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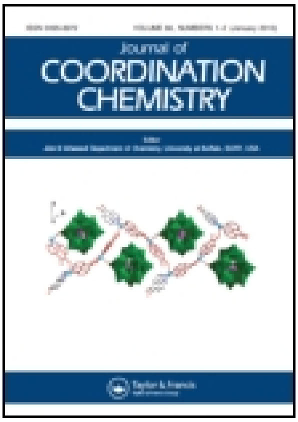

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C-H···$O_{nitrate}$ synthon assisted molecular assembly of hydrogen bonded Ni(II) and Cu(II) complexes

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C–H···O$_{nitrate}$ synthon assisted molecular assembly of hydrogen bonded Ni(II) and Cu(II) complexes

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Two Schiff base metal complexes [Cu–SPETN·NO_3 (**1**) and Ni–SPETN·NO_3 (**2**) [SPETN = 2,2′-[propane,1,3-diylbis(nitrilomethyldyne)pyridyl,phenolate]] with hydrogen bonding groups have been synthesized and characterized by single-crystal X-ray diffraction. In both of the compounds nitrates occupy a crystallographic general position. In **1** the lattice nitrates are on the 2_1 screw axis while in **2** they are at the crystallographic inversion center. C–H···O$_{nitrate}$ synthons (formed by the nitrate anions and peripheral hydrogen bonding groups of the metal complexes) are non-covalent building blocks in molecular-assembly and packing of the cationic Schiff base metal complexes ($M = Ni^{2+}$, Cu^{2+}), resulting in 2-D hydrogen bonded networks. The Cu···Cu non-bonding contact in **1** is 3.268 Å while the Ni–Ni bonding distance in **2** is 3.437 Å.

Keywords: Metal-organic complexes; Crystal engineering; C–H···O$_{nitrate}$ synthons; Molecular-assembly

1. Introduction

Crystal engineering moves from individual molecules to supramolecular description of crystal structures in which the molecules are considered as an assembly held together by noncovalent interactions [1, 2]. Hydrogen bonding has been called the master key of molecular recognition because it is the most reliable interaction in the toolkit of the crystal engineering, being both strong and directional [2]. The combined influence of all hydrogen bonds in the crystal structures of salts [3–5] can make a large impact on the resulting network [6] because complementary H-bonds can efficiently bind counter-anions and/or solvents in a structure and contribute to shaping the hierarchy of supramolecular assembly [7].

Further study of intermolecular interactions is of fundamental importance to hydrogen bonded organic and metal-organic supramolecular structure, because these interactions determine crystal structures, while the structures determine most of the important physical and chemical properties of solids. In particular, the directional interactions resulting from multiple hydrogen bonding with neighbours are explored in crystal engineering [1]. The structures of molecular organic and metal-organic solids are determined by summation of

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weak intermolecular forces. The C–H···O interaction, though weak, is not van der Waals but electrostatic and resembles conventional O–H···O/N and N–H···O/N hydrogen bonds in its geometrical properties [8]. Nitrate, although not inherently basic, can act as a potential C–H···O acceptor. C–H···$O_{nitrate}$ synthons play an important role in hydrogen bonded metal-organic crystals of Ni–triazolate [7a] together with other conventional O–H···O and N–H···O synthons and reflects a collective impact on the crystal packing. Recently the author reported the role of neutral C–H···O synthon towards self-assembly of a 1-D Cu-picolinate coordination polymer into a 2-D hydrogen bonded network [9] and they do play an important role in crystal packing.

Since, anions have the ability to influence the crystal packing as potential hydrogen bond acceptors, hydrogen bonds to anions can be utilized for tuning the topology of a molecular network [10, 11]. A "free or non-coordinated" anion [7a] can influence a framework by instigating preferable supramolecular recognition because metal bound anion has a restricted stereoelectronic option of forming intermolecular interactions. To strategically design and synthesize a metal-organic supramolecular network, a set of cationic complexes with "in-built" C–H groups as a source of hydrogen bond donor with metal nitrates as a nitrate source have been chosen.

A given set of molecules will yield a given set of crystal structures if they are capable of leading to a given set of supramolecular synthons [12]. In metal-organic complexes, if a ligand is likely to form a particular set of synthons (after complexation), then these structural patterns will recur in the overall metal-organic systems that result. There is general consensus that C–H···O bonds determine crystal packing, particularly when stronger hydrogen bonding is absent [1]. Herein, I design metal complexes with C–H···$O_{nitrate}$ synthons in their crystal structures.

The preparation and crystal structures of two new cationic Schiff base complexes, Cu–SPETN·NO_3 (**1**) and Ni–SPETN·NO_3 (**2**), are reported. **1** and **2** are stabilized by an intricate array of H-bonding interactions between the peripheral C–H groups and non-coordinated nitrates.

