J Chem Crystallogr (2009) 39:853–863
DOI 10.1007/s10870-009-9575-3

ORIGINAL PAPER

Synthesis and Characterization of Some Transition Metal Complexes with Mixed Adenine and Acetylacetonate Ligands: Crystal Structures of Solvated Complex {[$Cu(acac)_2$(adenine)]·EtOH} and {[$Cu(acac)_2$(adenine)]·DMF·H_2O}

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Received: 12 March 2008 / Accepted: 4 June 2009 / Published online: 14 July 2009

Abstract Metal complexes of divalent copper (**1–2**), cobalt (**3**), and nickel (**4**) with mixed ligands acetylacetone (acac) and adenine were prepared and characterized by IR, mass spectra, elemental and thermal analysis. The X-ray crystal structures of {[$Cu(acac)_2$(adenine)]·EtOH} complex (**1**) and {[$Cu(acac)_2$(adenine)]·DMF·H_2O} (**2**) were determined. Compound (**1**) crystallizes in the triclinic space group $P-1$ with $a = 7.547(3)$ Å, $b = 7.828(3)$ Å, $c = 17.791(6)$ Å, $\alpha = 79.538(6)°$, $\beta = 82.240(7)°$, $\gamma = 86.010(6)°$, $V = 1023.1(6)$ Å^3, and $Z = 2$. Complex (**1**) forms a hydrogen bonded 2:2 complex {[$Cu(acac)_2$(adenine)]$_2$:[EtOH]$_2$} arranged in bilayers. Complex (**2**) crystallizes in the triclinic space group $P-1$ with $a = 7.828(2)$ Å, $b = 8.095(2)$ Å, $c = 16.995(5)$ Å, $\alpha = 78.508(5)°$, $\beta = 84.949(5)°$, $\gamma = 89.285(5)°$, $V = 1051.2(5)$ Å^3, and $Z = 2$. Complex (2) also forms bilayers with H-bonded DMF. Thermal analysis TG and DSC of the compounds (25–800 °C, under N_2) reveals the disproportionation of ligands with the associated heat.

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Keywords Adenine · Acetylacetone · Thermal analysis · Complexes · X-ray crystal structure · Bilayers · H-bond

Introduction

The interaction of nucleic acids and 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].

Metal ions mediate the biochemistry of pyrimidine and purine nucleosides, nucleotides, and nucleic acids [2–4]. Successful synthetic and structural studies of pertinent metal complexes have largely been elucidated [5–9]. In contrast to the historically well studied metal amino acid and peptide complexes, interligand H-bonding is a ubiquitous aspect of these structures. The existence of such H-bonds in solution has been used (a) to guide the successful synthesis of complexes of unique type [1], (b) to interpret stability trends in solutions [5], (c) to explain the unusually stable chelate ring conformers found in Cr(III)-nucleotide enzyme inhibitors and substrates [10], and even (d) to rationalize the effectiveness of certain metallo-antineoplastic agents [11]. This latter suggestion draws additional support from the recent observation of interligand H-bonding on the complex formed between t-RNA and trans-$Pt(NH_3)_2Cl_2$.

The complexation of metal ions with adenine has been well studied and its binding site(s) has also been elucidated [12–14]. Various coordination sites have been observed for adenine in copper complexes as indicated by X-ray studies. Among the four nitrogens N(1), N(3), N(7) and N(9) of adenine, the N(9) is the most basic and hence bears a proton

rendering it the most preferred metal binding site. An example is the crystal structure of {[Cu(tren)(adeninato)]·ClO_4} where N(9) of adeninate anion is bound to Cu at the axial position, (tren = tris(2-aminoethyl)amine) [1]. The same mode of binding is observed in the crystal structure of {[Cu(tren)(adeninato)]·Cl·$2H_2O$} [15]. Adenine cation also coordinates through ring nitrogen N(9) in $[Cu(adenineH)_2Cl_2]^{2+}$ [16]. Both N(1) and N(3) are electronically favoured coordination sites for the metals. The crystal structure of {[Cu(MOBIDA)(adenine)H_2O]·H_2O} reveals the selective formation of rare Cu-N(3) adenine-H bound, {MOBIDA = [*N*-(*p*-methoxybenzyl)-imidiacetato]$^{2-}$} [17]. However, due to tautomerization of the imidazole hydrogen atom between N(7) and N(9), the nitrogens N(3) and N(9) have also been involved in metal binding [14]. Ternary complexes of transition metals with nucleic acid bases and some other ligands such as 1,10-phenanthroline, 2,2-dipyridyl, sulfosalicylic acid, amino acids, *N*,*N*′-tetramethylene ethylenediamine have been also synthesized and characterized [18–30].

We have interest in the structure of mixed ligand copper(II) complexes having acetylacetonato as primary ligand, and adenine as secondary ligand, because this N-rich nucleobase has proved to be a rather versatile metal-binding biomolecule, where the nucleobase species can be linked to the copper(II) atom by the N(9) donor (as monodentate) [1, 16, 31], or in a μ-N(3),N(9) bridging mode (oligomers) [15, 32, 33], or by N(7) or bridging μ-N(3),N(7) [34].

Additionally, acetylacetone is an intermediate product of organic synthesis reaction, which can be used as annexing agent in gasoline, lubricant and desiccant in paint [35]. Also it has been found to possess fungicidal and insecticidal activities [36]. Complexes of metal ions with acetylacetone have been the subjects of a wide variety of physical researches for many years. In recent years, the study on metal coordination of β-diketonate and its derivatives has attracted great interest, because metal complexes of β-diketonate derivatives can be good precursors in metal-organic chemical vapour deposition (MOCVD) for growing high Tc superconducting films [37–40]. The transition metal β diketone compounds were used extensively as starting materials in the early days of metallocene chemistry [41], and as electroluminescent materials [42, 43].

