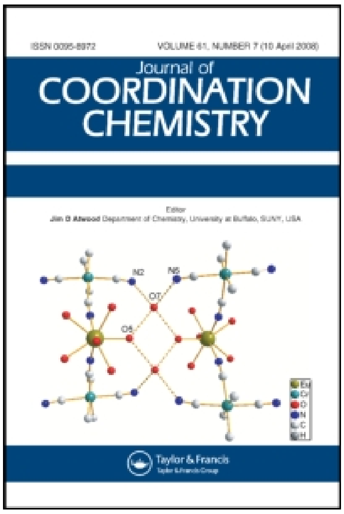

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Syntheses, weak interactions, and 3-D network structures of two salts based on $[Ni(i\text{-}mnt)_2]^{2-}$ (i-mnt^{2-}=iso-maleonitriled-ithiolate) anion with substituted pyridinium cation

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Syntheses, weak interactions, and 3-D network structures of two salts based on $[Ni(i\text{-}mnt)_2]^{2-}$ ($i\text{-}mnt^{2-}$ = iso-maleonitriledithiolate) anion with substituted pyridinium cation

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Two new salts, $[2\text{-NaMePy}]_2[Ni(i\text{-mnt})_2]$ (**1**) and $[2\text{-NaMe-4-MePy}]_2[Ni(i\text{-mnt})_2]$ (**2**) ($[2\text{-NaMePy}]^+$ = 1-(2′-naphthylmethyl)pyridinium, $[2\text{-NaMe-4-MePy}]^+$ = 1-(2′-naphthylmethyl)-4-methylpyridinium and $i\text{-mnt}^{2-}$ = iso-maleonitriledithiolate), have been prepared and characterized by elemental analyses, UV, IR, molar conductivity, and single crystal X-ray diffraction. The anions in **1** form a 1-D chain through short $C \cdots N$ interactions between the anions, while the cations in **2** stack a 1-D column *via* $C\text{–}H \cdots \pi$ and $\pi \cdots \pi$ stacking interactions between the cations. The effect of weak intramolecular interactions such as $C\text{–}H \cdots N$, $C\text{–}H \cdots S$, $C\text{–}H \cdots Ni$ hydrogen bonds, and $\pi \cdots \pi$ stacking interactions between the cations and the anions further generate a 3-D network structure. The change of the molecular topology of the countercation when the 4-substituted group in the pyridine ring is changed from H atom to CH_3 group results in different crystal system, space group, and the stacking mode of the cations and anions of **1** and **2**.

Keywords: Substituted pyridinium; *Bis*(iso-maleonitriledithiolate)nickel anion; Syntheses; Weak interactions; 3-D network structures

1. Introduction

Transition metal complexes of 1,2-dithiolenes are of interest in materials science owing to their application as building blocks in molecular-based materials showing magnetic, superconducting, and optical properties [1–7]. A number of maleonitriledithiolate (mnt) complexes have been investigated to prepare advanced molecular solids [8–12]. Introduction of inorganic or organic cations as counterions of $[M(mnt)_2]^-$ (where M is

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Ni(III), Pd(III), or Pt(III) ion) tunes the stacking pattern of the $[M(mnt)_2]^-$ anions giving molecular materials with unusual magnetic properties [13–17]. However, little attention has been paid to the construction of $M(i\text{-}mnt)^{n-}$ (i-mnt = iso-maleonitriledithiolate) with organic cations, as exemplified by $[(n\text{-}C_4N_9)_4N]_2[Ni(i\text{-}mnt)_2$ [18], $[BzDMAP]_2[Ni(i\text{-}mnt)_2]$ (BzDMAP = benzyl-4-dimethylaminopyridinium) [19], and $[Bz\text{-}2\text{-}NH_2Py]_2[Ni(i\text{-}mnt)_2]$ ($Bz\text{-}2\text{-}NH_2Py$ = benzyl-2-aminopyridinium) [20]. In continuing research on the effect of organic cations on the structure and properties of $M(i\text{-}mnt)^{n-}$ complexes, we have prepared two new salts, $[2\text{-}NaMePy]_2[Ni(i\text{-}mnt)_2]$ (**1**) and $[2\text{-}NaMe\text{-}4\text{-}MePy]_2[Ni(i\text{-}mnt)_2]$ (**2**) ($[2\text{-}NaMePy]^+$ = 1-(2′-naphthylmethyl)pyridinium, $[2\text{-}NaMe\text{-}4\text{-}MePy]^+$ = 1-(2′-naphthylmethyl)-4-methylpyridinium, and $i\text{-}mnt^{2-}$ = iso-maleonitriledithiolate). Weak interactions such as $C–H\cdots N$, $C–H\cdots S$, $C–H\cdots\pi$, $C–H\cdots Ni$ hydrogen bonds, $\pi\cdots\pi$ stacking interactions and UV, IR, molar conductance, and crystal structures have been investigated.