2. Experimental

2.1. *Materials and methods*

$Cu(NO_3)_2 \cdot 4H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were purchased from Finar Chemicals. Salicylaldehyde, 1,3-diaminopropane, and pyridine-2-carboxaldehyde were purchased from Sigma Aldrich. All reagents and solvents were of commercial grade and used without purification. The infrared spectra as KBr pellets from 4000 to 500 cm^{-1} and Nujol from 600 to 100 cm^{-1} were recorded with a Bruker IFS66 Spectrometer. Thermogravimetric analysis (TGA) was carried out with a STA 409C TGA instrument.

2.2. *Synthesis of 1 and 2*

To a stirred methanolic solution (10 mL) of pyridine-2-carboxaldehyde (1 mmole) and salicylaldehyde (1 mmole), methanolic solution (10 mL) of 1,3-diamino propane (1 mmole) was added dropwise and the resulting reaction mixture was stirred at 50 °C for 2 h. The yellow reaction mixture obtained was cooled at room temperature and 10 mL methanolic solution of 1 mmole metal nitrate salt ($M = Cu^{2+}$ (**1**) and Ni^{2+} (**2**))

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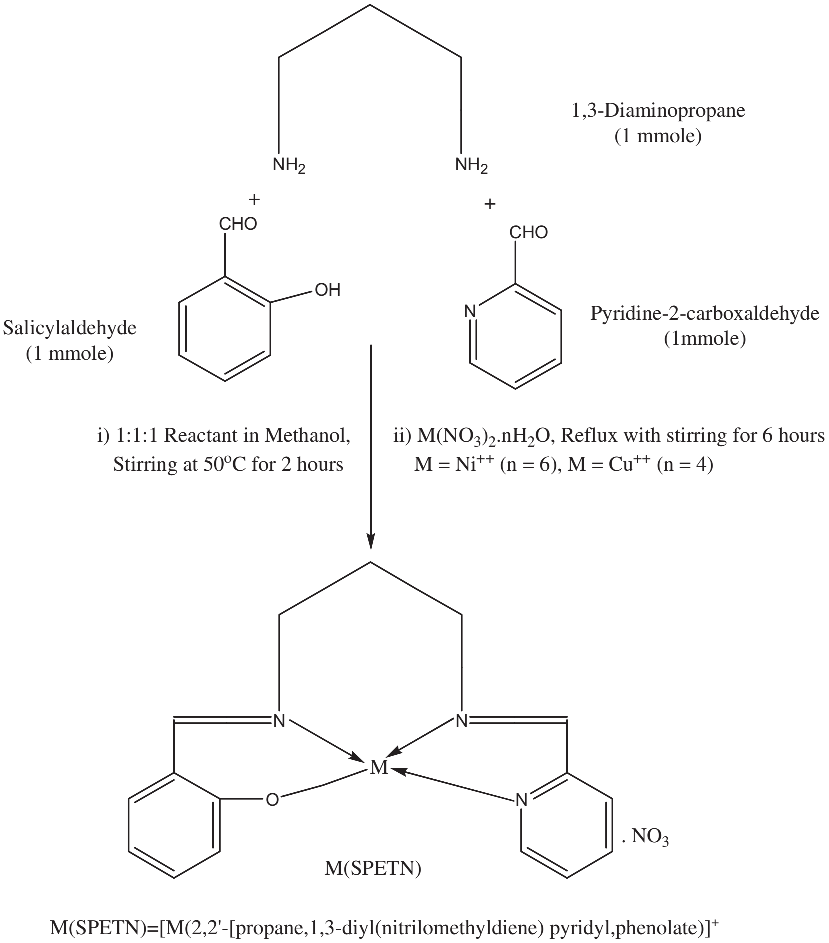

Scheme 1. Schematic representation of the reactions for **1** and **2**.

was added dropwise to the ligand solution. The resulting solution was refluxed with stirring for 6 h. The solution [red (**1**) and green (**2**)] obtained was filtered and left for crystallization at room temperature (scheme 1). After 15 days single crystals suitable for X-ray single crystallography were collected. The crystal structure and refinement data are tabulated in table 1.

2.3. *X-ray crystallography*

Single crystal of **1** with dimensions $0.48 \times 0.32 \times 0.29\,\text{mm}^3$ and **2** with dimensions $0.6 \times 0.4 \times 0.2\,\text{mm}^3$ were mounted on a Rigaku Mercury375R/M CCD (XtaLAB mini) diffractometer using graphite monochromated Mo-Kα radiation equipped with a Rigaku low temperature gas spray cooler. In these cases, data were processed with the Rigaku Crystal Clear software [13]. Structure solutions and refinements were performed using SHELX97 [14] using WINGX suite [15].