Recently, there is considerable interest in the chemistry of tetrakis(μ-carboxylato)M(II) complexes with nucleic bases and their derivatives because these complexes function as antitumor agent against many types of tumors by causing inhibition of DNA replication and protein synthesis. Examples of such carboxylate complexes are Rh with azathiopurine [44], Rh with 9-ethyladenine and 9-ethylguanine [45, 46], Re with 9-ethyladenine [47] and 9-ethylguanine [48], Ru with adenine [49], Pt with cytosine, 6-fluorocytosine, 6-methylisocytosine, guanine and benzotriazole [50].

We have recently studied the in vitro biological effect of copper adenine complex {[Cu_2(adenine)$_4Cl_2$]Cl_2·2EtOH} [51–53]. The study demonstrated binding of the complex to DNA, decrease in cell viability, inhibitory effect on Taq polymerase; inhibition of transcription; inhibition of NADH oxidation in isolated rat liver sub-mitochondrial (SMP) particles, reducing thus the level of ATP and inhibition of C_2C_{12} myoblast differentiation into myotubes [53].

Here in, we report the synthesis, characterizations and thermal stabilities of Cu(II), Ni(II) and Co(II) adenine complexes (**1**–**4**). We also report the crystal structure of the complexes {[Cu(acac)$_2$(adenine)]·EtOH} (**1**) and {[Cu(acac)$_2$(adenine)]·DMF·H_2O} (**2**) where acetylacetone acts as a bidentate ligand and adenine as a monodentate ligand through N(7).

Experimental

All chemicals were of analytical reagent grade and used directly without further purification. The metal acetylacetonate complexes were prepared according to literature review [54–61].

Physical Measurements

The elemental analysis was measured with a Perkin Elmer 1400C analyser. Infrared spectra were recorded on a JASCO FTIR 410 instrument by using pressed KBr plates in the 4,000–500 cm^{-1}. The electronic spectra were taken on a UV–Vis SP-3000 OPTIMA Spectrophotometer. Thermogravimetric-differential scanning calorimetry (TG-DSC) curves were recorded on SETARAM LABSYS Thermal analyser in the flow of N_2 within the 25–800 °C temperature range, with a heating rate of 3 °C/min. Mass spectra was done at the Microanalytical Lab, University of Surrey UK.

Single crystals suitable for X-ray crystallographic analysis were selected following examination under a microscope. Intensity data were collected at 100(2) K on a Bruker-AXS SMART APEX/CCD diffractometer using Mo_{ka} radiation (λ = 0.7107 Å). The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program. The structures were solved using direct methods and refined by full-matrix least-squares on $|F|^2$. All non-hydrogen atoms (and hydrogen atom of methanol oxygen) were refined anisotropically. All other hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their bonded atoms. All crystallographic calculations were conducted with the SHELXTL 6.1 program package. A summary of data collection, structure refinement for complexes (**1**) and (**2**) are given in Table 1. Selected bond lengths and bond angles are given in Table 2.

Table 1 Crystal data and structure refinement for (**1**) and (**2**)

Compound	{[Cu(acac)$_2$(adenine)]·EtOH}	{[Cu(acac)$_2$(adenine)]·DMF·H$_2$O}
Empirical formula	C17 H25 Cu N5 O5	C18 H28 Cu N6O6
Formula weight	442.96	488.00
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P-1$	$P-1$
a (Å)	7.547(3)	7.828(2)
b (Å)	7.828(3)	8.095(2)
c (Å)	17.791(6)	16.995(5)
α (°)	79.538(6)	78.508(5)
β (°)	82.240(7)	84.949(5)
γ (°)	86.010(6)	89.285(5)
Volume (Å^3)	1023.1(6)	1051.2(5)
Z	2	2
Dx (g cm^{-3})	1.438	1.513
μ (mm^{-1})	1.105	1.087
Crystal size (mm^3)	0.12 × 0.10 × 0.06	0.30 × 0.20 × 0.10
Θ Range (°)	1.17–28.25	1.23–28.31
Reflections collected	4,985	6,378
Independent reflections	3,999 [$R_{(int)} = 0.0453$]	4,585 [$R_{(int)} = 0.0212$]
Absorption correction	SADABS	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.518	1.000 and 0.118
Data/restraints/parameters	3999/0/256	4585/0/315
Goodness-of-fit on F^2	1.020	1.003
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0779$, $wR_2 = 0.1754$	$R_1 = 0.0556$, $wR_2 = 0.1597$
R indices (all data)	$R_1 = 0.1198$, $wR_2 = 0.2045$	$R_1 = 0.0644$, $wR_2 = 0.1708$
Largest diff. peak and hole (eÅ^{-3})	1.284 and −1.056	0.961 and −0.995

PLATON was used to generate the ORTEP diagram whereas all other figures were prepared using Material Studios v. 2.2.

Preparation of Metal Complexes

*Preparation of Adenine Bis(2,4-pentanedionato) Copper(II) Complex: {[Cu(acac)$_2$(adenine)]·EtOH} (**1**)*

To a solution of adenine in boiling ethanol (1 mmol), was added a solution of Cu(acac)$_2$ (1 mmol) in chloroform. The obtained solution was refluxed for 2 h, after which the solution is concentrated and filtered. The blue solution was evaporated for a few weeks at room temperature to yield blue crystals suitable for X-ray measurements (25% yield).

Elemental analysis: % Calcd. for $CuC_{17}H_{25}N_5O_5$: C = 46.10, H = 5.69, N = 15.81; Found: C = 46.96, H = 5.77, N = 16.05; MS data [Cu(acac)$_2$(adenine)]: m/z = expected 396.08, Found 396.80; RA = 85%.

*Preparation of Adenine Bis(2,4-pentanedionato) Copper(II) Complex: {[Cu(acac)$_2$(adenine)]·DMF·H$_2$O} (**2**)*

The same experiment was repeated as above, but using adenine in DMF instead of ethanol; yield 40%.