2. Experimental

2.1. *Materials and methods*

All reagents used in the syntheses were of analytical grade. The starting materials 1-(2′-naphthalenayl)pyridinium bromide ([2-NaMePy]Br), 1-(2′-naphthalenayl)-4-methylpyridinium bromide ([2-NaMe-4-MePy]Br), and potassium iso-maleonitriledithiolate ($K_2(i\text{-}mnt)\cdot H_2O$) were synthesized following literature procedures [18, 21]. Elemental analyses were run on a Model 240 Perkin–Elmer C, H, and N instrument. IR spectra were recorded on a Nicolet Avatar 360 FT-IR ($400–4000\,cm^{-1}$ region) spectrophotometer in KBr pellets. Electronic spectra were recorded on a SHIMADZU UV-4000 spectrophotometer. All solution concentrations were *ca* $10^{-5}\,mol\,L^{-3}$ in CH_3CN. Molar conductivity was measured on a DDS-11A conductivity instrument using a platinum electrode.

2.2. *Synthesis of $[2\text{-}NaMePy]_2[Ni(i\text{-}mnt)_2]$ (1) and $[2\text{-}NaMe\text{-}4\text{-}MePy]_2[Ni(i\text{-}mnt)_2]$ (2)*

The salt **1** was prepared by direct combination of $NiCl_2\cdot 6H_2O$, $K_2(i\text{-}mnt)\cdot H_2O$ and [2-NaMePy]Br in 1 : 2 : 2 molar ratio. The green precipitate that formed was filtered off, washed with water, and dried under vacuum. Yield: 88%. Anal. Calcd for $C_{40}H_{28}NiN_6S_4$: C, 61.58; H, 3.69; N, 10.71%. Found: C, 61.62; H, 3.62; N, 10.78%. IR spectrum (cm^{-1}): 3116(w), 3041(w), 2941(w), 2205(s), 1626(m), 1481(m), 1425(s), 1153(m), 1049(w), 890(m), 805(m), 756(m), 680(m), and 477(m).

The procedure for **2** is similar to that for **1**. Yield: 87%. Anal. Calcd for $C_{42}H_{32}NiN_6S_4$: C, 62.42; H, 4.03; N, 10.36%. Found: C, 62.46; H, 3.99; N, 10.40%. IR spectrum (cm^{-1}): 3078(w), 2979(w), 2912(w), 2200(s), 1640(s), 1568(m), 1509(m), 1468(m), 1399(s), 1377(m), 1205(w), 1091(m), 936(m), 890(m), 853(m), 771(m), 752(m), 694(w), 609(m), 534(m), 482(m), and 474(m).

The brown single crystals suitable for X-ray structure analysis were obtained by evaporating solutions of **1** and **2** in mixed MeCN and *i*-PrOH (v/v = 1 : 2).

Table 1. Crystallographic data for **1** and **2**.