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Table 1. Crystal structure and refinement data for **1** and **2**.

	1	**2**
Empirical formula	$C_{16}H_{16}CuN_4O_5$	$C_{16}H_{16}NiN_4O_5$
Formula weight	407.87	386.91
Temperature (K)	150	150
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\ -1$ (No. 2)
Unit cell dimensions		
a (Å)	7.007(4)	6.912(6)
b (Å)	10.821(10)	10.692(11)
c (Å)	20.615(18)	11.162(11)
α (°)	90.00	110.501(12)
β (°)	93.34	94.285(14)
γ (°)	90.00	92.153(7)
Volume (Å^3)	1560.4	768.7(13)
Z	4	2
Density (calculated) (mg m^{-3})	1.736	1.672
Absorption coefficient (mm^{-1})	1.401	1.300
F (000)	680	384
Crystal size	0.48 × 0.32 × 0.29	0.6 × 0.4 × 0.2
θ Range for collection	2.1–27.5	2.1–27.5
Absorption correction	Multi-scan	Multi-scan
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.119	1.199
R indices [$I > 2\mathrm{sigma}(I)$]	$R1 = 0.0436$; $wR2 = 0.1190$	$R1 = 0.0899$; $wR2 = 0.2758$
R (all data)	$R1 = 0.0502$; $wR2 = 0.136$	$R1 = 0.0956$; $wR2 = 0.2889$
Largest diff. peak and hole (e Å^3)	0.645 and −1.645	2.206 and −1.372

3. Results and discussion

3.1. *Description of the crystal structures of 1 and 2*

The single-crystal X-ray diffraction studies reveal that **1** crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit of **1** consists of two components: a cationic building block [Cu–(SPETN = 2,2′-[propane, 1,3-diylbis (nitrilomethyldyne) pyridyl, phenolate]$^+$ and a nitrate. The copper sites exhibit "4 + 1" square pyramidal geometry with the basal plane defined by one pyridyl nitrogen, two nitrilomethyldiene nitrogens, and one phenolate oxygen; the apical site is occupied by another phenolate oxygen. The Cu···Cu non-bonding contact for **1** is 3.268 Å and this is unexceptional. In **1**, the peripheral C–H of the complex together with nitrate forms a heterosynthon constituted with six C–H···O_{nitrate} hydrogen bonds, out of which one nitrate oxygen acts as a bifurcated acceptor (figure 1).

The nitrate together with the cationic building block is arranged around the crystallographic 2_1 screw axis. The anions are not only responsible for charge neutrality, but are also involved in H-bonding interactions via their oxygens with nearby cationic units resulting in the formation of 1-D sheets, which are further assembled by another C–H···O_{nitrate} synthon yielding a 2-D H-bonded metallo-supramolecular network (figure 2). The synthon-**I** in **1** is a chelating synthon; these chelating synthons are themselves connected with other C–H···O_{nitrate} hydrogen bonds of 2.563 and 2.615 Å.

Single crystal X-ray diffraction studies reveal that **2** has triclinic centrosymmetric space group $P{-}1$ (number 2). Nickel in [Ni(2,2′-[propane,1,3-diylbis(nitrilomethyldyne)pyridyl, phenolate])]$^+$ is coordinated by three nitrogens, one from pyridine and two from imine, and one phenolate oxygen resulting in square planar geometry. An effective Ni–Ni

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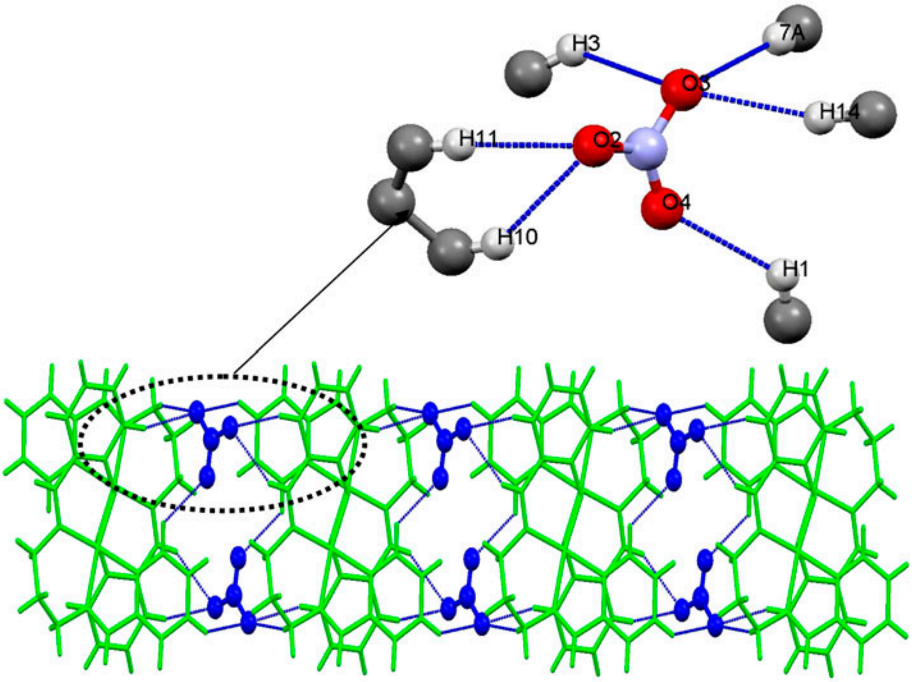

