=O)$ of hydrogen bonded –COOH, 1720 and 1693; $\delta(H_2O)+\nu_{as}(COO)$, 1595; $\delta(NH_2)$ and $\delta(N^+-H)$, 1537 (shoulder) and 1495 (peak), respectively; $\nu(C-O)+\delta(O-H)$ of –COOH, 1404; and $\nu_s(COO)$, 1381. A large difference $\Delta = \nu_{as}(COO)-\nu_s(COO) = 214\ cm^{-1}$ suggests the main ionic character of the Cu(II)–O(carboxyl) bonds [40]. The electronic spectrum shows an unsymmetrical d–d band at $\nu_{max} = 13\,260\ cm^{-1}$ (with a shoulder $\sim 8360\ cm^{-1}$) in agreement with the elongated octahedral chromophore $CuNO_3+N+O$. The powder ESR spectrum at r.t. is quasi-isotropic type with $\sim g_{//} = 2.17 > g_{av} = 2.14 > \sim g_{\perp} = 2.13 > 2.03$, which yields no useful g value information but is in accordance with a d_{x2-y2} Cu(II) ground state, long metal–metal separations $(Cu(1)-Cu(1^i) = 7.053(1)$ Å) and local molecular axes clearly misaligned in the crystal [41]. A plot of χ data versus T (K) $(T = 79–290$ K) is linear $(1/\chi = (1/C)T-(\theta/C)$ with a statistical r^2 factor of 0.9965)

according to a Curie–Weiss behaviour, $\chi = C/(T-\theta)$ [31]. The Curie constant is $C = 0.43$ K emu mol^{-1} with Weiss constant of $\theta = 7.46$. The estimated value of μ_{eff} for Cu(II) atom is 1.86 BM, according to the structure reported here.

4. Concluding remarks

We can consider that the chelated anions $[Cu(HEDTA)(H_2O)]^-$ and $[Ni(NTA)(H_2O)_2]^-$ [16] display different mechanisms to recognise the adeninium(1+) ion. The former by means of an ion pair stabilised by two inter-ionic hydrogen bonds, and the latter, as a secondary ligand also reinforced by an inter-ligand $NTA-AdeH_2^+$ hydrogen bond. In addition, ion-pairs of compound **1** recognise themselves forming a slightly slipped π,π-stacking interaction between the six-membered rings of anti-parallel symmetry related adjacent $AdeH_2^+$ cations. In contrast, such aromatic π,π-ring stacking seems not to take part in the crystal packing of the related compound $[Ni(NTA)(AdeH_2)(H_2O)]\cdot 2.5H_2O$ [16].

5. Supplementary material

Acknowledgements

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