Salt	**1**	**2**
Temperature (K)	293(2)	293(2)
Empirical formula	$C_{40}H_{28}NiN_6S_4$	$C_{42}H_{32}NiN_6S_4$
Formula weight	779.65	807.71
λ (Å)	0.71073	0.71073
Space group	$C2/c$	$P\bar{1}$
Crystal system	Monoclinic	Triclinic
Unit cell dimensions (Å, °)		
a	19.617(4)	10.1271(7)
b	10.9158(15)	10.6782(7)
c	19.780(3)	11.1814(7)
α	90	71.161(1)
β	117.626(7)	65.243(1)
γ	90	62.357(1)
Volume (Å^3)	3752.7(11)	960.17(11)
Z	4	1
D_{Calcd} (g cm^{-3})	1.38	1.397
μ (Mo-Kα) (mm^{-1})	0.777	0.762
θ range (°) for data collection	2.2–25.0	2.0–25.0
Observed data [$I > 2\sigma(I)$]	2373	2551
Reflections collected	9368	5809
Independent reflections	3301	3333
$R_{(\mathrm{int})}$	0.031	0.027
Goodness-of-fit on F^2	1.07	1.007
R_1	0.0376, 0.0577	0.0287, 0.0346
wR_2	0.1007, 0.1103	0.0847, 0.0865
Largest different peak and hole (e Å^{-3})	0.40 and −0.21	0.24 and −0.13

2.3. *Determination of crystal structure*

Crystallographic data for **1** and **2** were collected using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) by $\phi - \omega$ scan mode on a Smart APEX CCD area detector. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares, employing Bruker's SHELXTL [22]. All non-hydrogen atoms were refined with anisotropic thermal parameters. All H atoms were placed in calculated positions, assigned fixed isotropic displacement parameters 1.2 times the equivalent isotropic U value of the attached atom, and allowed to ride on their respective parent atoms. Crystal data are summarized in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Crystal structures*

A perspective view of the molecular structure of **1**, which crystallizes in the monoclinic space group $C2/c$, is shown in figure 1. The nickel(II) of $[\mathrm{Ni(i\text{-}mnt)_2}]^{2-}$ anion is situated at a center of symmetry of a square planar complex in which two $[\mathrm{2\text{-}NaMePy}]^+$ ions are related to each other by the symmetry center. The terminal N atom of CN groups are tipped out of the coordination plane with deviations from the plane being 0.1101 Å for N(1) and −0.4004 Å for N(2). The S–Ni–S bond angle within the five-membered ring is

Table 2. Selected bond lengths, bond angles, and dihedral angles for **1** and **2**.

Salts (Å, °)	**1**	**2**
Ni(1)–S(1)	2.1916(10)	2.2024(8)
Ni1)–S(2)	2.2132(9)	2.2049(7)
S(1)–C(1)	1.717(2)	1.728(2)
S(2)–C(1)	1.722(3)	1.728(2)
N(1)–C(3)	1.135(5)	1.144(4)
N(2)–C(4)	1.138(5)	1.141(4)
N(3)–C(15)	1.488(4)	1.503(3)
N(3)–C(16)	1.322(4)	1.327(4)
N(3)–C(20)	1.329(5)	1.339(3)
C(1)–C(2)	1.368(4)	1.364(3)
C(2)–C(3)	1.426(5)	1.425(4)
C(2)–C(4)	1.426(4)	1.426(4)
S(1)–Ni(1)–S(2)	78.62(3)	78.96(3)
S(1)–Ni(1)–S(2)#1	101.38(3)	101.04(3)
S(1)–C(1)–S(2)	108.50(17)	108.34(11)
S(1)–C(1)–C(2)	124.2(2)	125.8(2)
S(2)–C(1)–C(2)	127.3(2)	125.8(2)
C(1)–C(2)–C(3)	120.9(3)	121.1(2)
C(1)–C(2)–C(4)	121.9(3)	120.5(3)
C(3)–C(2)–C(4)	117.1(3)	118.4(2)
N(1)–C(3)–C(2)	178.8(3)	178.2(2)
N(2)–C(4)–C(2)	178.0(4)	177.0(3)
N(3)–C(15)–C(14)	111.5(2)	111.9(2)
N(3)–C(16)–C(17)	120.2(4)	120.6(3)
C_{Ar}–CH_2–N_{Py} and $\Phi_{Ar}(\theta_1)$	63.7	109.8
C_{Ar}–CH_2–N_{Py} and $\Phi_{Py}(\theta_2)$	60.5	145.1
Φ_{Ar} and $\Phi_{Py}(\theta_3)$	94.8	86.1

Symmetry transformations used to generate equivalent atoms: $\#1 = -x+1, -y+1, -z$.