Figure 1. Complex **1**. View of the crystal lattice along the *a* axis showing heterosynthon (inset), constituted with six C–H···$O_{nitrate}$ hydrogen bonds. Note the formation of a 1-D supramolecular chain.

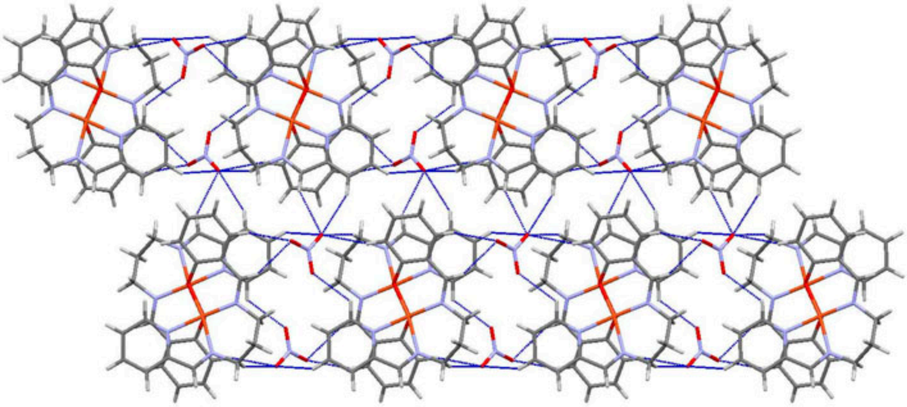

Figure 2. Complex **1**. View of 2-D H-bonded metallo-supramolecular network. Nitrates are bound to the cations around the 2_1 screw axis.

bonding distance is 3.437 Å; consequently, the metal in the dimer has square pyramidal geometry.

The nitrates are at a crystallographic inversion center and are responsible for charge neutrality. Oxygen of nitrate with the peripheral C–H forms a heterosynthon of seven C–H···$O_{nitrate}$ hydrogen bonds (figure 3). The cationic units are assembled by C–H···$O_{nitrate}$ synthons

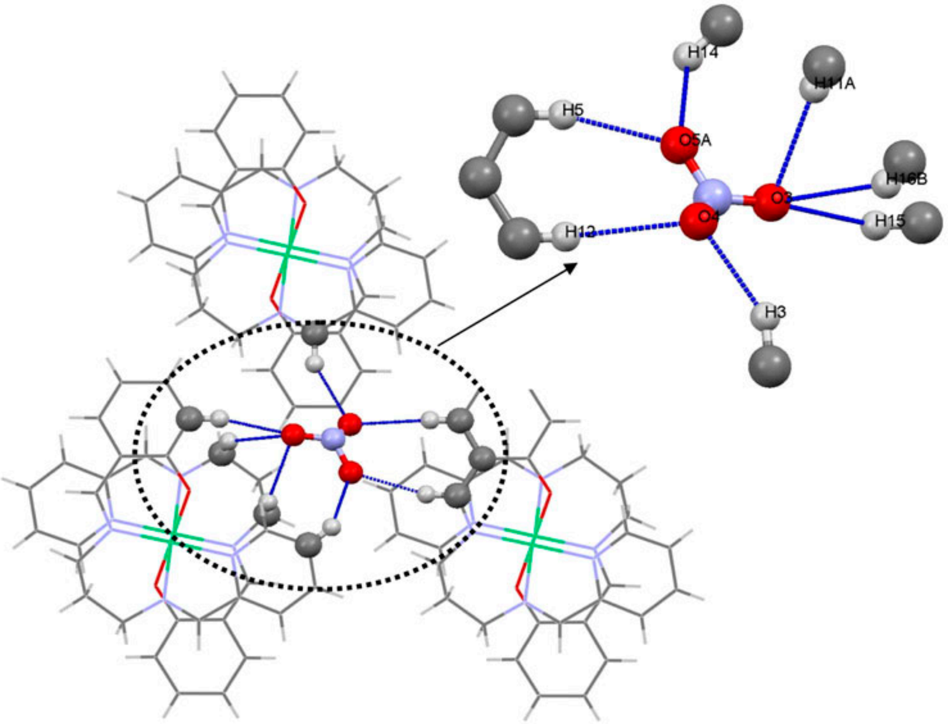

Figure 3. View of the crystal lattice showing seven C–H···O$_{nitrate}$ heterosynthons (inset) in **2**.