*Preparation of Adenine Bis(2,4-pentanedionato) Cobalt(II) Metal Complex: [Co(acac)$_2$(adenine)] (**3**)*

To a boiling ethanol solution of adenine (1 mmol) was added cobalt(II) acetylacetonate (1 mmol). The solution was refluxed for 2 h, after which the obtained product was filtered, washed with ethanol, and dried in a desiccator under P_2O_5. Elemental analysis: Calcd. for $C_{15}CoH_{19}N_5O_4$: C = 45.91, H = 4.846, N = 17.857; Found: C = 45.326, H = 4.985, N = 18.5; MS data: m/z = expected 391.27, Found 391.2.

Table 2 Heavy-atom interatomic distances (Å) and angles (°)

	Bond lengths			Bond angles	
	(1)	(2)		(1)	(2)
(a) The primary coordination sphere about the copper atom					
Cu–O(11)	1.943(4)	1.947(2)	O(11)–Cu–O(12)	93.34(18)	92.64(11)
Cu–O(12)	1.955(4)	1.949(2)	O(21)–Cu–O(11)	86.22(18)	86.21(10)
Cu–O(21)	1.937(4)	1.938(2)	O(22)–Cu–O(12)	85.09(17)	85.32(11)
Cu–O(22)	1.934(4)	1.938(2)	O(22)–Cu–O(21)	94.34(18)	93.88(10)
Cu–N(31)	2.328(5)	2.287(3)	O(22)–Cu–O(11)	171.47(17)	167.95(10)
			O(21)–Cu–O(12)	173.17(17)	170.68(10)
			N(31)–Cu–(O12)	88.37(17)	93.26(11)
			N(31)–Cu–(O11)	93.92(17)	100.13(10)
			N(31)–Cu–(O21)	98.46(17)	96.05(10)
			N(31)–Cu–(O22)	94.41(17)	91.85(10)
(b) The acetylacetonato molecule					
O(21)–C(21)	1.288(7)	1.269(4)	C(11)–O(11)–Cu	123.7(4)	124.6(2)
C(22)–C(21)	1.399(8)	1.399(5)	O(11)–C(11)–C(12)	125.2(6)	125.6(3)
C(23)–C(22)	1.394(8)	1.401(5)	C(11)–C(12)–C(13)	125.6(6)	123.8(3)
C(23)–O(22)	1.276(7)	1.265(4)	C(13)–O(12)–Cu	123.2(4)	125.0(2)
C(23)–C(25)	1.504(8)	1.510(5)	C(12)–C(13)–C(15)	118.8(6)	118.4(3)
C(21)–C(24)	1.496(8)	1.504(5)	O(12)–C(13)–C(15)	116.2(6)	115.8(3)
O(11)–C(11)	1.277(7)	1.272(4)	O(11)–C(11)–C(14)	116.3(6)	116.3(3)
C(11)–C(12)	1.397(8)	1.401(5)	C(14)–C(11)–C(12)	118.6(6)	118.1(3)
C(12)–C(13)	1.395(9)	1.405(5)	C(12)–C(13)–O(12)	125.0(6)	125.8(3)
C(13)–C(15)	1.511(8)	1.509(5)			
C(14)–C(11)	1.512(9)	1.508(5)	O(22)–C(23)–C(22)	124.9(6)	125.4(3)
C(13)–O(12)	1.27(8)	1.263(4)	C(23)–C(22)–C(21)	126.1(6)	124.8(3)
			C(22)–C(21)–O(21)	124.6(6)	125.7(3)
			C(21)–O(21)–Cu	124.4(4)	124.5(2)
			C(23)–O(22)–Cu	124.8(4)	125.1(2)
			C(22)–C(23)–C(25)	119.3(6)	118.7(3)
			O(22)–C(23)–C(25)	115.8(5)	116.0(3)
			C(24)–C(21)–C(22)	119.0(6)	118.3(3)
			C(24)–C(21)–O(21)	116.3(5)	116.0(3)
(c) The adenine molecule					
N(35)–C(34)	1.313(8)	1.342(5)	N(35)–C(34)–N(34)	119.7(6)	117.9(3)
C(34)–N(34)	1.363(8)	1.344(5)	N(35)–C(34)–C(35)	123.3(6)	123.2(3)
N(34)–C(33)	1.332(8)	1.345(5)	C(34)–N(34)–C(33)	118.1(6)	118.6(3)
C(33)–N(33)	1.337(8)	1.329(5)	N(34)–C(33)–N(33)	130.4(6)	129.0(3)
N(33)–C(32)	1.348(7)	1.346(5)	C(33)–N(33)–C(32)	110.1(5)	110.9(3)
C(32)–C(35)	1.369(8)	1.382(5)	N(33)–C(32)–C(35)	127.6(6)	126.6(3)
C(34)–C(35)	1.438(8)	1.408(5)	C(32)–C(35)–C(34)	116.7(6)	117.0(3)
C(35)–N(31)	1.385(7)	1.392(4)	N(31)–C(35)–C(32)	111.2(5)	110.3(3)
N(31)–C(31)	1.309(7)	1.315(5)	C(35)–C(32)–N(32)	105.3(5)	105.9(3)
C(31)–N(32)	1.367(7)	1.362(4)	C(32)–N(32)–C(31)	105.8(5)	106.4(3)
N(32)–C(32)	1.393(8)	1.371(4)	N(32)–C(31)–N(31)	113.6(5)	113.6(3)
			C(31)–N(31)–C(35)	104.2(5)	103.9(3)
			N(34)–C(34)–C(35)	117.0(5)	118.8(3)
			N(31)–C(35)–C(34)	132.0(5)	132.8(3)
			C(35)–N(31)–Cu	138.2(4)	137.8(2)
			C(31)–N(31)–Cu	117.4(4)	118.3(2)
			N(33)–C(32)–N(32)	127.1(5)	127.5(3)

*Preparation of Adenine Bis(2,4-pentanedionato) Nickel(II) Metal Complex: [Ni(acac)$_2$(adenine)].0.5 Ethanol (**4**)*

To a solution of adenine (1 mmol) in boiling ethanol was added nickel(II) acetylacetonate (1 mmol) in ethanol. The solution was refluxed for 2 h, after which the obtained product was filtered, washed with ethanol, and dried in a desiccator under P_2O_5. Elemental analysis: Calcd. for $C_{16}NiH_{24}N_5O_{4.5}$: C = 46.08, H = 5.76, N = 16.80; Found: C = 45.23, H = 5.33, N = 17.7.

