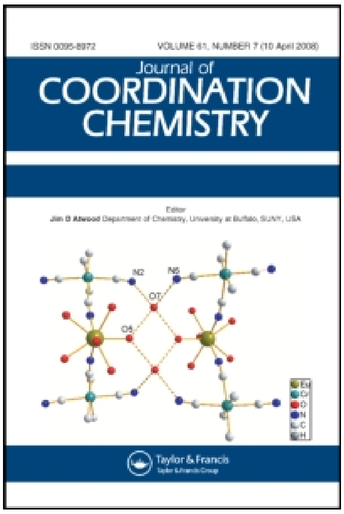

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Combining Coordination Chemistry and Hydrogen Bonds: Synthesis, Crystal Structures and Thermal Behavior of the Complexes Aqua(2,2'-Bipyridine- N , N ')-(Malonamide- O , O ')-M(II) Dinitrate (M = Cu, Ni)

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COMBINING COORDINATION CHEMISTRY AND HYDROGEN BONDS: SYNTHESIS, CRYSTAL STRUCTURES AND THERMAL BEHAVIOR OF THE COMPLEXES AQUA(2,2′-BIPYRIDINE-*N*,*N*′)-(MALONAMIDE-*O*,*O*′)-M(II) DINITRATE (M = Cu, Ni)

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Complexes have been isolated from reaction of $M(NO_3)_2 \cdot xH_2O$ (M = copper(II), nickel(II)) with bipy (bipy = 2,2′-bipyridine, $C_{10}H_8N_2$) and malonamide (L = malonamide, $CH_2(CONH_2)_2$) in a mixture of ionized water : ethanol. Complete single crystal structure determinations have been carried out for both compounds, which display monomer structures $[Cu^{II}(L)(bipy)(H_2O)] \cdot (NO_3)_2$ (**I**) and $[Ni^{II}(L)(bipy)(H_2O)_2] \cdot (NO_3)_2$ (**II**). The molecular structure of **I** shows that the copper atom has a slightly distorted square pyramidal coordination. Two nitrogen atoms from the chelating bipy and two oxygen atoms from the malonamide ligand build the basal plane and a water molecule fills the apical position. The nickel complex **II** has octahedral coordination. Hydrogen bonding plays an important role consolidating the crystal structure. The two compounds have been characterized through thermogravimetric (TG) and calorimetric analyses (DSC).

Keywords: Copper(II) and nickel(II) complexes; Malonamide; 2,2′-bipyridine; Thermal behavior

INTRODUCTION

The use of transition metal complexes of chelating 2,2′-bipyridine (bipy) to generate multidimensional infinite arrays or networks via hydrogen bonding is an area of general interest in metal-coordination chemistry [1,2]. These hydrogen-bonding interactions have long been considered to be of importance in biological systems [3] and in crystal engineering [4].

The purpose of involving metals may be: (i) purely structural, e.g. providing linkages or controlling network connectivity or (ii) functional, e.g. the introduction

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of metal-based photophysical or magnetic properties or, in the channel structures, perhaps even metal-based reactive sites [3,5].

When considering the involvement of transition metals in crystal engineering, several decades of well-established principles in coordination chemistry and organometallic chemistry provide a foundation. Specifically, the linking of transition metal-containing molecular building blocks can draw upon the principles for both design and synthesis of the molecular units. This existing knowledge base includes information about coordination number and coordination geometries for a wide variety of transition metal ions, as well as qualitative or quantitative information on the thermodynamic and kinetic stability of many types of metal–ligand bonds [6].

Our aim in this work has been to combine this well-established molecular inorganic chemistry with aspects of supramolecular organic chemistry where hydrogen bonds combine the most favorable aspects of directionality and strength among intermolecular interactions. While weaker than covalent bonds or even coordinate bonds, they offer greater flexibility and there are well-developed principles for fostering mutual recognition by functional groups through hydrogen bonding [4]. Thus, amide groups bearing self-recognizing hydrogen-bonding groups can be used to construct hydrogen-bonded assemblies with predictable topologies [7].