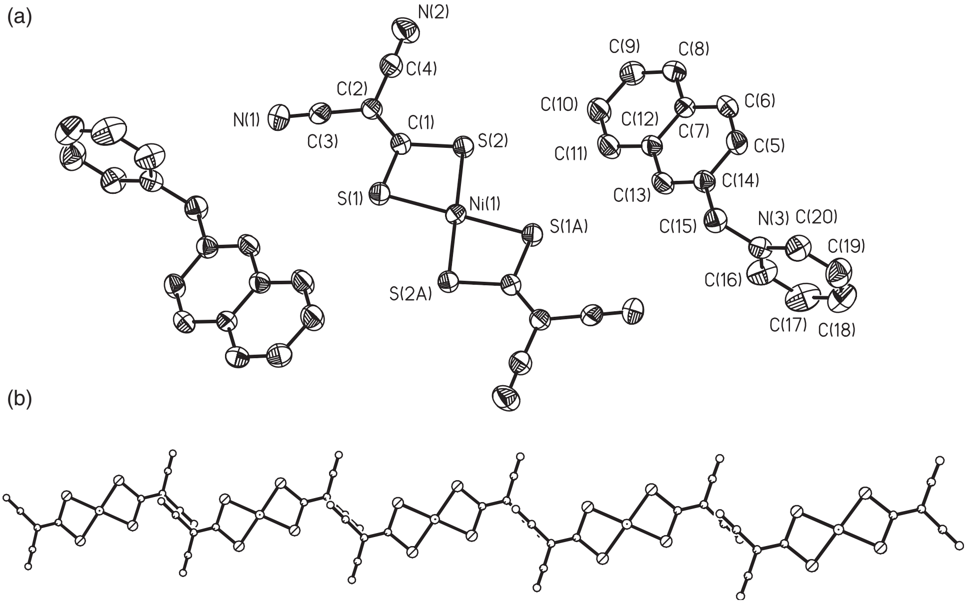

Figure 1. (a) ORTEP plot (30% probability ellipsoids) showing the molecule structure of **1**. (b) The 1-D chain of the anions through short C···N interactions.

