Syntheses and Crystal Structures of Tetrakis(arylamidine)nickel(II) Chloride and Bis[2,4-dipyridyl-1,3,5-triazapentadienato]nickel(II)

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The reaction of $LiN(SiMe_3)_2$ with arylnitrile, followed by the addition of anhydrous $NiCl_2$ gives ionic complexes of the general formula $[Ni\{H_2NC(Ar)=NH\}_4]Cl_2$ (Ar = Ph **1**, *p*-tolyl **2**). When the above reaction is carried out with cyanopyridine instead of arylnitrile under the same reaction conditions, neutral complexes of the general formula $[\{HN=C(Py)N=C(Py)NH\}_2Ni]$ (Py = 4-pyridyl, **3**; 3-pyridyl, **4**] are obtained. Compound **1** undergoes a metathesis reaction with sodium benzoate to give the neutral complex $[(PhCO_2)_2Ni\{H_2NC(Ph)=NH\}_4]$ (**5**). Magnetic susceptibility measurements show that **1**–**4** are diamagnetic and that **5** is paramagnetic with two unpaired electrons. These results suggest that **1**–**4** are d^8 square-planar complexes and **5** is an octahedral complex. The solid state structures of compounds **1**–**5** were determined by X-ray crystallography. Structural analyses reveal that **1** and **2** form a one-dimensional network through charge-assisted hydrogen bonds; whereas **5** forms a one-dimensional network through hydrogen bonds only. In complexes **3** and **4**, the 2,4-dipyridyl-1,3,5-triazapentadienyl ligand behaves as a bidentate ligand forming a six-membered ring with the metal ion.

Introduction

Lithium amidinates, which can be readily generated in situ through the reaction of lithium amide with α-hydrogen-free nitriles RCN,[1] are very versatile reagents for organic and organometallic syntheses. They are the preferred bases for the formation of ketone enolates,[2] generating low steady-state concentrations of some relatively unstable carbanions,[3] and for the preparation of dithiadiazole heterocycles[4] and π-electron rich phosphorus-nitrogen hetero-donor ligands.[5] Amidinates possess a very diverse and rich coordination chemistry. As anionic ligands, they can behave as mono- and bidentate ligands when coordinated by a single metal atom, and as bridging bidentate ligands when coordinated by two metal atoms. Amidinates form coordination compounds with virtually every metal in the periodic table, ranging across the main group and transition metal series, and into the lanthanides.[6] There is a growing interest in the coordination of amidinate ligands by first-row transition metals, with the goal of creating new catalysts that have industrial use.[7] Usually these compounds were prepared by the reaction of the corresponding lithium amidinates, generated in situ, with metal halides. Metal complexes with bulky,[8] asymmetrical[9] or pendant substituents[10] on amidinato ligands, bridged amidinato ligands[11] or oxalic amidinato ligands[12] have also been synthesized. Recently, the coordination chemistry of related β-diketiminato ligands has also received increasing attention;[13] however, there are very few reports on the isoelectronic 1,3,5-triazapentadienato ligands. Herein we report on the reaction of anhydrous nickel(II) chloride with lithium *N*,*N*′-bis(trimethylsilyl)arylamidinate, $[(Me_3Si)N(Li)C(Ar)-N(SiMe_3)]$ (Ar = phenyl, tolyl, 4-pyridyl, 3-pyridyl), generated in situ from the reaction of $LiN(SiMe_3)_2$ with either benzonitrile, *p*-tolunitrile, 4-cyanopyridine or 3-cyanopyridine. Depending on the nature of the aryl group, the reactions gave either tetrakis(arylamidine)nickel(II) chloride $[Ni\{H_2NC(Ar)=NH\}_4]Cl_2$ (Ar = Ph 1, *p*-tolyl 2) or bis[2,4-dipyridyl-1,3,5-triazapentadienato]nickel(II) $[\{HN=C(Py)-N=C-(Py)NH\}_2Ni]$ (Py = 4-pyridyl, **3**; 3-pyridyl, **4**) complexes (Scheme 1). This is in contrast to the reaction of $NiCl_2{\cdot}0.3C_4H_{10}O_2$ and $[MCl_2(PhCN)_2]$ (M = Pd or Pt) with lithium *N*,*N*′-diphenylbenzamidinate, [PhN(Li)-C(Ph)NPh], which gave the dimeric and monomeric bis(amidinato) complexes, $[Ni_2\{PhNC(Ph)NPh\}_4]$[14a] and $[M\{PhNC(Ph)NPh\}_2]$ (M = Pd, Pt),[14a,14b] respectively, in the solid state.

Results and Discussion

Synthesis and Structural Characterization

Yellow crystals of tetrakis(arylamidine)nickel(II) chloride $[Ni\{H_2NC(Ar)=NH\}_4]Cl_2$ (Ar = Ph, **1**; *p*-tolyl, **2**) were obatined in good yields (67 and 76%, respectively) when $LiN(SiMe_3)_2$ was reacted with one equivalent of benzonitrile or tolunitrile in THF, followed by the addition of half an

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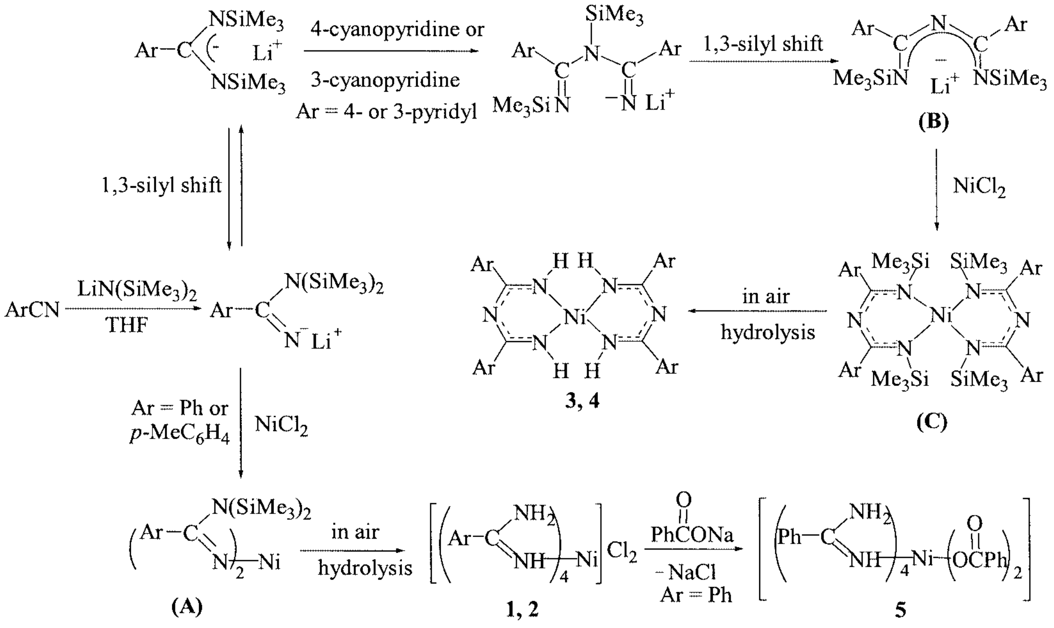