In the present work, we report the synthesis, structure and thermal behavior of two new malonamide copper (II) and nickel (II) complexes, $[Cu(L)(bipy)(H_2O)]\cdot(NO_3)_2$ (**I**) and $[Ni(L)(bipy)(H_2O)_2]\cdot(NO_3)_2$ (**II**) (bipy = 2,2′-bipyridine, L = malonamide).

EXPERIMENTAL

Instrumentation

Elemental analyses (carbon, hydrogen and nitrogen) were performed with an EA 1108 CHNS-O automatic analyzer. Thermal analyses (TG-DSC) were carried out on a Netzsch STA 409 EP simultaneous thermal analyzer in a dynamic atmosphere of dinitrogen (flow rate: $70\,mL\,min^{-1}$). The sample (8 mg) was heated from ambient to 400°C in an alumina crucible at a rate of $5°C\ min^{-1}$ with inert alumina as reference. The TG curves were analyzed as percentage mass loss as a function of temperature. The numbers of decomposition steps were identified using the derivative thermogravimetric curve (DTG). The DSC curves were analyzed as differential scanning calorimetric (ΔT (μV)).

Synthesis

The reagents and solvents employed in the synthesis were used without further purification. Copper complex **I** was synthesized by adding an ethanol solution (15 mL) of 2,2′-bipyridine (0.39, 2.5 mmol) to an aqueous suspension of copper nitrate hemipentahydrate (0.58 g, 2.5 mmol). To the resulting solution was added an aqueous solution (20 mL) of malonamide (0.50 g, 5 mmol) with continuous stirring for 30 min. From the resulting blue solution ($pH \cong 5$), filtered and cooled at room temperature, blue crystals appeared after several days suitable for X-ray diffraction studies (Table I). Yield: 650 mg ($\cong 57\%$, based on $Cu(NO_3)_2\cdot 5/2H_2O$). Anal. Calcd. for $[Cu(L)(bipy)(H_2O)]\cdot(NO_3)_2(\%)$ (**I**); C, 33.52; H, 3.89; N, 18.04. Found: C, 33.42;

H, 4.05; N, 17.99. The synthetic method of **II** is similar to that for **I** except that $Cu(NO_3)_2 \cdot 5/2H_2O$ was replaced by $Ni(NO_3)_2 \cdot 6H_2O$. From the resulting violet-solution (pH ≅ 6), filtered and cooled at room temperature, violet crystals appeared after several days suitable for X-ray diffraction studies (Table I). Yield: 700 mg (≅ 59%, based on $Ni(NO_3)_2 \cdot 6H_2O$). Anal. Calcd. for $[Ni(L)(bipy)(H_2O)] \cdot (NO_3)_2$(%) (**II**): C, 32.60; H, 4.21; N, 17.54. Found: C, 32.32; H, 4.29; N, 17.65.

X-ray Structure Determination

The single crystals used for data collection were attached to thin glass fibers and data collection was performed on an Enraf-Nonius MACH3 diffractometer by ω-scan techniques using graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). Intensity data were collected in the θ ranges 2.82–29.97°. A summary of the selected crystallographic data and structure refinement for Complexes **I** and **II** is given in Table I. For **I** and **II**, the data were corrected for L_p effects. No absorption corrections were applied in **II** because of poor face definition. In **II**, space groups P1 and P-1 were consistent with the triclinic Laue symmetry. The structure solved and refined normally in space group P-1, and some reflections from high resolution (Å) were removed before the anisotropic refinement. The coordinates of the metal atoms were determined by direct methods (SIR92 [8]) and the remaining nonhydrogen atoms were located from successive Fourier difference syntheses. The structures were refined by full-matrix