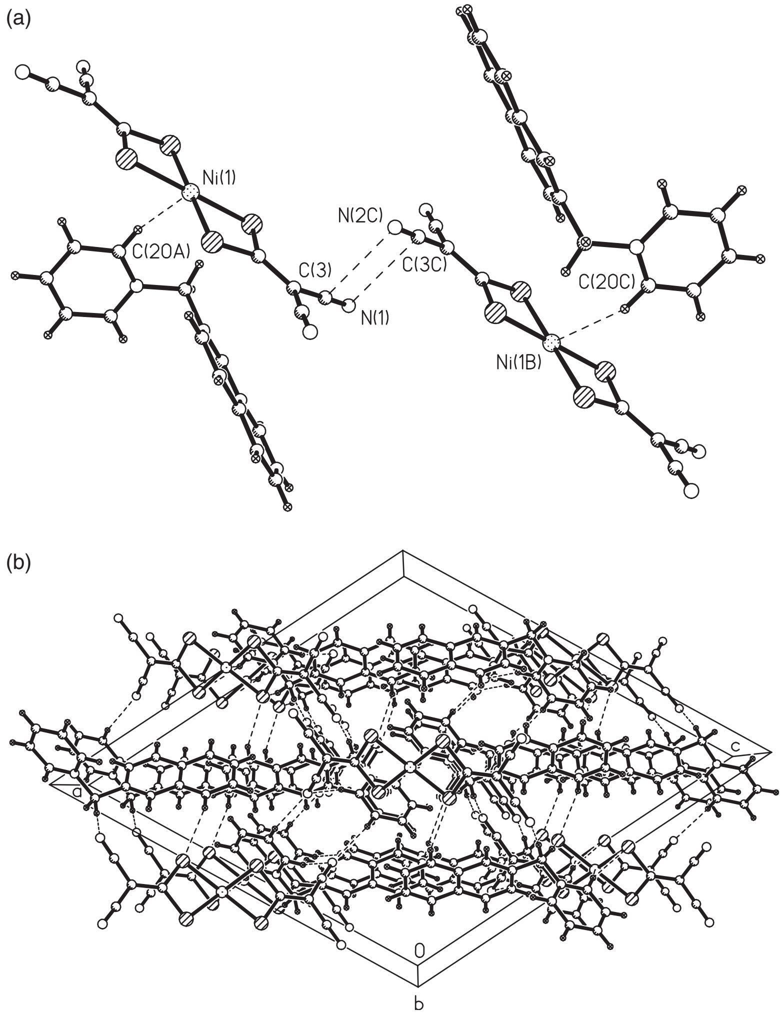

Figure 2. (a) Weak C $\cdots$ N stacking interaction between the anions and C–H $\cdots$ Ni hydrogen bond between cation and anion for **1**. (b) The packing diagram for **1** as viewed along the *b*-axis.

78.62(3)° and the average Ni–S bond distance is 2.2024 Å (table 2); these values are in agreement with those of previously reported $[Ni(i\text{-}mnt)_2]^{2-}$ salts [18–20]. The $[2\text{-}NaMePy]^{+}$ cation adopts a conformation in which the naphthyl ring and pyridine ring are twisted to the C(14)–C(15)–N(3) reference plane with dihedral angles of 63.7°(θ_1) and 60.5°(θ_2), respectively. In addition, the naphthyl ring and the pyridine ring make a dihedral angle of 94.8°(θ_3). The $[Ni(i\text{-}mnt)_2]^{2-}$ anions form a 1-D chain [figure 1(b)] through short C(2) $\cdots$ N(1^{i}) interaction between CN groups of the anions with a C $\cdots$ N distance of 3.539 Å (symmetry code (i): $x-1/2$, $y+1/2$, z) [figure 2(a)]. Complicated weak interactions between the anions and the cations further generate a 3-D network structure [figure 2(b)]: C–H $\cdots$ Ni hydrogen bond between the anion and cation with distance of 3.796 Å between C(20) and Ni(1^{ii}) (symmetry code (ii): $-x-1$, y, $-z+1/2$) [figure 2(a)]; two C–H $\cdots$ N hydrogen bonds, and three C–H $\cdots$ S hydrogen bonds (table 3). Although regular weak hydrogen bonding is very common, weak hydrogen bonding with Ni is rare but not unprecedented [20, 23, 24], which is similar to the C–H $\cdots$ Cu observed in the literature [25, 26].

To understand how the countercation affects the molecule structure and the packing pattern of the $[Ni(i\text{-}mnt)_2]^{2-}$ anion, $[2\text{-}NaMe\text{-}4\text{-}MePy]_2[Ni(i\text{-}mnt)_2]$ (**2**) is prepared by utilizing the starting material [2-NaMe-4-MePy]Br instead of [2-NaMePy]Br. As shown in figure 3(a), although the coordination geometry for the $Ni(i\text{-}mnt)_2]^{2-}$ anion and the $[2\text{-}NaMe\text{-}4\text{-}MePy]^+$ cation of **2** are essentially identical to those described above for **1**, the dihedral angles θ_1, θ_2, and θ_3 are 109.8°, 145.1°, and 86.1° for $[2\text{-}NaMe\text{-}4\text{-}MePy]^+$, respectively, markedly different from those in **1**. The deviation of C(21) from the pyridine ring is 0.0042 Å. The cations stack into a 1-D column [figure 3(b)] by two interactions: (1) the C–H $\cdots\pi$ interactions between C(21) and the naphthyl rings with a distance of 3.514 Å between C(21) and the center of the C(7)C(8)C(9)C(10)C(11)C(12)

Table 3. Intermolecular hydrogen bonds for **1**.