Scheme 1

equivalent of anhydrous nickel chloride and workup in air. However, when two equivalents of 4-cyanopyridine or 3-cyanopyridine were used instead of benzonitrile in the above reaction, yellow crystals of bis[2,4-dipyridyl-1,3,5-triazapentadienato]nickel(II) [{HN=C(Py)N=C(Py)NH}$_2$Ni] (Py = 4-pyridyl, **3**; 3-pyridyl, **4**), with 30 and 28% yields, respectively were obtained. Magnetic susceptibility measurements show that compounds **1−4** are all diamagnetic. This suggests that compounds **1−4** are d^8 square-planar Ni^{II} complexes. The solid state structures of these four compounds were determined by X-ray crystallography. Perspective drawings of compounds **1−4** are shown in Figure 1, 3, 5 and 6, respectively. Selected bond lengths and angles are given in Table 1.2

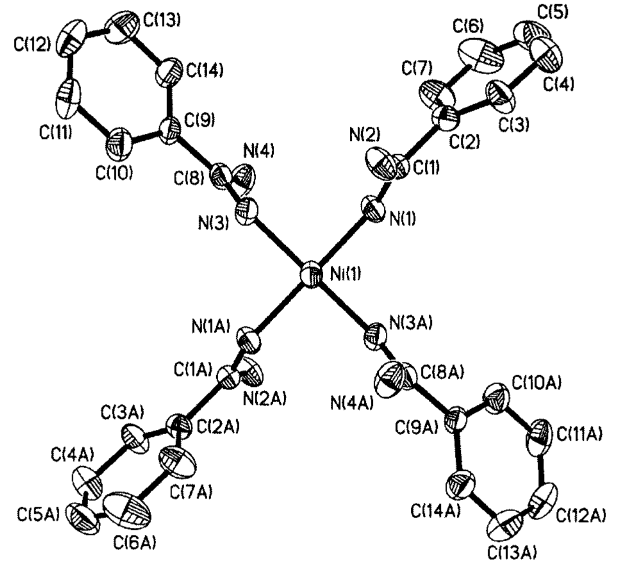

Figure 1. A perspective view of the cation of compound **1**; hydrogen atoms are omitted for clarity

The crystal structure of **1**, shown in Figure 1, reveals that the dication is centrosymmetric and that the nickel center has a square-planar geometry, the N(1)−Ni(1)−N(3) angle is 90.49(18)° and the Ni−N(coordinated) distances are 1.895(4) [Ni(1)−N(1)] and 1.885(4) Å [Ni(1)−N(3)]. The C(1)−N(1) [1.276(6) Å] and C(1)−N(2) [1.337(6) Å] distances of the N−C−N framework indicate that N(1) and N(2) are imino and amino nitrogens, respectively. The C(1)−N(2) distance, which is intermediate between a C−N single (1.47 Å) and double (1.30 Å) bond length, reflects some degree of delocalization within the N−C−N framework. The N(1)C(1)N(2) and N(3)C(8)N(4) planes form dihedral angles of 36.9 and 40.2° with the C(2)- and C(9)-phenyl planes, respectively. The distance between Ni(1B) and Cl(1A) is 3.271 Å, which is longer than the sum of the ionic radii of the Ni^{II} cation and chloride anion. This indicates that the Ni(1B) and Cl(1A) ions are held together by electrostatic attractive forces and that complex **1** is a d^8 square-planar complex. The fact that **1** is diamagnetic further supports this. The distance between Cl(1A) and N(2A) is 3.225 Å and is similar to that of the N···Cl distance of 3.332(5) Å between a NH group and a Cl$^-$ anion involved in H-bonding.[15] The distance between Cl(1A) and the hydrogen atom bonded to N(2A) is 2.416 Å, which is the same as that between Cl(1D) and the hydrogen atom bonded to N(2AB), and is within the range (2.2−2.6 Å) observed for M−Cl···H−N distances.[16] This indicates that there is a hydrogen-bonding interaction between the chloride ion and the amino group of the benzamidine ligand. It is evident that each chloride ion interacts with one cation through electrostatic forces and with another through hydrogen−bonding. Through these interactions, the com-