Results and Discussion

Complex (**1**) was prepared by mixing Cu(acac)$_2$ in chloroform with adenine in ethanol (Eq. 1), while with adenine in DMF complex (**2**) is obtained. But when the same preparation was repeated in presence of ammonium chloride a different copper complex is formed with a proposed dimeric structure [Cu$_2$adenine$_4$Cl$_2$]Cl$_2$·2EtOH (**5**) [53], where four adenine ligands bridges two copper ions (through μ-N3,N7) and the chloride ions occupying the axial positions (Eq. 2).

$$\mathrm{Cu(acac)_2 + adenine} \xrightarrow{\mathrm{EtOH}} \mathrm{Cu(acac)_2(adenine)\cdot EtOH} \quad (1)$$

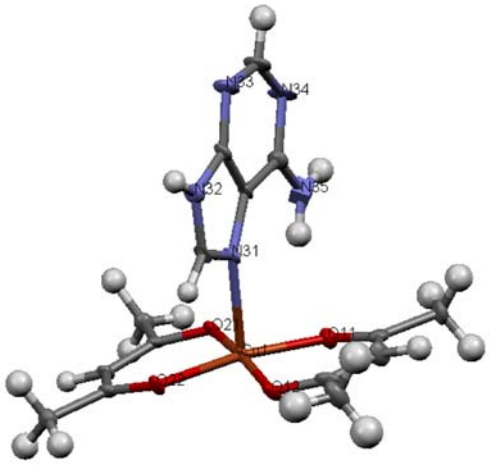
$$2\mathrm{Cu(acac)_2} + 4\ \mathrm{adenine} + 4\mathrm{Cl^-} \xrightarrow{\mathrm{EtOH}} \left[\mathrm{Cu_2(adenine)_4(Cl_2)}\right]\mathrm{Cl_2\cdot 2EtOH} \quad (2)$$

Single Crystal X-ray Structures of Copper Acetylacetonato Adenine Complexes: {[Cu(acac)$_2$(adenine)]·EtOH} (**1**) and {[Cu(acac)$_2$(adenine)]·DMF·H$_2$O} (**2**)

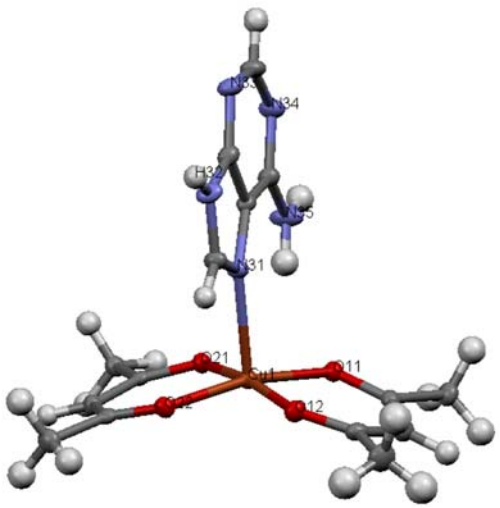
Description of the structure of the asymmetric unit of (**1**) and (**2**).

The basic unit structures for complexes (**1**) and (**2**) are shown in Fig. 1a and b, respectively.

In both complexes (**1**) and (**2**), the coordination geometry about the copper atom is distorted square pyramidal with the two bidentate molecules of acetylacetone anion defining the equatorial plane and one molecule of adenine occupying the axial position through ^{7}N(31) (Fig. 1). ^{7}N(31) is a purine site which is accessible for complexation in nucleosides, nucleotides and single-stranded and double-stranded nucleic acids. This makes the complex a possible model for the type of interactions which occur in enzyme metal-nucleic acid ternary species[2]. The Cu-^{7}N adenine bond length is 2.328 Å in complex (**1**) and 2.287 Å in complex (**2**) (Table 2), these values are significantly greater than those found in copper glycylglycinato, copper sulphate and copper chloride of N(9)-methyladenine



Basic structural unit for [Cu(acac)$_2$(adenine)] occurring in complex (**1**).



Basic structural unit for [Cu(acac)$_2$(adenine)] occurring in complex (**2**).

Fig. 1 **a** Basic structural unit for [Cu(acac)$_2$(adenine)] occurring in complex (**1**). **b** Basic structural unit for [Cu(acac)$_2$(adenine)] occurring in complex (**2**)

complexes, where the bond lengths are 2.021, 1.995, and 2.004 Å, respectively [62–64]. The observed elongation is probably related to the steric factors associated with the interligand hydrogen-bond formation.

The crystal structure of several copper adenine complexes reported in the literature indicated the formation of monomeric, dimeric or polymeric species where adenine acts as monodentate, or bridging bidentate. The preference for binding is controlled by the basicity as such: N9 > N1 > N7 > N3 > N6. The adenine binds to copper through either N3 in adenine *N*-benzyliminodiacetato Cu(II)complexes [17, 34], N7 in the present work and in N-substituted iminodiacetato-copper(II) chelates [34], or bridging binding mode μ-N3,N7 as well [34], or N9 in [Cu(tren)(adeninato)]ClO$_4$ where tren is tris(2-aminoethyl)amine[1] and in [Cu(tren)(adeninato)]Cl·2H$_2$O [15], μ-N7,N9 in [Cu$_2$(NBzIDA)$_2$