TABLE I Summary of crystal data and structure refinements for **I** and **II**

		I	*II*
Empirical formula		C13H18CuN6O9	C13H20NiN6O10
Formula weight		465.87	479.03
Color		blue	violet
Crystal system		monoclinic	triclinic
Space group		P21/c	P-1
Unit cell dimensions			
a (Å)		12.527(2)	7.314(1)
b (Å)		8.447(l)	9.771(2)
c (Å)		18.035(2)	14.113(3)
α (°)			78.33(3)
β (°)		102.94(0)	86.36(3)
γ (°)			81.61(3)
V (Å^3)		1859.9(4)	976.6(3)
Z		4	2
D_{calc} (g cm^{-3})		1.656	1.622
μ_{calc} (Cu Kα) (mm^{-1})		1.237	1.059
F(000)		948	492
Index ranges		$-17 \leq h \leq 0$	$-10 \leq h \leq 10$
		$-11 \leq k \leq 11$	$-13 \leq k \leq 0$
		$-24 \leq l \leq 25$	$-19 \leq l \leq 19$
Reflections collected		10880	5935
Independent reflections		5396	5625
Observed reflections [I ≥ 2σ(I)]		3005	4582
Indices [I ≥ 26(I)]	R_1	0.045	0.036
	wR_2	0.115	0.122
R indices [all dates]	R_1	0.114	0.059
	wR_2	0.1425	0.1455
Largest difference peak and hole (e Å^{-3})		0.599, −0.391	0.654, −0.411

least-squares techniques. All hydrogen atoms were located at the calculated positions except for those of water molecules, and they were assigned a fixed displacement and constrained to ideal geometry with N–H = 0.86 Å. The thermal parameters of calculated hydrogen atoms were related to those of their parent atoms by $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{N})$. All calculations were performed with the SHELXL97 [9] program. Atomic scattering factors and anomalous scattering corrections are from the literature [10]. The final geometrical calculations and the graphical manipulations were carried out with PARST95 [11] and PLATON [12] programs, respectively. The weighting scheme chosen for **I** was $w = 1/[\sigma^2(F_o^2) + (0.0760P)^2 + 0.0973P]$ whereas for **II** $w = 1/[\sigma^2(F_o^2) + (0.1656P)^2 + 1.3447P]$ where $P = (F_o^2 + 2F_o^2)/3$.

RESULTS AND DISCUSSION

Selected bond length and angles for **I** and **II** are shown in Table II.

Structural Description

The molecular structures of **I** and **II**, which are depicted in Figs. 1(a,b) show the asymmetric units with the crystallographic numbering schemes. Figure 1(a) shows the copper atom as a slightly distorted square pyramid. Two nitrogen atoms from the chelating bipy and two oxygen atoms from the malonamide ligand build the basal plane with a water molecule at the apical position. The charges are counterbalanced by two uncoordinated nitrate anions. The Cu–$\mathrm{O_{malonanude}}$ bond distance (mean value 1.940(3) Å) lies within the range observed in the two polymorphic compounds $[\mathrm{Cu^{II}(malonamide)_2(NO_3)_2}]$ recently reported by Rodríguez-Martín *et al.* [13]. The average Cu–$\mathrm{N_{bipy}}$ (1.976(2) Å) distance also agrees with those reported for other bipy–copper (**II**) complexes [3,14].

Figure 1(b) shows the nickel atom with an octahedral coordination comprised of two malonamide O atoms, two N atoms from one chelating bipy group and two water O atoms. The charges are counterbalanced by two uncoordinated nitrate anions. The N-donor ligands show a *trans*-arrangement of two O-donor atoms around the $\mathrm{Ni^{II}}$. The bond lengths Ni–$\mathrm{O_{malonamide}}$ (mean value 2.019(2) Å) are slightly shorter than those observed in $[\mathrm{Ni^{II}(malonamide)_2(H_2O)_2}]\cdot(\mathrm{NO_3})_2$, recently reported [13]. The Ni–$\mathrm{N_{bipy}}$ bond distances (mean value 2.048(5) Å) are slightly shorter than the Ni–$\mathrm{O_{Water}}$ bonds lengths (mean value 2.047(2) Å). These values are in accord with other bipy–nickel (II) complexes described in the literature [15].