Table 1. Selected bond lengths (Å) and bond angles (°) for compounds **1−4**

1		**2**		**3**		**4**	
Ni(1)−N(1)	1.895(4)	Ni(1)−N(1)	1.861(4)	Ni(1)−N(1)	1.876(3)	Ni(1)−N(1)	1.847(2)
Ni(1)−N(3)	1.885(4)	Ni(1)−N(3)	1.867(4)	Ni(1)−N(2)	1.856(3)	Ni(1)−N(2)	1.855(2)
C(1)−N(1)	1.276(6)	C(1)−N(1)	1.307(6)	C(1)−N(1)	1.309(4)	C(1)−N(1)	1.307(3)
C(1)−N(2)	1.337(6)	C(1)−N(2)	1.337(6)	C(1)−N(3)	1.348(4)	C(1)−N(3)	1.341(3)
C(8)−N(3)	1.286(6)	C(9)−N(3)	1.297(6)	C(7)−N(3)	1.338(4)	C(7)−N(3)	1.354(3)
C(8)−N(4)	1.328(6)	C(9)−N(4)	1.335(6)	C(7)−N(2)	1.322(5)	C(7)−N(2)	1.307(3)
C(1)−C(2)	1.498(7)	C(1)−C(2)	1.467(7)	C(1)−C(2)	1.505(5)	C(1)−C(2)	1.496(3)
C(8)−C(9)	1.466(7)	C(9)−C(10)	1.472(7)	C(7)−C(8)	1.505(4)	C(7)−C(8)	1.493(3)
N(1)−Ni(1)−N(3)	90.49(18)	N(1)−Ni(1)−N(3)	90.18(17)	N(1)−Ni(1)−N(2)	89.12(13)	N(1)−Ni(1)−N(2)	89.14(9)
C(1)−N(1)−Ni(1)	130.6(4)	C(1)−N(1)−Ni(1)	131.6(4)	Ni(1)−N(1)−C(1)	129.5(2)	Ni(1)−N(1)−C(1)	128.01(17)
C(8)−N(3)−Ni(1)	132.3(4)	C(9)−N(3)−Ni(1)	131.3(4)	Ni(1)−N(2)−C(7)	128.6(2)	Ni(1)−N(2)−C(7)	129.85(18)
N(1)−C(1)−N(2)	121.5(5)	N(1)−C(1)−N(2)	120.1(5)	N(1)−C(1)−N(3)	125.7(3)	N(1)−C(1)−N(3)	126.7(2)
N(1)−C(1)−C(2)	120.7(5)	N(1)−C(1)−C(2)	122.2(5)	C(1)−N(3)−C(7)	120.1(3)	C(1)−N(3)−C(7)	119.96(19)
N(3)−C(8)−N(4)	119.7(5)	N(3)−C(9)−N(4)	119.9(5)	N(3)−C(7)−N(2)	127.0(3)	N(3)−C(7)−N(2)	124.4(2)
N(3)−C(8)−C(9)	122.3(5)	N(3)−C(9)−C(10)	122.1(5)	N(1)−C(1)−C(2)	121.0(3)	N(1)−C(1)−C(2)	119.2(2)
				N(2)−C(7)−C(8)	119.3(3)	N(2)−C(7)−C(8)	121.2(2)

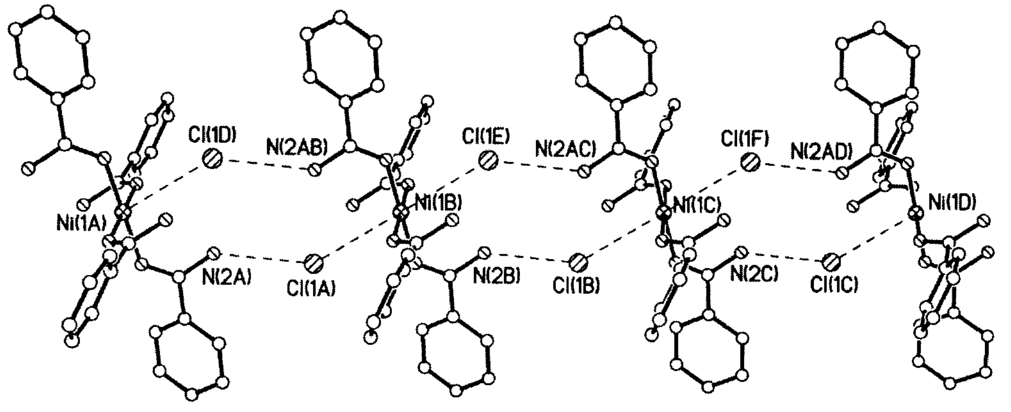

Figure 2. Crystal packing diagram for **1** showing the electrostatic and hydrogen-bonding interactions in a one-dimensional network

plex cations and chloride anions are arranged in a regular manner to form a one-dimensional network structure (Figure 2).

The solid state structure of **2** is very similar to that of **1** (Figure 3). There is centrosymmetry about the Ni center and the dication adopts a square-planar geometry with a N(1)−Ni(1)−N(3) angle of 90.18(17)°. The bond lengths between the nickel center and the coordinated nitrogen atoms are 1.861(4) [Ni(1)−N(1)] and 1.867(4) Å [Ni(1)−N(3)]. The C−N distances for the N(1)−C(1)−N(2) framework are 1.307(6) [C(1)−N(1)] and 1.337(6) Å [C(1)−N(2)], and for the N(3)−C(9)−N(4) framework are 1.297(6) [C(9)−N(3)] and 1.335(6) Å [C(9)−N(4)]. These distances again indicate some degree of delocalization within the N−C−N framework. The N(1)C(1)N(2) and N(3)C(9)N(4) planes form dihedral angles of 38.2 and 34.4° with the C(2)- and C(10)-phenyl planes, respectively. As is the case for **1**, the distance between the nickel center and the chloride atom is 3.287 Å, implying that there is an electrostatic interaction between the two ions. The N···Cl distance between Cl(1A) and N(2AB) is 3.225 Å, and the Cl···H−N distance between Cl(1A) and the hydrogen atom bonded to N(2AB), which is the same as that between

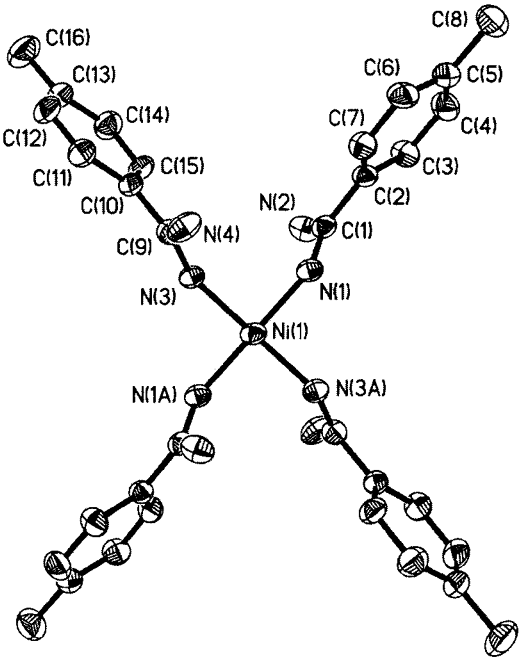

Figure 3. A perspective view of the cation of compound **2**; hydrogen atoms are omitted for clarity