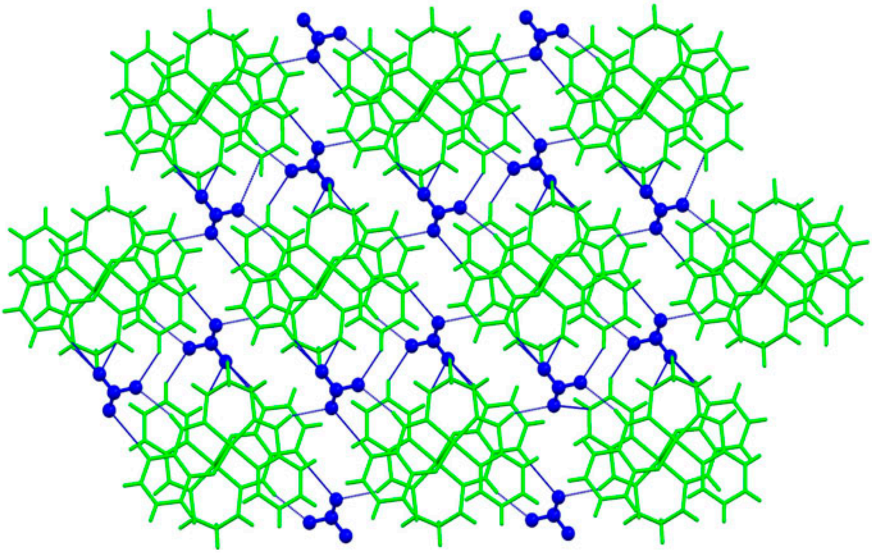

Figure 4. View of 2-D H-bonded metallo-supramolecular network in **2**. Nitrates are bound to the cations (one oxygen of nitrate is disordered and has been deleted for clarity).

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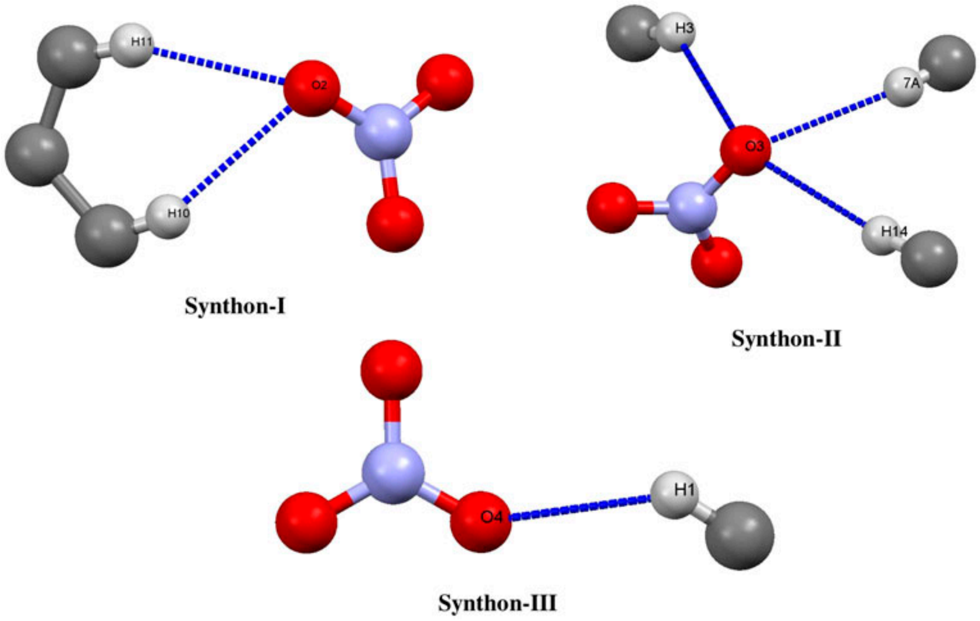
resulting in a 2-D H-bonded metallo-supramolecular network (figure 4). The synthon-**I** in **2** is a cyclic dimer; these cyclic dimers are themselves connected with C–H···O_{nitrate} hydrogen bonds of 2.433 and 2.709 Å. The geometrical parameters of C–H···O_{nitrate} hydrogen bonds in **1** and **2** are listed in table 2.