The individual pyridine rings are nearly planar with the dihedral angle between the pyridine rings [N1C1C2C3C4C5] and [N2C6C7C8C9C10] is 2.43(9)° for **I** and 1.52(3)° for **II**. The N ⋯ N *bite* of bipy is 82.0(1) and 80.34(1) Å for **I** and **II**, respectively, which fall in the normal range. The *bite* angles N1–$\mathrm{CuI^{II}}$–N2 82.00(11)° and N1–$\mathrm{Ni^{II}}$–N2 80.34(8)° for **I** and **II**, respectively, are far from the ideal one of 90° because of the constrained geometry of the bipy-ring system [16]. These values are in agreement with other compounds reported [3,13–15]. The $\mathrm{Cu^{II}}$ **I** and $\mathrm{Ni^{II}}$ **II**, lie 0.223(4) and 0.036(5) Å above the [N1N2O1O2] mean plane toward the coordinated water molecule. Average C–C and C–N bond lengths within the rings and the inter-ring C5–C6 bond (Table II) are in good agreement with those currently given in the literature for the noncoordinated [16] and coordinated bipy ring [3,13–15].

TABLE II Selected bond lengths (Å) and bond angles (°) for **I** and **II** E.D.S.′S in parentheses

I				*II*			
Bond lengths				Bond lengths			
Cu(1)–O(1)	1.951(2)	C–C$_{\mathrm{bpy}}$	1.377(5)	Ni(1)–O(1)	2.008(2)	C–C$_{\mathrm{bpy}}$	1.381(4)
Cu(1)–O(2)	1.929(2)	C–N$_{\mathrm{bpy}}$	1.342(4)	Ni(1)–O(2)	2.031(2)	C–N$_{\mathrm{bpy}}$	1.342(3)
Cu(1)–N(1)	1.978(3)	C(5)–C(6)$_{\mathrm{bpy}}$	1.479(4)	Ni(1)–N(1)	2.053(2)	C(5)–C(6)$_{\mathrm{bpy}}$	1.485(3)
Cu(1)–N(2)	1.974(2)	C–C$_{\mathrm{malonamide}}$	1.501(4)	Ni(1)–N(2)	2.042(2)	C–C$_{\mathrm{malonamide}}$	1.514(4)–1.517(3)
Cu(1)–O(1W)	2.248(2)	C–N$_{\mathrm{malonamide}}$	1.297(4)–1.304(3)	Ni(1)–O(1W)	2.084(2)	C–N$_{\mathrm{malonamide}}$	1.307(3)–1.310(3)
		C–O$_{\mathrm{malonamide}}$	1.248(3)–1.252(3)	Ni(1)–O(2W)	2.085(2)	C–O$_{\mathrm{malonamide}}$	1.242(3)–1.244(3)
Bond angles				Bond angles			
O(1)–Cu(1)–O(2)	91.24(8)	O(2)–Cu(1)–O(1W)	94.51(8)	O(1)–Ni(1)–O(2)	89.73(8)	O(2)–Ni(1)–O(2W)	86.25(8)
O(1)–Cu(1)–O(1W)	95.42(8)	O(2)–Cu(1)–N(1)	165.40(10)	O(1)–Ni(1)–O(1W)	91.69(8)	O(2)–Ni(1)–N(1)	175.46(7)
O(1)–Cu(1)–N(1)	92.58(10)	O(2)–Cu(1)–N(2)	91.20(10)	O(1)–Ni(1)–N(1)	94.19(8)	O(2)–Ni(1)–N(2)	95.67(8)
O(1)–Cu(1)–N(2)	166.80(10)	N(1)–Cu(1)–N(2)	82.00(11)	O(1)–Ni(1)–N(2)	174.25(7)	O(2W)–Ni(1)–N(1)	91.51(8)
O(1W)–Cu(1)–N(1)	99.15(9)			O(1W)–Ni(1)–N(1)	91.09(8)	O(2W)–Ni(1)–N(2)	89.22(8)
O(1W)–Cu(1)–N(2)	97.31(9)			O(1W)–Ni(1)–N(2)	90.19(8)	N(1)–Ni(1)–N(2)	80.34(8)