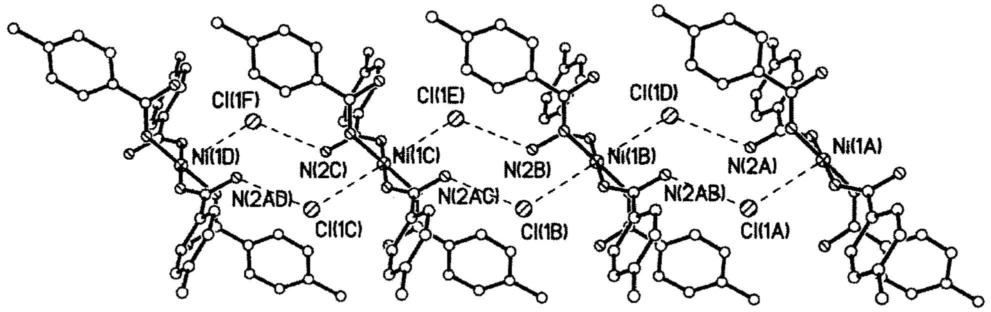

Figure 4. Crystal packing diagram for **2** showing the electrostatic and hydrogen-bonding interactions in a one-dimensional network

Cl(1D) and N(2A), is 2.505 Å. These distances indicate that there is a hydrogen-bonding interaction between the chloride ion and the nitrogen atom of the amino group. Likewise, the complex cations and chloride anions in **2** are arranged in a regular manner through charge-assisted hydrogen bonds to form a one-dimensional network structure (Figure 4).

What is perhaps remarkable in the solid state structures of **1** and **2** is the presence of both electrostatic interactions and hydrogen bonds, which link the cations and anions together to form a loose one-dimensional polymeric structure. Schröder and co-workers have also reported similar weak electrostatic forces and hydrogen-bonding interactions in a palladium complex ligated by a urea-functionalized thioether macrocycle.[15] These types of hydrogen bonds are regarded as medium-strong in strength.[17] Recently, there has been a growing interest in the use of charge-assisted hydrogen bonds for the generation of H-bonded molecular networks.[18]

The solid state structures of **3** and **4** are very similar. Structural analyses reveal that both **3** and **4** are centrosymmetric with the nickel(II) ion adopting a square-planar geometry. In complex **3**, shown in Figure 5, the nickel(II) ion is located at the center of the plane defined by the four nitrogen atoms of the two bidentate 1,3,5-triazapentadienyl ligands, $[HN=C(4\text{-}Py)-N=C(4\text{-}Py)-NH]^{-}$, with Ni−N distances of 1.876(3) [Ni−N(1)] and 1.856(3) Å [Ni−N(2)], and a N(1)−Ni(1)−N(2) angle of 89.12(13)°. Each bidentate 1,3,5-triazapentadienyl ligand forms a six-membered ring with the metal ion. The six-membered ring is almost planar, with a mean deviation of 0.0035 Å from the plane. Within the 1,3,5-triazapentadienyl ligand, the C(1)−N(1) (1.309(4) Å), C(1)−N(3) (1.348(4) Å), C(7)−N(3) (1.338(4) Å) and C(7)−N(2) (1.322(5) Å) distances are very similar, indicating complete delocalization within the N−C−N−C−N framework. The plane of the six-membered ring forms dihedral angles of 3.0 and 44.7° with the N(4)- and N(5)-pyridyl planes, respectively. Solid state packing effects presumably account for such a large difference in the above-mentioned angles.

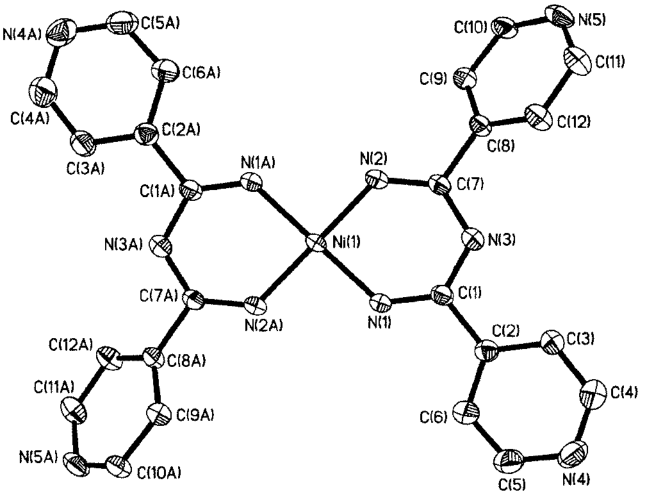

Figure 5. A perspective view of compound **3**. Hydrogen atoms are omitted for clarity

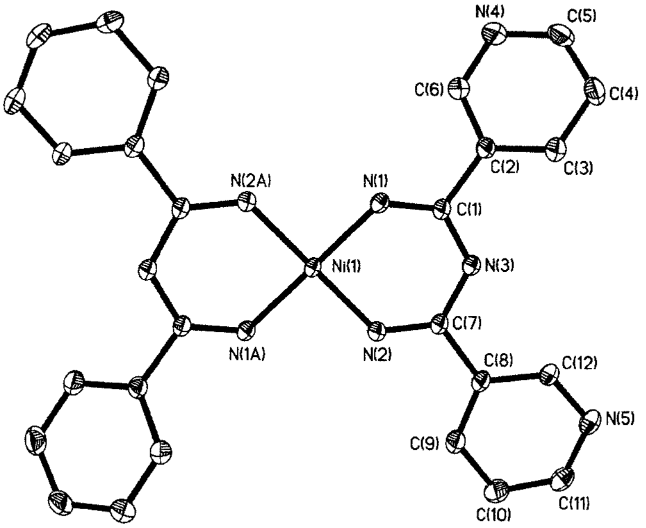

Figure 6. A perspective view of compound **4**; hydrogen atoms are omitted for clarity

Figure 6 shows the nickel(II) ion of **4** positioned at the center of the N(1)N(2)N(1A)N(2A) plane, with Ni−N distances of 1.847(2) [Ni(1)−N(1)] and 1.855(2) Å [Ni(1)−N(2)], and a N(1)−Ni(1)−N(2) angle of 89.14(9)°. Each bidentate 1,3,5-triazapentadienyl ligand forms a six-membered ring with the metal ion. The six-membered ring is almost planar, with a mean deviation of 0.0583 Å from the plane. Within the 1,3,5-triazapentadienyl ligand, the similarity between the C(1)−N(1) [1.307(3) Å], C(1)−N(3) [1.341(3) Å], C(7)−N(3) [1.354(3) Å] and C(7)−N(2)

[1.307(3) Å] distances shows complete delocalization within the N−C−N−C−N framework. The plane of the six-membered ring forms dihedral angles of 33.8 and 9.9° with the N(4)- and N(5)-pyridyl planes, respectively.