In crystal packing of **1** and **2**, nitrates play an important role in complementing the non-covalent binding forces in stabilization. The propagation of the low-dimensional structure to a 2-D framework is basically due to robust hydrogen bonding interactions involving a variety of supramolecular synthons (figures 5, and 6) emanating through the molecular recognition of lattice nitrates.

Table 2. The geometrical H-bond parameters in **1** and **2** (Å) and (°).

1			
C–H(11)···O(2)	144.35	H(11)···O(2)	2.459
C–H(10)···O(2)	146.46	H(10)···O(2)	2.557
C–H(3)···O(3)	136.15	H(3)···O(3)	2.587
C–H(7A)···O(3)	157.18	H(7A)···O(3)	2.543
C–H(14)···O(3)	160.61	H(14)···O(3)	2.527
C–H(1)···O(4)	127.74	H(1)···O(4)	2.539
2			
C–H(12)···O(4)	158.83	H(12)···O(4)	2.709
C–H(5)···O(5A)	163.05	H(5)···O(5A)	2.433
C–H(3)···O(4)	151.05	H(3)···O(4)	2.358
C–H(16B)···O(3)	139.36	H(16B)···O(3)	2.584
C–H(15)···O(3)	154.15	H(15)···O(3)	2.492
C–H(11A)···O(3)	136.64	H(11A)···O(3)	2.539
C–H(14)···O(5A)	133.40	H(14)···O(5A)	2.363



Synthon-I

Synthon-II

Synthon-III

Figure 5. Variety of C–H···O_{nitrate} heterosynthons in **1**.

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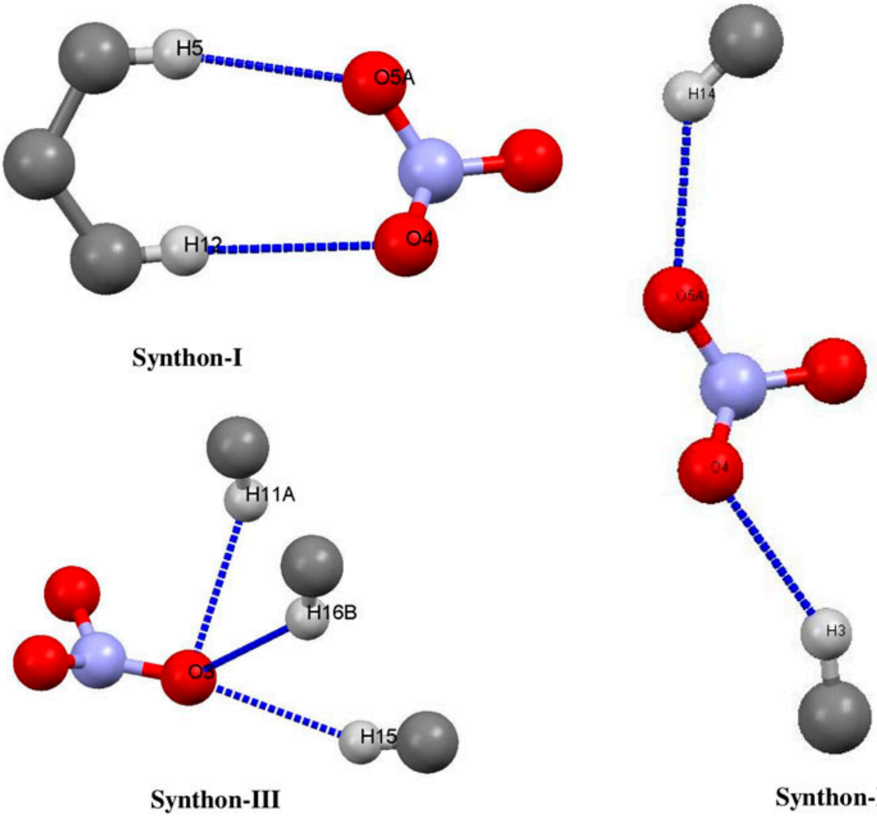

Synthon-I

Synthon-III

Synthon-II

Figure 6. Variety of C–H···$O_{nitrate}$ heterosynthons in **2**.

The interaction patterns in these two structures are an artifact of C–H···$O_{nitrate}$ hydrogen bonds. The crystal structure of **1** may therefore be described as a linear array of molecules held together by chelating synthon-**I** made with C–H···$O_{nitrate}$ hydrogen bonds in which nitrate receives hydrogen bonds from two equivalent peripheral C–H groups leading to a catemer motif and is believed to have an important role in the extensive hydrogen bonding [figure 7(a)]. The cyclic dimers synthon-**I** in **2** are linked to one another through formation of C–H···O hydrogen bonds between the lattice nitrate and peripheral C–H [figure 7(b)]. Although nitrates in the reported complexes have both inversion and twofold symmetry, the resulting architectures are almost equienergetic and, in principle, both patterns are reasonable possibilities in **1** and **2**.