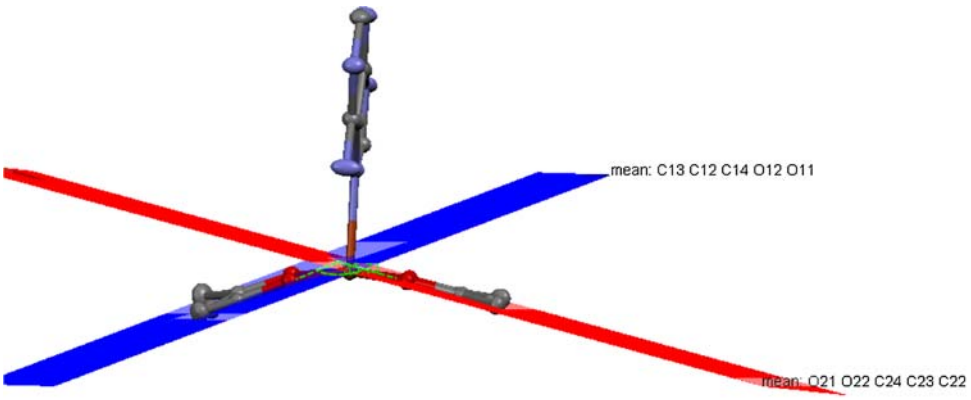


Fig. 2 The planes of acetylacetonato ligands in (**2**) forming an angle of 35.71°

$(H_2O)_2$(μ-N7,N9-Adenine]·$3H_2O$ where NBzIDA = *N*-benzyliminodiacetate(2-) [65] and μ-N3,N9 in several dimeric structures as in the following examples: The first one is $[Cu_2(adeninato)_4(H_2O)_2]\cdot 2H_2O$. The dimmer has similar structure to that of copper acetate with four bridging adenine anions, coordinated through N3 and N9 of adenine while copper occupying the axial site [66]. Similar dimeric structures occur in $[Cu_2(Adenine)_4(H_2O)_2](ClO_4)_4\cdot 2H_2O$ [32], and $[Cu_2(Adenine)_4Cl_2]Cl_2\cdot 6H_2O$ [33], involving bridging neutral adenine through N3 and N9 with the axial site occupied by water in the first complex and chloride in the second one. While under acidic conditions, unidentate coordination via only N9 has been observed in the roughly tetrahedral complex $[Cu(AdH)_2Cl_2]Cl_2$, where AdH is adeninium ions [16].

In our recent work, $[Cu_2(adenine)_4Cl_2]Cl_2\cdot 2EtOH$ (**5**) was prepared with a possible dimeric structure. The complex has demonstrated a potential anticancer activity, the cytotoxic effect was attributed to the availability of N1 and N6 of coordinated adenine to H-bond with thymine of DNA [51].

The Cu–O distances range [1.935–1.954 Å] in complex (**1**) and [1.938–1.949] in complex (**2**) are close to those reported in related complexes [67–69] (Table 2). The bond lengths and angles in the adenine and acetylacetone anion in the two complexes are in agreement with those found in the literature [59, 70], (Table 2).

The nine atom framework of the adenine ligand is planar with 0.58 and 0.35 deg. fold about the C(32)–C(35) bond in complexes (**1**) and (**2**), respectively, as has been commonly observed in many other coordinated and uncoordinated purine systems [47].

The copper atom is above the plane formed by acetylacetonate oxygen atoms O(11), O(12), O(21), and O(22) by 0.13 Å in complex (**1**) and 0.036 Å in complex (**2**). In both complexes, the exocyclic angles at ^{7}N(31) are highly dissymmetric with [Cu–N(31)–C(35)] angle being about 20.8° and 19.5° larger than that Cu–N(31)–C(31) angle in (**1**) and (**2**), respectively.

In complexes (**1**) and (**2**), the two acetylacetonato molecules are not coplanar. The angle formed between two planes of acetylacetonato ligands is equal to 3.06° in (**1**) between [O22 C23 O21 C21 C22] and [C11 C12 C13 O12 O11] planes, while it is equal to 35.71° in (**2**) between [O21 O22 C24 C23 C22] and [C13 C12 C14 O12 O11], see Fig. 2.

H-bonding

i. Complex (1)

Intramolecular. The NH_2 group in complex (**1**) is involved in intramolecular hydrogen bonds with the two acetylacetonates oxygen. H-Bonds distances and angles are: H···A = 2.433 Å, D···A = 3.229 Å, D–H = 0.88 Å, D–H···A = 150.74° where D–H···A is N(35)–H(35A)···O(12); while H···A = 2.450 Å, D···A = 3.203 Å, D–H = 0.88 Å, D–H···A = 143.89° where D–H···A is N(35)–H(35A)···O(22).

Intermolecular. In complex (**1**), ethanol molecules and $Cu(acac)_2$(adenine) units interact by H-bond forming 2:2 complex: $\{[Cu(acac)_2(adenine)]_2{:}[EtOH)_2]\}$. Two intermolecular H-bonds exist between each pair of adenine and ethanol molecules, Fig. 3. Each ethanol molecule bridges two adenine molecules through H-bonds. (O(1 M)–H(1 M)) of ethanol acts as H-bond donor to the ^{3}N(33) atom of adenine in one complex molecule, and as a H-bond acceptor from the ^{9}N(32)–H(32) of adenine in an opposite complex molecule.

The nucleobases form centro-symmetric adenine···$(ETOH)_2$···adenine aggregates in which the N(9) and N(3) of each adenine interact with two symmetry related lattice EtOH molecules by means of H-bonds. This preferable type of interaction prevents copper(II) from forming dimeric copper complexes through μ-N3, N9 bridging adenine as previously discussed [14, 32, 33, 53].

The H-bond distances and angles for complex (**1**), are: H···A = 1.955 Å, D···A = 2.734 Å, D–H = 0.815 Å, D–H···A = 159.64° (where D–H···A is ^{9}N(32)–H(32)···O (1 M). Also, H···A = 1.873 Å, D···A = 2.774 Å, D–H = 0.945 Å, D–H···A = 158.62° (where D–H···A is O(1 M)–H(1 M)···N(33).