In the literature, Lappert and co-workers reported on the formation of metal β-diketiminate complexes by the nucleophilic addition reaction of PhCN with $LiCHR_2$ or LiCHRR′.[19] The typical character of these complexes is that the ligands $[N(R^1)=C(R^2)-C(R^3)=C(R^4)-N(R^5)]^-$ form six-membered chelate rings with the metal cations. Many similar diimine ligands and complexes are also known.[20] However, there are only a few examples of transition metal complexes with the anionic 1,3,5-triazapentadienyl ligand $[HN=C(R)-N=C(R)-NH]^-$. One complex is formed by the evaporation of a methanol solution of nickel chloride hexahydrate and acetamidine,[21] the second from reacting acetonitrile with a dinuclear nickel complex $[Ni_2(\mu\text{-}OH)_2(tpa)_2](ClO_4)_2$ [tpa = tris(2-pyridylmethyl)amine],[22] and the third from reacting triazine with copper acetate.[23] The synthetic route in this paper provides a new and convenient method for the preparation of complexes with 1,3,5-triazapentadienyl ligands.

A plausible mechanism for the formation of the compounds **1**−**4** is depicted in Scheme 1. The nitrile is first attacked by $LiN(SiMe_3)_2$, giving a lithium ketimide. Reaction with benzonitrile or tolunitrile and $NiCl_2$ gives a nickel ketimide intermediate, **A**, which hydrolyzes during workup in air to give **1** or **2**, respectively. However, if 4-cyanopyridine or 3-cyanopyridine is used instead of benzonitrile or tolunitrile, the resulting lithium ketimide undergoes a rapid 1,3-silyl shift, giving a lithium *N*-silylated amidinate, which then attacks another 4-cyanopyridine. This is followed by a 1,3-silyl shift to produce the 1,3,5-triazapentadienyllithium intermediate, **B**, which then reacts with $NiCl_2$ to give the intermediate **C**, which hydrolyzes during workup in air to give **3** or **4**. We also found that varying the ratio of $LiN(SiMe_3)_2$ to the organic nitrile did not alter the results. For example, when the ratio of $LiN(SiMe_3)_2$ to benzonitrile was changed to 1:2 and that of $LiN(SiMe_3)_2$ to 4-cyanopyridine to 1:1, **1** and **3** were the only isolable products from the respective reactions. No other nickel complexes were isolated. This suggests that the resultant ketimide-amidinate $[(4\text{-}Py)C(NSiMe_3)_2]^-$ from 4-cyanopyridine reacts rapidly with another molecule of 4-cyanopyridine, thus producing the 1,3,5-triazapentadienyl anion $[(SiMe_3)NC(4\text{-}Py)NC(4\text{-}Py)N(SiMe_3)]^-$; whereas the resultant ketimide-amidinate $[PhC(NSiMe_3)_2]^-$ from benzonitrile does not react further with benzonitrile. To further support this, we also examined the hydrolysis reaction of the intermediate formed between $LiN(SiMe_3)_2$ and the organic nitriles. The $[M + 1]^+$ peak corresponding to the phenyl amidine $[PhC(=NH)NH_2]$ and the 2,4-dipyridyl-1,3,5-triazapentadiene $[HN=C(4\text{-}Py)-N=C(4\text{-}Py)-NH_2]$ was observed in the positive ESI mass spectra of the hydrolysis products obtained from the hydrolysis reaction of the intermediate derived from benzonitrile and 4-cyanopyridine, respectively. This is in agreement with the fact that the pyridyl group is a stronger electron-withdrawing substituent than the phenyl group. Therefore, the nitrile carbon atom is activated to a greater degree by the pyridyl group than the corresponding phenyl group, thus rendering it more susceptible to nucleophilic attack.

Compound **1** undergoes a metathesis reaction with sodium benzoate to give bis(benzoato)tetrakis(benzamidine)nickel(II) $[(PhCO_2)_2Ni\{H_2NC(Ph)=NH\}_4]$ (**5**) in a moderate yield (Scheme 1). Unlike **1**, which is diamagnetic, **5** is paramagnetic and has an effective magnetic moment (μ_{eff}) of 2.64 μ_B, which corresponds to two unpaired electrons. This suggests that **5** is a d^8 octahedral Ni^{II} complex. This is confirmed by the solid state X-ray structure of **5**. A perspective drawing of **5** is shown in Figure 7. Selected bond lengths and angles are given in Table 2. **5** has a distorted octahedral geometry, the two benzoato ligands are in a *trans* disposition, with N−Ni−N angles of 91.73(12) [N(1)−Ni(1)−N(3)], 176.10(12) [N(1)−Ni(1)−N(5)] and 89.39(12)° [N(1)−Ni(1)−N(7)], and a O(1)−Ni−O(3) angle of 177.51(10)°. The bond lengths between the nickel center and the coordinated nitrogen atoms are 2.075(3) [Ni(1)−N(1)], 2.073(3) [Ni(1)−N(3)], 2.096(3) [Ni(1)−N(5)] and 2.077(3) Å [Ni(1)−N(7)], and those between the nickel center and the coordinated oxygen atoms are 2.153(3) [Ni(1)−O(1)] and 2.195(3) Å [Ni(1)−O(3)]. Similar to **1** and **2**, the C(1)−N(1) (1.277(5) Å) and C(1)−N(2) (1.338(5) Å) bond lengths of the benzamidine ligand are indicative of a carbon−nitrogen double bond and single bond, respectively. The C(8)−N(3) (1.286(4) Å) and C(8)−N(4) (1.332(4) Å), C(15)−N(5) (1.270(5) Å) and C(15)−N(6) (1.338(5) Å), and C(22)−N(7) (1.284(4) Å) and C(22)−N(8) (1.338(4) Å) bond lengths also indicate that they are double and single bonds, respectively. The N(1)C(1)N(2), N(3)C(8)N(4), N(5)C(15)N(6) and N(7)C(22)N(8) planes form dihedral angles of 27.2, 36.0, 26.7 and 38.1° with the C(2)-, C(9)-, C(16)- and C(23)-phenyl planes, respectively. The benzoato ligands are almost