D–H $\cdots$ A	d(D $\cdots$ H)	d(H $\cdots$ A)	d(D $\cdots$ A)	∠(DHA)
C(11)–H(11) $\cdots$ S(1)#1	0.93	2.78	3.630(3)	152.0
C(15)–H(15B) $\cdots$ N(1)#1	0.97	2.46	3.400(5)	162.0
C(16)–H(16) $\cdots$ N(2)#2	0.93	2.50	3.294(5)	144.0
C(17)–H(17) $\cdots$ N(2)#3	0.93	2.51	3.382(5)	156.0
C(19)–H(19) $\cdots$ N(1)#4	0.93	2.62	3.411(6)	143.0
C(20)–H(20) $\cdots$ S(2)#5	0.93	2.76	3.649(4)	160.0

Symmetry transformations used to generate equivalent atoms: $\#1 = -x+1, -y+1, -z$; $\#2 = x+1/2, y+1/2, z$; $\#3 = -x+3/2, y+1/2, -z+1/2$; $\#5 = x+1, y, z$; $\#4 = -x+3/2, -y+1/2, -z$.

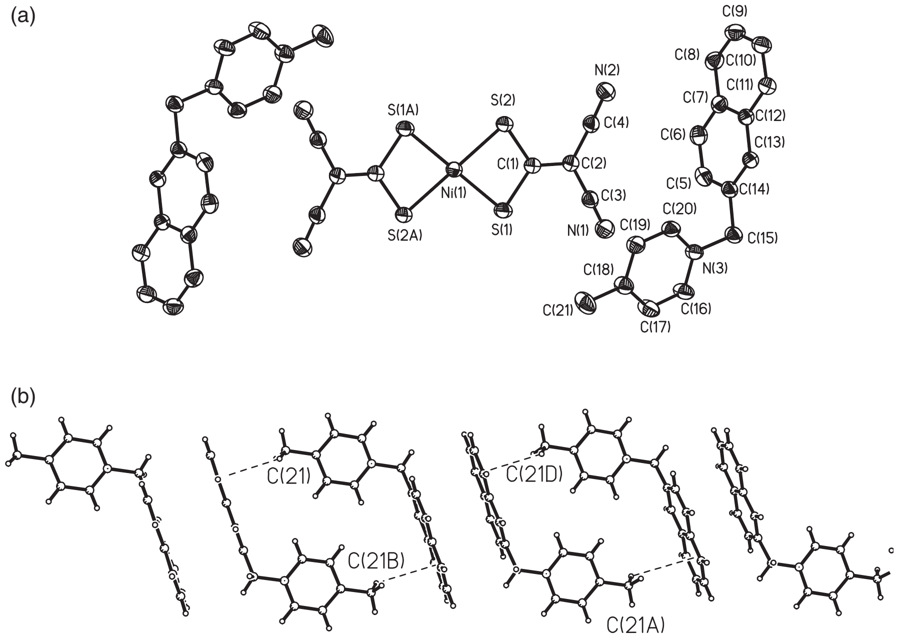

Figure 3. (a) ORTEP plot showing the structure of **2**. (b) The 1-D column of the cations through C–H $\cdots\pi$ and $\pi\cdots\pi$ interaction between the cations of **2**.

ring; (2) the $\pi \cdots \pi$ stacking interactions between the naphthyl rings with a distance of 3.458 Å. Three weak intermolecular interactions are observed between the cations and anions of **2** [figure 4(a)]. One is a C(16)–H(16) $\cdots$ N(2) hydrogen bond, with a C(16) $\cdots$ N(2^{iii}) distance of 3.258 Å (symmetry code (iii): $x-1$, y, z). Another is $\pi \cdots \pi$ stacking interaction between the CN group and pyridine ring, with a distance between N(1) of CN group and the centroid of pyridine of 3.472 Å. The third is a C–H $\cdots$ Ni hydrogen bond, with a C(13) $\cdots$ Ni(1^{iv}) distance of 3.690 Å (symmetry code (iv): $-x+2$, $-y+1$, $-z+1$). The corresponding distances and angles of H-bonding contacts are summarized in table 4. These interactions in the crystal structure generate a 3-D network [figure 4(b)].