Although similar reaction conditions were used for the preparation of **1** and **2**, with the same Schiff base, and both structures have nitrate as a structure directing agent, the complexes have unique structural features. In **1** the lattice nitrates are on the 2_1 screw axes while in **2** they are at crystallographic inversion centers. Both exploit the in-built peripheral hydrogen bonding of the cationic metal Schiff-base complexes. The anionic layer of nitrate anions in both complexes not only is a template controlling the formation of the layered network but also influences the interlayer separation and packing.

The representative structural unit in **1** and **2** is C–H···O_{nitro} heterosynthon, acting as non-covalent building blocks in molecular assembly and packing of metal-organic

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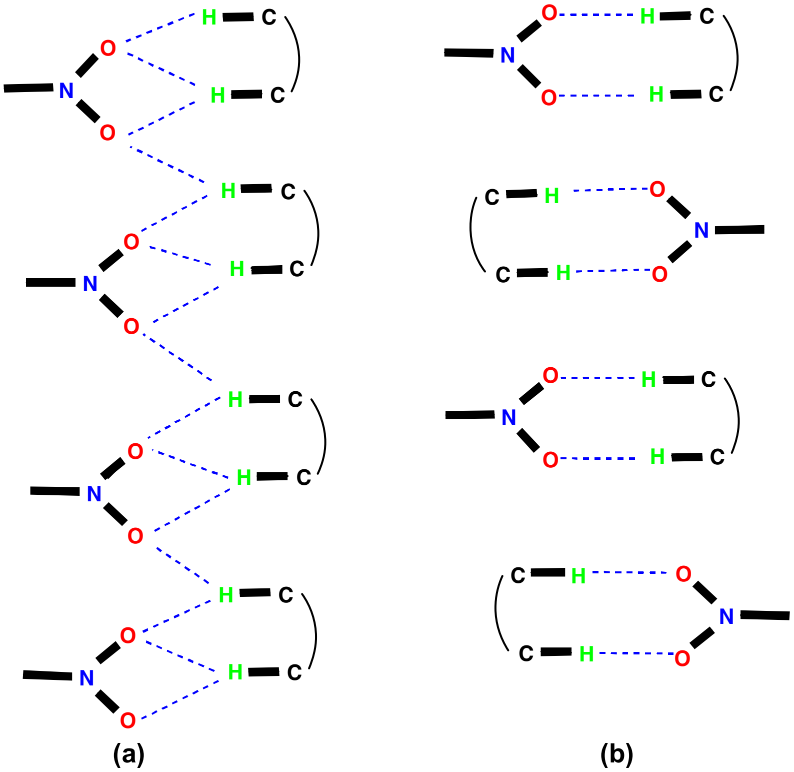

Figure 7. Schematic representation (a) chelated C–H···O hydrogen bonding synthon-**I** forming catemer; (b) cyclic C–H···O hydrogen bonded dimer synthon-**I**.

supramolecular structure. In **1**, one of the nitrate oxygens is bonded with two different hydrogens [chelated hydrogen bond] while one C–H hydrogen is bonded with two different nitrates, confirming that donors as well as acceptor are bifurcated; this trend is found throughout the crystal structure. The important synthon in **1** is the chelated hydrogen bonding synthon-**I** (figure 5) of one nitrate oxygen with C–H hydrogens from two groups while in **2** it is a cyclic C–H···O hydrogen bonded dimer synthon-**I** (figure 6). In effect, the interactions are the same but the dimensionality of the synthons is different. This means the crystal energies may be similar and this could be a possible rationale for obtaining different structures in the Cu and Ni cases.

Both structures are an outcome of anionic–neutral type of non-covalent interactions. Since, H-bonded molecular assemblies comprising oppositely charged donor and acceptor have enhanced electrostatic character, the hydrogen bonds in such assemblies are stronger (10-20 $\mathrm{kcal\,mol^{-1}}$) than those present in assemblies of neutral components [16]. In the networks of **1** and **2**, hydrogen bonding between nitrates in the crystal lattice and peripheral tectons (C–H) is of ionic-neutral type. In both the structures, hydrogen bonds work cooperatively with covalent interactions and are capable of "maneuvering" complex ions into desirable motifs.