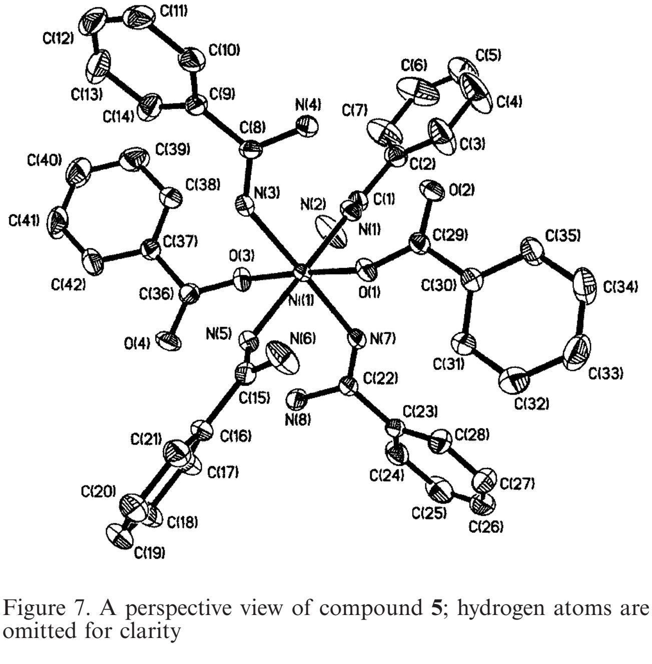

Figure 7. A perspective view of compound **5**; hydrogen atoms are omitted for clarity

Table 2. Selected bond lengths (Å) and bond angles (°) for compound **5**

Ni(1)−N(1)	2.075(3)	Ni(1)−N(3)	2.073(3)
Ni(1)−N(5)	2.096(3)	Ni(1)−N(7)	2.077(3)
Ni(1)−O(1)	2.153(3)	Ni(1)−O(3)	2.195(3)
C(1)−N(1)	1.277(5)	C(1)−N(2)	1.338(5)
C(1)−C(2)	1.497(5)	C(8)−N(3)	1.286(4)
C(8)−N(4)	1.332(4)	C(8)−C(9)	1.495(5)
C(15)−N(5)	1.270(5)	C(15)−N(6)	1.338(5)
C(15)−C(16)	1.497(5)	C(22)−N(7)	1.284(4)
C(22)−N(8)	1.338(4)	C(22)−C(23)	1.490(5)
C(29)−O(1)	1.260(4)	C(29)−O(2)	1.252(4)
C(29)−C(30)	1.499(5)	C(36)−O(3)	1.268(4)
C(36)−O(4)	1.243(5)	C(36)−C(37)	1.505(5)
N(1)−Ni(1)−N(3)	91.73(12)	N(1)−Ni(1)−N(5)	176.10(12)
N(1)−Ni(1)−N(7)	89.39(12)	N(1)−Ni(1)−O(1)	91.63(11)
N(1)−Ni(1)−O(3)	90.18(11)	N(3)−Ni(1)−N(5)	90.00(11)
N(3)−Ni(1)−N(7)	178.81(13)	N(3)−Ni(1)−O(1)	94.39(11)
N(3)−Ni(1)−O(3)	87.27(11)	N(5)−Ni(1)−N(7)	88.90(12)
N(5)−Ni(1)−O(1)	91.72(11)	N(5)−Ni(1)−O(3)	86.41(11)
N(7)−Ni(1)−O(1)	85.18(11)	N(7)−Ni(1)−O(3)	93.13(11)
O(1)−Ni(1)−O(3)	177.51(10)	C(1)−N(1)−Ni(1)	135.5(3)
C(8)−N(3)−Ni(1)	136.3(3)	C(15)−N(5)−Ni(1)	138.4(3)
C(22)−N(7)−Ni(1)	135.5(3)	C(29)−O(1)−Ni(1)	133.4(3)
C(36)−O(3)−Ni(1)	131.2(3)	N(1)−C(1)−N(2)	120.3(4)
N(1)−C(1)−C(2)	123.7(4)	N(3)−C(8)−N(4)	121.1(3)
N(3)−C(8)−C(9)	122.9(3)	N(5)−C(15)−N(6)	120.0(4)
N(5)−C(15)−C(16)	122.8(4)	N(7)−C(22)−N(8)	121.4(3)
N(7)−C(22)−C(23)	122.8(3)	O(1)−C(29)−O(2)	124.0(4)
O(1)−C(29)−C(30)	117.1(4)	O(3)−C(36)−O(4)	124.8(4)
O(1)−C(36)−C(37)	118.8(3)		

planar. The dihedral angle between the O(1)C(29)O(2) plane and the C(30)-phenyl plane is 7.7°, and that between the O(3)C(36)O(4) plane and the C(37)-phenyl plane is 2.5°. Figure 8 shows one entity selected from its packing diagram. It is evident that the non-coordinating oxygen atoms of the two carbonyl groups of the benzoato ligands of one molecule interact with the non-coordinating nitrogen atoms of the amino group of two neighboring molecules through hydrogen bonds to form a one-dimensional infinite network. The distance between O(2A) and N(8B) is 2.891 Å, and that between O(2A) and the hydrogen atom bonded to N(8B) is 2.156 Å. The distance between O(4B) and N(4A) is 2.886 Å, and that between O(4B) and the hydrogen atom bonded to N(4A) is 2.070 Å.