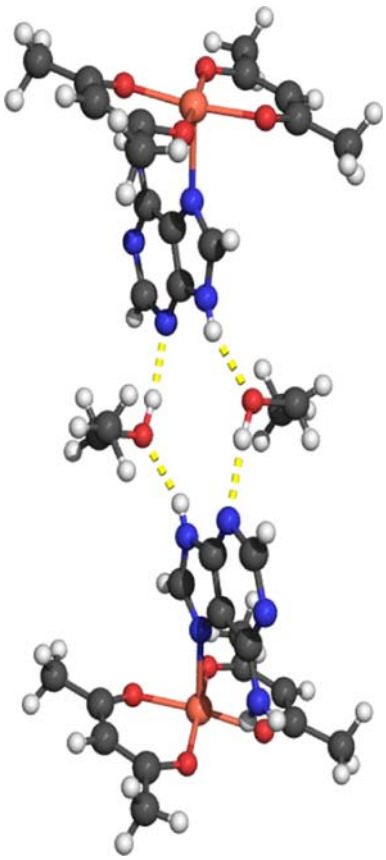


Fig. 3 Hydrogen bonded 2:2 complex $\{[Cu(acac)_2(adenine)]_2:[EtOH]_2\}$ in (**1**)

ii. Complex (2)

Intramolecular H-bond. The NH_2 group in complex (**2**) is involved in hydrogen bonds through H(35A) with the two acetylacetonate oxygen atoms O(12) and O(22) as follows: H···A = 2.458 Å, D···A = 3.245 Å, D–H = 0.88 Å, D–H···A = 149.05° when D–H···A is N(35)–H(35A)···O(12); and H···A = 2.413 Å, D···A = 3.177 Å, D–H = 0.88 Å, D–H···A = 45.39° where D–H···A is N(35)–H(35 A)···O(22).

Intermolecular H-bond. The adenine acts in complex (**2**), as a hydrogen bond donor to O(41) atom of dimethylformamide molecule through the ^{9}N(32). The bond distances and angle are as follows: H···A = 1.845 Å, D···A = 2.716 Å, D–H = 0.88 Å, D–H···A = 170.04° (where D–H···A is N(32)–H(32)···O(41). Adenine molecule is also involved in one hydrogen bond with a water molecule through the ^{3}N(33) and the O(51), where the H atom of water is not resolved, (D···A = 2.883 Å).

Crystal Packing

$Cu(acac)_2$(adenine) units in (**1**) are arranged in an opposite way forming a bilayer. Crystal packing in (**1**) also shows $Cu(acac)_2$(adenine) bilayers alternating with ethanol molecule bilayers in a view down "*x*" axis, the bilayers interact through H-bonding, Fig. 4.

$Cu(acac)_2$(adenine) units in (**2**) are packed along "*a*" axis forming bilayers. The $Cu(acac)_2$(adenine) bilayers alternate with DMF molecule bilayers as shown in Fig. 5. The two bilayers interact through H-bonding. Complex (**2**) showed a closely related arrangement of $Cu(acac)_2$(adenine) and DMF bilayers compared to the $Cu(acac)_2$(adenine) and methanol bilayers occurring in (**1**).

Noncovalent interactions (hydrogen bonds and π–π stacking interactions) play a major role in the supramolecular structure of copper adenine complexes [17, 34], where these interactions are similar to the noncovalent forces present in DNA double-helix structure (hydrogen bonds involving the complementary DNA bases and arene–

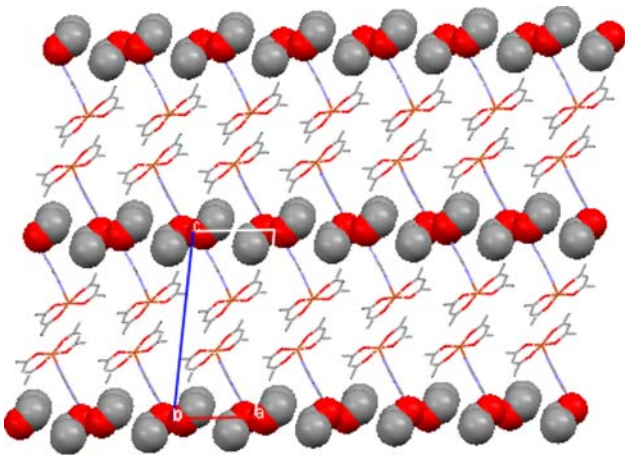


Fig. 4 View of bilayers down "*x*" axis with ethanol solvent. Alternating $Cu(acac)_2$(adenine) and ethanol bilayers interact by H-bonding in complex (**1**)

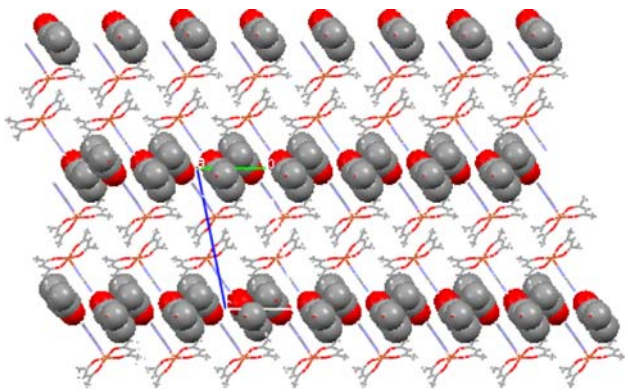


Fig. 5 View of bilayers down "*a*" axis with DMF solvent. Alternating $Cu(acac)_2$(adenine) and DMF bilayers interact by H-bonding in complex (**2**)

arene π-stacking of the planar heterocycles of the nucleobases) [15].

In the present work, π–π interaction is absent but the presence of intermolecular H-bond with the lattice solvents cause formation of bilayers and govern the mode of molecular packings in the crystal and is responsible for stabilization of complex (**1**) and (**2**) having a weak bonding through (N7) compared to N9.