Derivatives of benzylpyridinium (abbreviated as $[\mathrm{RBzPy}]^{+}$) serve as flexible cations which can be adjusted *via* modifying the nature of the groups on the aromatic rings; the molecular configuration is determined by three dihedral angles (θ_1, θ_2, and θ_3) [27]. The stacking pattern of the salts based on $[\mathrm{Ni(i\text{-}mnt)_2}]^{2-}$ depends strongly upon the molecular topology of the countercation. With methyl in the 4-position of the pyridine

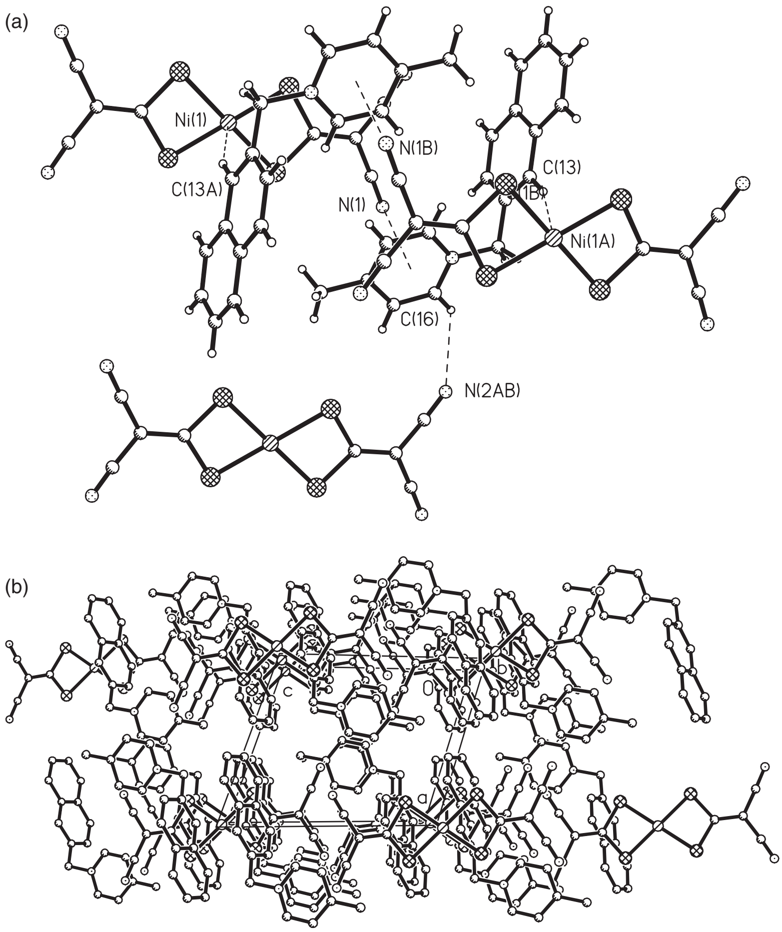

Figure 4. (a) The $\pi \cdots \pi$ stacking interaction and C–H $\cdots$ N, C–H $\cdots$ Ni hydrogen bonds between cations and anions for **2**. (b) The packing diagram for **2** as viewed along the *b*-axis.

Table 4. Intermolecular hydrogen bonds for **2**.