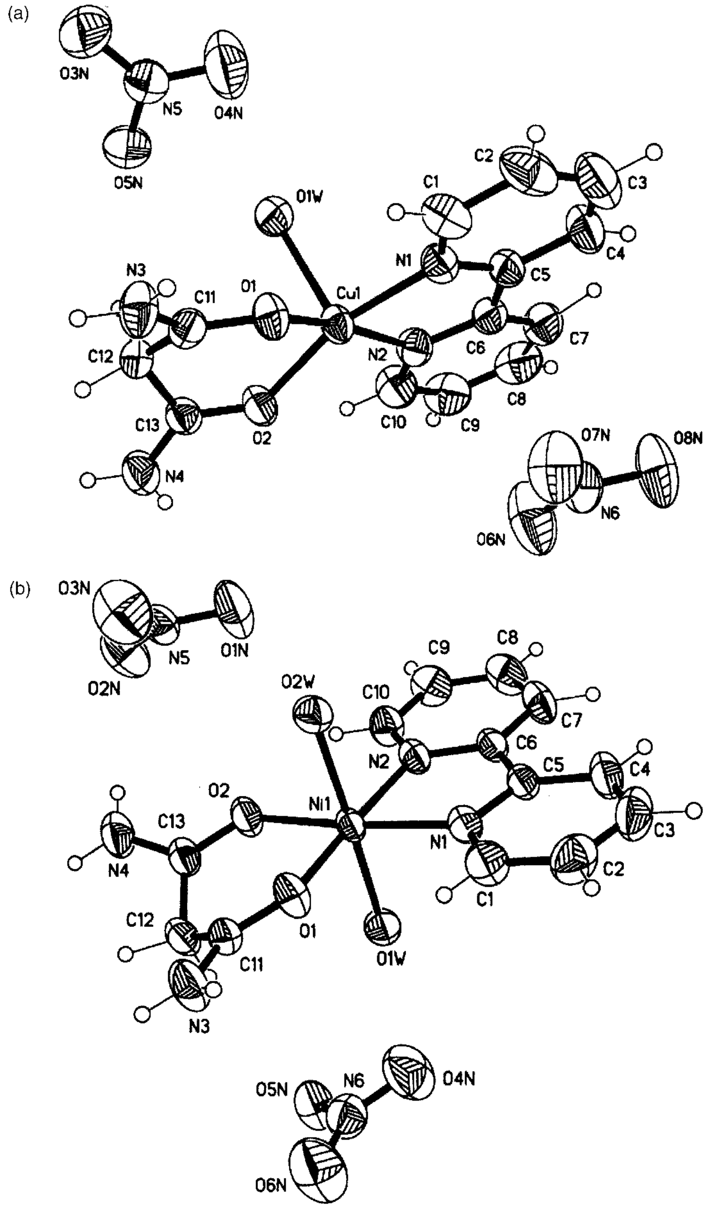


FIGURE 1 Perspective view of the complexes (a) $[Cu^{II}(L)(bipy)(H_2O)]\cdot(NO_3)_2$ (**I**) and (b) $[Ni^{II}(L)(bipy)(H_2O)_2]\cdot(NO_3)_2$ (**II**). In both compounds with the atom-labeling scheme, the displacement ellipsoids are drawn at the 50% probability level where hydrogen atoms have been omitted for clarity; [L = malonamide].

The bond lengths C–C, C–N and C–O of the malonamide ligand are in Table II. These values are similar to $[M^{II}(malonamide)_2(NO_3)_2]$ $[M^{II} = Cu, Co]$; $[Ni^{II}(malonamide)_2(H_2O)_2(NO_3)_2]$ complexes [13].

The malonamide ligand is in a six-member boat coordination [13], with $Q = 0.513(3)$ and $\phi = 125.7(4)°$ for **I** and $Q = 0.487(0)$ and $\phi = -171.1(0)°$ for **II**.