Infrared Spectra

The five possible nitrogen binding sites of adenine are the pyrimidine N(1) and N(3), the imidazole N(7) and N(9) ring nitrogen, and the N(6) nitrogen of the exocyclic NH_2 group. The infrared spectra of adenine are available in the literature [71].

The region 3,500–3,000 cm^{-1} shows several bands, which may be attributed to NH_2 of adenine and OH stretching modes. The presence of a peak at 3,429 cm^{-1} for compound (**1**) is assigned for the presence of ethanol molecule in the complex lattice [72, 73]. Various possible sites for coordination of adenine with metal ions are reported in the literature, and the hydrogen bonds have been also taken into consideration. Adenine coordinate through ring nitrogen with appreciable shifts and occasional splitting of *v* C=C, *v* C=N and ring vibrations of the ligand (1,605–1,300 cm^{-1}) [74–79]. The δNH_2 mode of free adenine at 1,674 cm^{-1} undergoes shifts to about 1,650 cm^{-1} as large as expected for those corresponding to H-bounded or N-bounded adenine complexes. The contribution of N(3) and N(9) nitrogens of adenine of complex (**1**) in hydrogen bonding is well observed by a shift in stretching and deformations of the corresponding NH and >C=N groups. In all complexes, the frequencies corresponding to *v* N(9) atom of adenine reveal no coordination to the metal ions but only a contribution in hydrogen bonding. N(9)–H band of adenine shifts towards lower frequency due to hydrogen bonding with ethanolic oxygen as in complex (**1**). The 1,232 cm^{-1} of adenine due to *v* N(7)–C(8) show no appreciable shift in wavelength upon complexation as in the case of complexes (**1**) and (**4**) [72, 75].

The *v*(>C=O) band which occurs at 1,622 cm^{-1} for free acetylacetone shifts to lower frequencies after complexation: The carbonyl stretch of acetylacetonate ligand is clearly observed at 1,582, 1,589 and 1,576 cm^{-1} in complexes (**1**), (**3**) and (**4**).

Thermal Analysis

Thermal analysis plays an important role in studying the structure and the properties of the metal complexes [80, 81]. Cu(II), Co(II) and Ni(II) complexes (**1**–**4**) with mixed ligands adenine and acetylacetonate were studied by thermogravimetric analysis from room temperature to 800°K in nitrogen atmosphere. The TG curves were drawn as % mass loss versus temperature (TG) curve. Heat flow curve were