D–H$\cdots$A	d(D$\cdots$H)	d(H$\cdots$A)	d(D$\cdots$A)	∠(DHA)
C(16)–H(16)$\cdots$N(2)#1	0.93	2.62	3.258(4)	127.0
C(13)–H(13)$\cdots$Ni(1)#2	0.93	2.805	3.690(2)	159.6
C(21)–H(21)$\cdots\pi$ (C7–C12 ring)#3	0.96	3.009	3.514(2)	114.2

Symmetry transformations used to generate equivalent atoms: #1 = $x-1$, y, z; #2 = $-x+2$, $-y+1$, $-z+1$; #3 = $-x+2$, $-y+1$, $-z+1$.

ring of the cation, the dihedral angles θ_1, θ_2, and θ_3 change markedly (table 2). By comparing the structures of **1** and **2** with the 4-substituted group in the pyridine ring changed from H to CH_3, the crystal system, space group, and the stacking mode of the cations and anions are different. In addition, C–H$\cdots$N, C–H$\cdots$S, C–H$\cdots$Ni C–H$\cdots\pi$ hydrogen bonds, C$\cdots$N short interactions, and $\pi\cdots\pi$ stacking interactions play important roles in the molecular stacking and stabilization of **1** and **2**.

3.2. *Infrared spectra*

The infrared spectra of **1** and **2** are consistent with the structural data presented above. Bands at 3116, 3041, 2941 cm^{-1} for **1** and 3078, 2979, 2912 cm^{-1} for **2** are due to C–H stretches in the aromatic rings and the methylene. The CN stretching bands lie at 2205 cm^{-1} for **1** and 2210 cm^{-1} for **2**. Bands at 1626 cm^{-1} for **1** and 1640, 1568, and 1509 cm^{-1} for **2** are attributable to ν(C=N), ν(C=C) stretching bands for the pyridine and naphthalene rings. The ν(C=C) of $[i\text{-}mnt]^{2-}$ is at 1481 cm^{-1} for **1** and 1468 cm^{-1} for **2**, similar to those of $[(n\text{-}C_4N_9)_4N]_2[Ni(i\text{-}mnt)_2]$ [18].

3.3. *UV–Vis spectra and molar conductivities*

The UV–Vis absorption spectra of **1** and **2** in CH_3CN from 200 to 900 nm are attributed to nickel portions of these compounds. Bands of **1** at 225, 250, 287, 344, 452 nm and at 225, 249, 286, 343, 498 nm for **2** are assigned as $L(\pi)\rightarrow M$, $L(\sigma)\rightarrow M$, $L(\sigma)\rightarrow M$, $L\rightarrow L^*$ and $M\rightarrow L$, respectively, similar to those of $[(n\text{-}C_4N_9)_4N]_2[Ni(i\text{-}mnt)_2]$ [18]. Molar conductivities of **1** and **2** at $10^{-3}\,mol\,L^{-3}$ in CH_3CN are 264.4 and 251.1 $S\,cm^2\,mol^{-1}$, indicating 2 : 1 electrolytes [28].

4. Conclusion

Two new salts based on $[Ni(i\text{-}mnt)_2]^{2-}$, $[2\text{-}NaMePy]_2[Ni(i\text{-}mnt)_2]$ (**1**) and $[2\text{-}NaMe\text{-}4\text{-}MePy]_2[Ni(i\text{-}mnt)_2]$ (**2**) have been prepared and characterized. The anions in **1** form a 1-D chain through short C$\cdots$N interactions between the anions, while the cations in **2** stack a 1-D column *via* C–H$\cdots\pi$ and $\pi\cdots\pi$ stacking interactions between the cations. The effect of weak intramolecular interactions such as C–H$\cdots$N, C–H$\cdots$S, C–H$\cdots$Ni hydrogen bonds, and $\pi\cdots\pi$ stacking interactions between the cations and the anions further generate a 3-D network. The change of the molecular topology of the countercation when the 4-substituted group in the pyridine ring is changed from H to

CH_3 results in a different crystal system, space group, and stacking mode of the cations and anions of **1** and **2**.

Supplementary material

The detailed crystallographic data of **1** and **2** have been deposited at the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-695843 and No. CCDC-695844. Copies of the data may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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