Figures 2(a,b) show the crystal packing of the compounds. Hydrogen bonding plays an important role consolidating the crystal structure (Table III). The amine groups are hydrogen bonded to the NO_3^- anions. There are also some weak C–H···O contacts, which involve the carbon atoms of the CH_2 in malonamide ligand and of the bipy

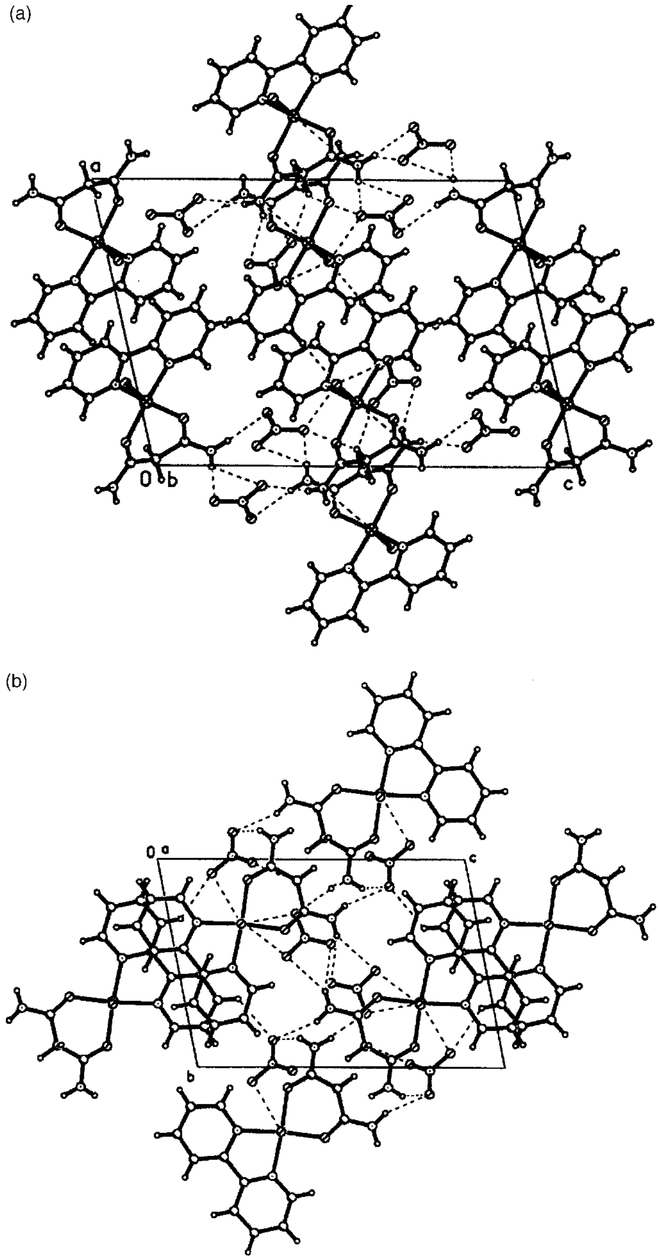
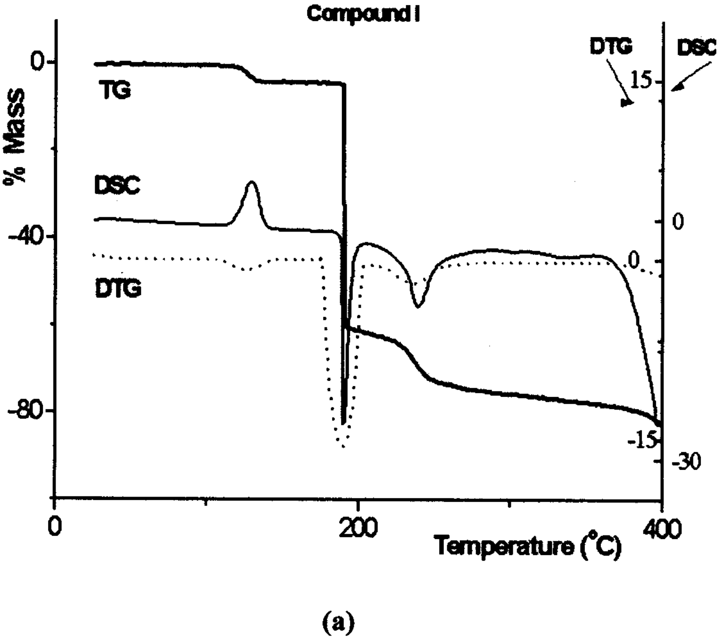