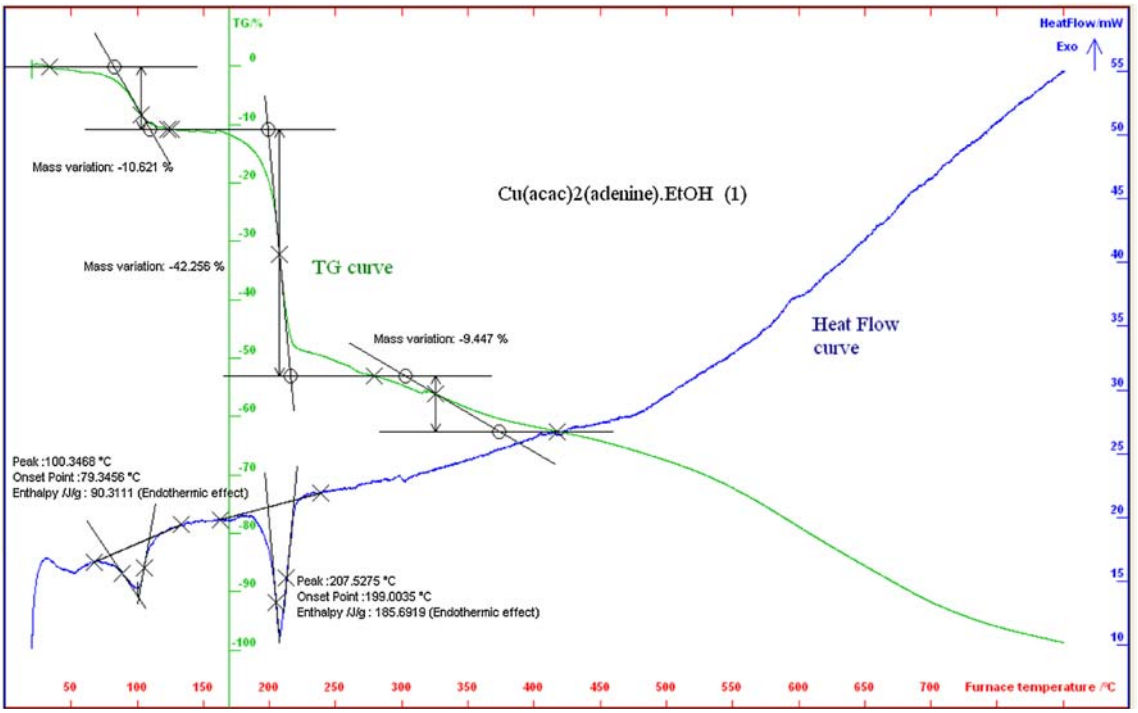


Fig. 6 Thermal analysis of complex (**1**) {[$Cu(acac)_2$(adenine)]·EtOH}

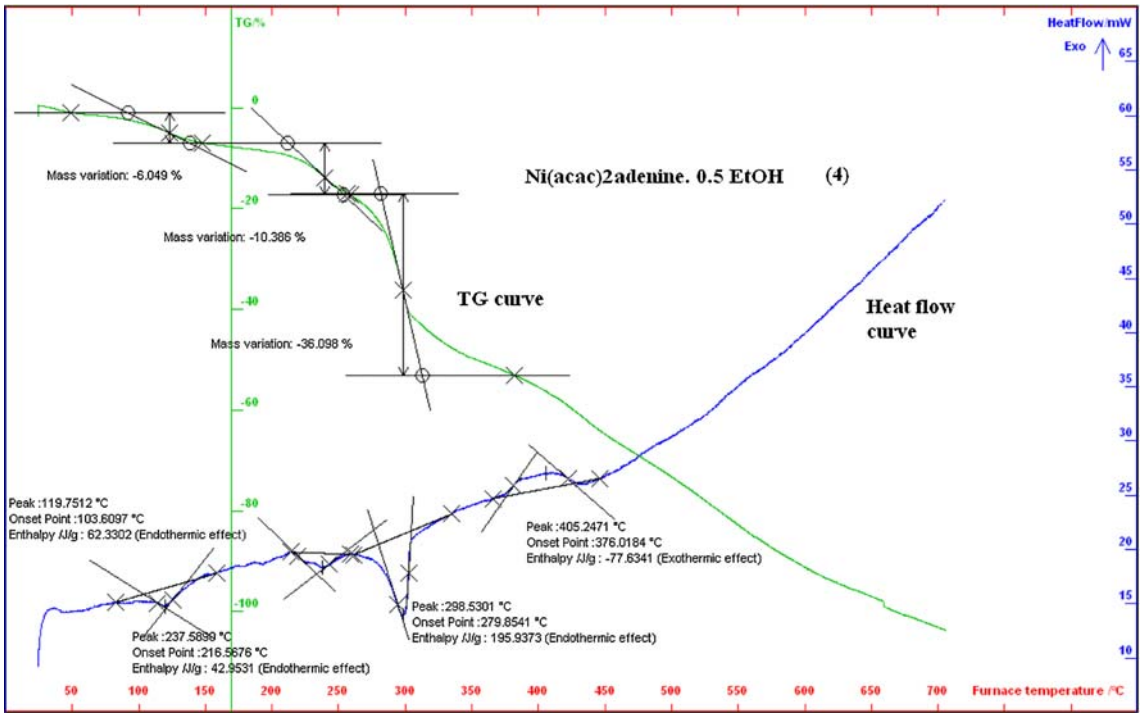


Fig. 7 Thermal analysis of complex (**4**) {[Ni(acac)$_2$(adenine)]·0.5EtOH}

Table 3 Thermal analysis data, TG and DSC for the complexes

Compound	Fragment loss	Theoretical mass loss	Experimental mass loss	T (°C)	ΔH (J/g)	Process
Adenine	$N_3C_4H_3$	68.89	66.50	362.90	891.67	Endo
	N_2CH_2	31.11	30.00	666.62	375.61	Endo
(**1**)	EtOH	10.4	10.62	100.35	90.31	Endo
	2 Acac	44.72	42.26	207.52	185.69	Endo
	N_2CH_2 (Ad)	9.48	9.45	323.9		
	$N_3C_4H_3$ (Ad) Cu	35.34	34.45	616.3		
(**2**)	H_2O	3.69	3.70	95.76	30.02	Endo
	0.5 DMF	7.48	7.42	152.2	18.66	Endo
	0.5 DMF + acac + CH_3CO (acac)	36.58	36.51	202.52	117.05	Endo
	CH_3COCH (acac) + $N_3C_4H_3$(Ad)	30.53	30.45	439.15		
	N_2CH_2 (Ad)	8.61	8.36			
(**3**)	acac + CH_3COCH (acac)	39.64	37.98	279.66	498.87	Endo
	CH_3CO (acac)	11.00	10.95	450.7		
	$N_3C_4H_3$ (Ad)	23.79	22.34	595.14	−327.70	Exo
(**4**)	0.5 EtOH	5.55	6.05	119.75	62.33	Endo
	CH_3CO (acac)	10.37	10.39	237.59	42.95	Endo
	acac + C_3H_4O (acac)	37.37	36.10	298.53	195.94	Endo
	Ni + Ad	46.71	46.64	405.25	−77.63	Exo
				450–800		
Cu (acac)$_2$	0.96 Cu (acaca)$_2$		96.77	272.32	464.62	Endo
				363.66	265.8	Exo

drawn vs. temperature as (DSC) curves. Typical TG-DSC curves are presented in Figs. 6 and 7. The temperature ranges and percentage mass losses of the decomposition reaction are given in Table 3, together with the associated heat.

Thermal analysis of bisacetylacetone copper complex $[Cu(acac)_2]$ shows two peaks due to the loss of acetylacetone ligands, one endothermic at 272 °C and another exothermic at 364 °C. The second peak is typical for acetylacetone ligand signalling its presence in the acetylacetone adenine complexes of copper, cobalt and nickel, Table 3; Figs. 6 and 7. Adenine shows two important decomposition pathways: one peak occurring at 362.90 °C with endothermic heat change of 891.67 J/g, another peak at 666.62 °C with endothermic heat change of 375.61 J/g. The TG curves of metal complexes (1–4) containing adenine ligands also shows similar decomposition patterns in these regions confirming the presence of adenine, Figs. 6 and 7; Table 3.

The complex $\{[Cu(acac)_2(adenine)]\cdot EtOH\}$ (**1**) loses the crystalline solvent ethanol at 100.35 °C. The % experimental mass loss = 10.62% and % theoretical mass loss = 10.40% with an endothermic process, $\Delta H = 90.31$ J/g. The other fragmentations losses are due to acetylacetone and adenine. The first one occurring at corresponds to the loss of two acetylacetonato ligand with experimental loss = 42.26% and theoretical loss = 44.72% with an endothermic heat of 185.69 J/g. The subsequent loss occurring at higher temperature is due to adenine, Fig. 6 and Table 3.

Supplementary Material

CCDC-281077 contains the supplementary crystallographic data for complex (**1**) while CCDC-676341 for complex (**2**) for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK.

Acknowledgments Thermal analyzer at BAU is provided by FP 6 European Commission Grants "MEDINDUS" Contract # 509159. Thanks to University of South Florida, Tampa for X-ray facilities.

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