Spectroscopic Properties of Compounds 1−5

The peaks in the ^{1}H NMR spectra of compounds **1** and **2** are very broad, although they are diamagnetic. This is probably due to the presence of free amidine ligands, which arise as a result of the dissociation of the complexes.[24] We were unable to locate the resonances for the NH protons of the amino and imino groups in the ^{1}H NMR spectra. However, the IR spectra of **1** and **2** exhibit strong multiple absorptions in the region between 3100−3500 cm^{-1} which are assigned to antisymmetric and symmetric NH and NH$_2$ stretching, and a strong absorption at 1645 cm^{-1} assigned to C=N stretching of the amidine ligands.[25] The medium strong bands around 1460 cm^{-1} can be assigned to the C−N single bond stretching. Both compounds do not show the molecular ion in their mass spectra. The LRMS (positive FAB) spectrum of **1** exhibits a peak at m/z = 453 corresponding to the [NiL$_3$Cl]$^+$ [L = PhC(=NH)NH$_2$] fragment for ^{35}Cl, and that of **2** shows a peak at m/z = 325 corresponding to the [NiL^1(L^1−H)]$^+$ [L^1 = p-CH$_3$C$_6$H$_4$C(=NH)NH$_2$; (L^1 − H) = p-CH$_3$C$_6$H$_4$C(NH)$_2$$^-$] fragment.

The protons at the terminal nitrogen atoms in compounds **3** and **4** are chemically equivalent, thus they have similar chemical shifts in the ^{1}H NMR spectra of **3** and **4** and appear as a singlet at δ = 7.56 for **3** and δ = 7.37 ppm for **4**. The pyridyl groups are each attached to the 1,3,5-triazapentadiento unit via a single bond, therefore, the four pyridyl rings, which are free to rotate in solution, are chemically equivalent and have similar chemical shifts. In the spectrum of **3**, the resonances for the 4-pyridyl protons appear as two doublets at δ = 8.73 (d, J = 4.4 Hz, 8 H) and 7.94 (d, J = 4.4 Hz, 8 H) ppm; whereas in the spectrum of **4**, the resonances for the 3-pyridyl protons appear as a singlet, two doublets and a doublet of doublets at δ = 9.17 (s, 4 H), 8.69 (d, J = 4.4 Hz, 4 H), 8.34 (d, J = 8.0 Hz, 4 H) and 7.51 (dd, J = 8.0, 4.4 Hz, 4 H) ppm, respectively. In their IR spectra, both compounds exhibit strong multiple absorptions, assigned to NH stretchings, in the region 3100−3500 cm^{-1}. Furthermore, there are other two strong absorption bands in their IR spectra. A strong broad multiple absorption band is seen between 1400−1500 cm^{-1}, and a strong single peak is seen around 1300 cm^{-1}. These can be assigned to the skeleton vibrations of the 1,3,5-triazapentadienyl ligand. The molecular ion peaks [M + H]$^+$ of

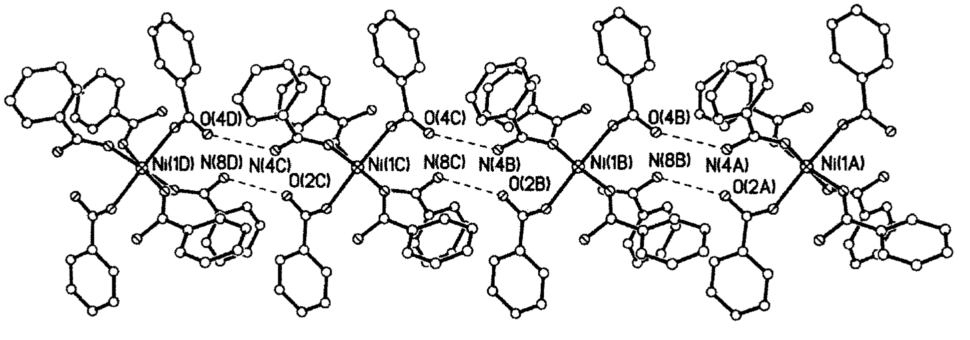

Figure 8. Crystal packing diagram for **5** showing the hydrogen-bonding in a one-dimensional network

both **3** and **4** are exhibited at m/z = 507 in their LRMS (positive FAB) spectra.

Due to the paramagnetic nature of compound **5**, we were unable to obtain an interpretable ^{1}H NMR spectrum. In the IR spectrum, in addition to the characteristic absorption bands of the benzamidine ligands, **5** also exhibits strong absorptions at 1680 and 1136 cm^{-1}, corresponding to the C=O and C−O stretches of the benzoato ligands, respectively. No molecular ion was observed in the mass spectrum of **5**. The highest mass peak observed in the LRMS (FAB+) of **5** was at m/z = 339, which corresponds to the $[(PhCOO)_2Ni + K]^+$ fragment.

Concluding Remarks

We have developed a convenient synthetic method for some new nickel(II) complexes containing the arylamidinato and 1,3,5-triazapentadienyl ligands. The formation of one-dimensional network structures in the solid state through charge-assisted hydrogen bonds is observed for **1** and **2**; while only hydrogen-bonding interactions are apparent in the crystal lattice of **5**. We have also investigated in detail the factors that control the type of product formed, and we observed that the products obtained depend on the nature of the aryl groups used in the starting arylnitrile.

Experimental Section

General Procedures: All reactions were carried out under nitrogen in flamed Schlenk-type glassware on a dual manifold Schlenk line, unless otherwise stated. Solvents were pre-dried by standard procedures. All chemicals used were of reagent grade, obtained from Aldrich or Fisher Scientific Chemical Company. The IR spectra (KBr pellets) were recorded with a Perkin−Elmer Paragon 1000PC or Nicolet Nagan-IR 550 Series II FTIR spectrometer, and NMR spectra with a Varian INOVA 400 spectrometer. Chemical shifts for the ^{1}H NMR spectra were referenced to internal deuterated solvents and then recalculated to TMS (δ = 0.00 ppm). Fast atom bombardment (FAB) low-resolution mass spectra were obtained with a Finnigan MAT SSQ-710 spectrometer in positive mode and reported as m/z. Magnetic susceptibilities were measured with a MSB-AUTO magnetic susceptibility balance. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