This study reflects the role of these synthons in mutual recognition of nitrates and peripheral C–H groups in molecular metal-organic crystals through formation of a cyclic

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C–H···O hydrogen bonded dimer synthon-**I** and chelated hydrogen bonding synthon-**I** (figure 7), and is the main driving force in crystal packing of the reported metallo-supramolecular network (**1** and **2**). These circumstances indicate that weak hydrogen bonds, especially C–H···O hydrogen bond, is an important interaction in metal-organic crystals.

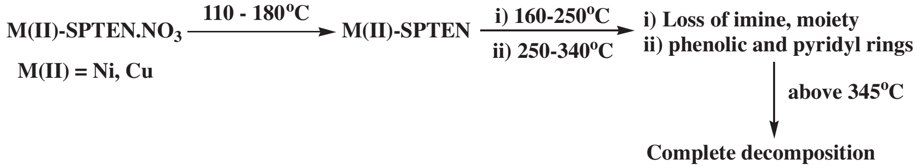
3.2. *Thermogravimetric analysis*

The hydrogen bonded structures of **1** and **2** are largely a consequence of interactions among the cationic [M^{2+}(2,2′-[propane,1,3-diylbis(nitrilomethyldyne)pyridyl, phenolate])$]^+$ building block (M^{2+} = Ni, Cu) and non-coordinated nitrates. The TGA curve for both compounds is nearly the same (scheme 2). Compound **1** and **2** of this study was analyzed by thermogravimetric analysis (TGA) under 20 mL min^{-1} of flowing nitrogen, while ramping the temperature at a rate of 10 °C min^{-1} from 30 to 615 °C. This association is quite strong as thermal gravimetric analysis (Supplementary material) for both and shows that the compound begins to lose weight between 110 and 360 °C. The removal of all nitrates takes place between 110 and 180 °C. The decomposition of imine takes place between 160 and 250 °C. Losses of pyridyl and phenolic rings occur between 250 and 340 °C. The complete decomposition of the compound takes place above 345 °C.

3.3. *IR spectroscopy*

Elemental analysis indicates that the complexes of SPETN with nickel and copper can be formulated as (ML)NO_3. The disappearance of the –OH band of the free ligand in the IR of metal complexes indicates that –OH is deprotonated and coordinated the metal. The C=N stretch shifts to low frequency upon coordination. These IR results indicate that the ligand is coordinated to nickel and copper via –N and –O. New IR bands at 420–430 cm^{-1} and 541–560 cm^{-1} are assigned to ν(Cu–O) and ν(Cu–N), respectively (Supplementary material). IR spectra of **1** and **2** in KBr and Nujol clearly point out the frequencies of free nitrate, νNi(1)–O and νNi–N bonds (Supplementary material). The νNi–O wagging frequency (637 cm^{-1}) for coordinated phenolic oxygen of this complex is higher than stretching (456 cm^{-1}) and rocking (443 cm^{-1}) frequencies. The stretching frequencies at 825 and 1384 cm^{-1} are for non-coordinated nitrate [17]. Frequencies at 191–290 cm^{-1} correspond to νNi–N.

The C=N stretch shifts from 1639 cm^{-1} in ligand to 1606 cm^{-1} in complex, confirming coordination via pyridyl nitrogen. νC=C$_{\mathrm{str}}$ at 1650–1450 cm^{-1}, νC–H$_{\mathrm{def}}$ at 900–700 cm^{-1} and νC–H$_{\mathrm{str}}$ at 3080 cm^{-1} correspond to the aromatic ring. The νC–H$_{\mathrm{str}}$ of aromatic ring got superimposed due to moisture.



Scheme 2. Schematic representation of TG-analysis of **1** and **2**.

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4. Conclusions

The present study exploits the peripheral hydrogen bonding groups for weak non-covalent interaction with nitrate forming an overall 2-D metallo-supramolecular network with $C–H\cdots O_{nitrate}$ as molecular junctions controlling the crystal packing. The molecular architecture of both the complexes evolves from two fundamental factors: (i) the peripheral hydrogen binding sites in metal complexes and (ii) the kind of counter anion. This study adds to the field of H-bonded framework materials formed by using metal complexes as secondary building block (tectons) via anion assisted supramolecular synthons. I anticipate expanded endeavors to fabricate and characterize systems with similar interactions that may extend a supramolecular synthon approach from molecular organic to metal-organic crystal engineering.

Supporting information available

X-ray crystallographic files in CIF format for the structures reported in this paper have been deposited to the Cambridge Crystallographic Data Center, CCDC Numbers 872208 (**1**) and 872209 (**2**). Copies of this information may be obtained free of charge form the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: C44 1223 336033; Email: deposit@ccdc.cam.ac.uk; Web: http://www.ccdc.cam.ac.uk/deposit].

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