FIGURE 2 View of the representative crystalline structure of (a) $[Cu^{II}(L)(bipy)(H_2O)]\cdot(NO_3)_2$ (**I**) and (b) $[Ni^{II}(L)(bipy)(H_2O)_2]\cdot(NO_3)_2$ (**II**), generated by the cross-linking of $N\text{–}H_{(malonamide)}\cdots O_{(nitrate)}$ bonds; [L = malonamide].

TABLE III Hydrogen bonds geometries in the crystal structure for **I** and **II** with E.D.S.′S in parentheses

I	$H\cdots A$ (Å)	$D-H\cdots A$ (°)	*Symmetry*	***II***	$H\cdots A$ (Å)	$D-H\cdots A$ (°)	*Symmetry*
$\text{N–H}_{(\text{malonamide})}\cdots\text{O}_{(\text{nitrate})}$				$\text{N–H}_{(\text{malonamide})}\cdots\text{O}_{(\text{nitrate})}$			
N(3)–H(3B)···O(6)	2.325(3)	147.2(2)	$-x, -y+1, -z$	N(3)–H(3A)···O(4)	2.404(1)	147.98(3)	$-x+2, -y+1, -z+1$
N(4)–H(4A)···O(3)	2.655(3)	123.4(2)	$x, +y+1/2, +z+1/2$	N(3)–H(3B)···O(3)	2.618(1)	161.44(2)	$-x+1, -y+2, -z+1$
N(4)–H(4B)···O(3)	2.573(3)	123.4(2)	$-x, -y, -z$	N(4)–H(4B)···O(6)	2.676(1)	119.50(3)	$-x+2, -y+2, -z+1$
$\text{C–H}_{(\text{malonamide})}\cdots\text{O}_{(\text{nitrate})}$				$\text{C–H}_{(\text{malonamide})}\cdots\text{O}_{(\text{nitrate})}$			
C(12)–H(12B)···O(5)	2.510(3)	135.7(2)	x, y, z	C(12)–H(12A)···O(5)	2.770(1)	147.54(5)	x, y, z
C(12)–H(12B)···O(7)	2.612(3)	135.7(2)	$x, +y+1, +z$				
$\text{C–H}_{(\text{bipy})}\cdots\text{O}_{(\text{malonamide})}$				$\text{C–H}_{(\text{bipy})}\cdots\text{O}_{(\text{malonamide})}$			
C(1)–H(1)···O(1)	2.459(2)	113.8(2)	x, y, z	C(1)–H(1A)···O(1)	2.604(1)	116.36(2)	x, y, z
C(10)–H(10)···O(2)	2.455(2)	113.7(2)	x, y, z	C(10)–H(10A)···O(2)	2.650(1)	116.91(2)	x, y, z
$\text{C–H}_{(\text{bipy})}\cdots\text{O}_{(\text{water})}$				$\text{C–H}_{(\text{bipy})}\cdots\text{O}_{(\text{water})}$			
C(4)–H(4)···O(1W)	2.741(2)	147.3(2)	$-x+1, -y+1, -z$	C(7)–H(7A)···O(1W)	2.661(1)	142.34(2)	$-x+2, -y+1, -z+2$
C(7)–H(7)···O(1W)	2.331(2)	160.8(2)	$-x+1, -y+1, -z$	C(7)–H(7A)···O(2W)	2.599(1)	137.63(2)	$-x+1, -y+1, -z+2$
$\text{C–H}_{(\text{bipy})}\cdots\text{O}_{(\text{nitrate})}$				$\text{C–H}_{(\text{bipy})}\cdots\text{O}_{(\text{nitrate})}$			
C(9)–H(9)···O(6)	2.670(3)	129.4(2)	$-x+1, +y-1/2, -z+1/2$	C(9)–H(9A)···O(1)	2.628(1)	151.94(3)	$-x+1, -y+2, -z+2$
C(9)–H(9)···O(8)	2.592(3)	138.6(2)	$-x+1, +y-1/2, -z+1/2$	C(9)–H(9A)···O(2)	2.737(1)	117.56(2)	$-x+1, -y+2, -z+2$



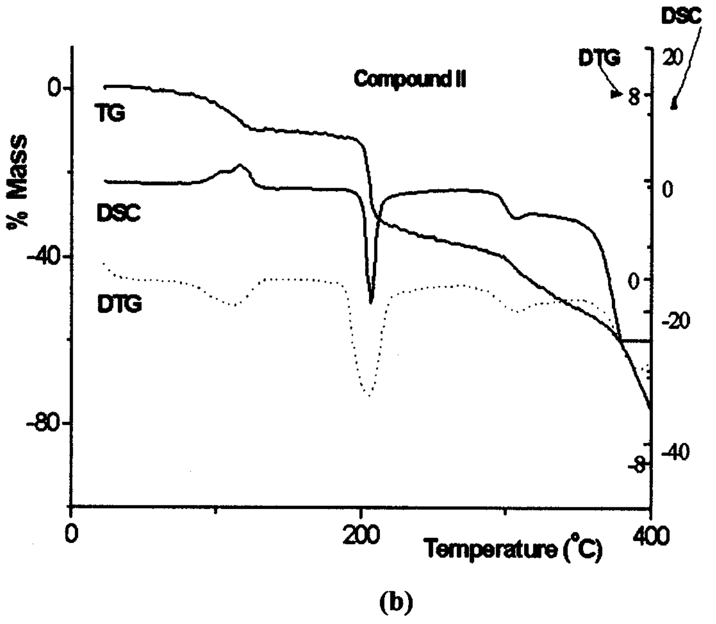


FIGURE 3 TG/DSC curves of (a) $[Cu^{II}(L)(bipy)(H_2O)]\cdot(NO_3)_2$ (**I**) and (b) $[Ni^{II}(L)(bipy)(H_2O)_2]\cdot(NO_3)_2$ (**II**), [L = malonamide; TG = % mass loss; DSC = ΔT (μV) and DTG = % min^{-1}].

ligand as hydrogen-donors, and nitrate oxygen atoms and water molecule O atoms as acceptors. There is no doubt that not all the C–H · · · O contacts can be considered as hydrogen bonds, but they are indicative of some polarization. Spectroscopists and crystallographers have long known the importance of C–H · · · O and C–H · · · OW hydrogen bonds but definitive evidence for their structural significance was given only a few years ago [17].

Thermogravimetric Analysis

In $[Cu^{II}(L)(bipy)(H_2O)]\cdot(NO_3)_2$ (**I**) (Fig. 3(a)), an endothermic process centered at 130°C (DSC) was observed as mass loss 3.99% (TG) $\{[DTG]_{Tpeak} = 127°C\}$ corresponding to the loss of one coordinated water molecule per formula unit (calculated value 3.86%). The compound $[Ni^{II}(L)(bipy)(H_2O)_2]\cdot(NO_3)_2$ (**II**) (Fig. 3(b)), presents a similar behavior to **I**, thus two endothermic processes on the DSC curve are observed. A shoulder and a peak at 104 and 117°C, respectively, as mass loss 9.26% (TG) $\{[DTG]_{Tpeak} = 111°C\}$ corresponding to the loss of two coordinated water molecules per formula unit (calculated value 7.52%). For both compounds, this process seems to take place in only one-step, suggesting that all of the water molecules are similar, as deduced from the crystallographic data (*comment above*). The range of temperature for weight loss corresponding to coordinated water molecules are in accord with other compounds reported [3,13,18]. The following stage, which occurs in the temperature ranges 144–400°C for **I** and 134–400°C for **II**, involves the combustion of part of the organic matter of the organic ligand [13,18b,19].

Acknowledgment

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Supplementary Material

Additional material consists of H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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