Tetrakis(benzamidine)nickel(II) Chloride (1): Benzonitrile (0.515 mL, 5.0 mmol) and $LiN(SiMe_3)_2$ (0.837 g, 5.0 mmol) were placed in THF (20 mL) at 0 °C. The resultant yellow solution was warmed to room temperature and stirred for an additional 2 h before cooling down to −78 °C. Anhydrous $NiCl_2$ (0.324 g, 2.5 mmol) was then added to the reaction mixture, after which it was stirred at −78 °C for 1 h before warming up to room temperature. The mixture was reacted overnight. The solvent was removed in vacuo and the residue was extracted with CH_2Cl_2 (2 × 10 mL) and the solution was filtered. Removal of the solvent in vacuo gave a dark red oily product. The product was dissolved in THF (20 mL) and the solvent was evaporated slowly to give yellow crystals of **1**. Yield: 0.512 g, 67%; m.p. 174−176 °C. IR (KBr): $\tilde{\nu}$ = 3335 s, 3179 s, 1645 vs, 1606 m, 1571 s, 1457 m, 1245 w, 1127 w, 781 w and 701 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.14 (br. s, 4 H, Ph), 8.02 (br. s, 8 H, Ph) and 8.41 (br. s, 8 H, Ph) ppm; we were unable to locate the resonance due to imino NH and amino NH_2 protons. LRMS (+FAB): m/z = 453 $[(NiL_3Cl)^+$, L = $PhC(=NH)NH_2]$ for ^{35}Cl. $C_{28}H_{32}Cl_2N_8Ni{\cdot}C_4H_8O{\cdot}0.5H_2O$ (691.33): calcd. C 55.60, H 5.98, N 16.21; found C 55.92, H 6.13, N 15.88.

Tetrakis(tolueneamidine)nickel(II) Chloride (2): Compound **2** was produced under the same reaction conditions and using the same procedures as for **1**; however, *p*-tolunitrile (0.586 g, 5.0 mmol) was used instead of benzonitrile. Yield: 0.635 g, 76%; m.p. 181−182 °C. IR (KBr): $\tilde{\nu}$ = 3326 s, 3188 s, 1645 s, 1612 s, 1565 m, 1519 w, 1460 m, 1262 w, 1133 w, 831 m, 734 m, 684 w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.67 (br. m, 12 H, Me), 7.73 and 7.83 (br. m, 16 H, C_6H_4) ppm. LRMS (+FAB): m/z = 325 $\{[NiL^1(L^1-H)]^+$; L^1 = $[p\text{-}CH_3C_6H_4C(=NH)NH_2]$, (L^1-H) = $[p\text{-}CH_3C_6H_4C(NH)_2^-]$. $C_{32}H_{40}Cl_2N_8Ni{\cdot}1.5H_2O{\cdot}0.4C_4H_8O$ (722.19): calcd. C 55.88, H 6.45, N 15.51; found C 55.86, H 6.37, N 15.26.

Bis[2,4-di(4-pyridyl)-1,3,5-triazapentadienato]nickel(II) (3): The procedure was similar to that of **1**. 4-Cyanopyridine (0.520 g, 5.0 mmol), $LiN(SiMe_3)_2$ (0.418 g, 2.5 mmol) and anhydrous $NiCl_2$ (0.162 g, 1.3 mmol) were used. The residue was extracted with methanol (2 × 10 mL) and the solution was filtered. Slow evaporation of the methanol solution gave yellow crystals of **3**. Yield: 0.201 g, 30%; m.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 3658 m, 3291 s, 3270 s, 3184 bw, 1601 m, 1577 m, 1533 vs, 1446 vs, 1411 s, 1315 s, 1063 m, 1003 w, 848 m, 759 s, 718 w and 595 w cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 7.56 (s, 4 H, NH), 7.94 (d, *J* = 4.4 Hz, 8 H, pyridyl) and 8.73 (d, *J* = 4.4 Hz, 8 H, pyridyl) ppm. MS (+FAB): m/z = 507 $[M + 1]^+$. $C_{24}H_{20}N_{10}Ni{\cdot}0.25CH_3OH{\cdot}H_2O$ (533.21): calcd. C 54.63, H 4.35, N 26.27; found C 54.59, H 4.24, N 26.29.

Bis[2,4-di(3-pyridyl)-1,3,5-triazapentadienato]nickel(II) (4): Compound **4** was produced under the same reaction conditions and using the same procedures as for **1**. 3-Cyanopyridine (0.312 g, 3.0 mmol), $LiN(SiMe_3)_2$ (0.250 g, 1.5 mmol) and anhydrous $NiCl_2$ (0.973 g, 0.75 mmol) were used. Yield: 0.112 g, 28%; m.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 3449 m, 3305 m, 3170 m, 1643 s, 1594 s, 1548 s, 1536 s, 1480 m, 1426 m, 1303 s, 1203 m, 1023 m, 815 m, 726 s, 704 m cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 7.37 (s, 4 H, NH), 7.51 (dd, *J* = 8.0, 4.4 Hz, 4 H, pyridyl), 8.34 (d, *J* = 8.0 Hz, 4 H, pyridyl), 8.69 (d, *J* = 4.4 Hz, 4 H, pyridyl) and 9.17 (s, 4 H, pyridyl) ppm. LRMS (+FAB): m/z = 507 $[M + 1]^+$. $C_{24}H_{20}N_{10}Ni{\cdot}CH_3OH{\cdot}1.5H_2O$ (566.25): calcd. C 53.03, H 4.81, N 24.74; found C 53.06, H 4.72, N 24.65.

Bis(benzoato)tetrakis(benzamidine)nickel(II) (5): After the preparation of **1** from benzonitrile (0.25 mL, 2.40 mmol), sodium benzoate (0.173 g, 1.20 mmol) was added to the THF mixture, and stirring was continued at room temperature for 48 h. The solvent was then removed in vacuo and dichloromethane (20 mL) was added to the residue and the solution was filtered. The solvent of the filtrate was removed in vacuo, a red oily product was obtained. The product was dissolved in THF (20 mL) and the solvent was evaporated slowly, giving pale yellow crystals of **5**. Yield: 0.261 g, 56%; m.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 3184 s, 3061 s, 1680 m, 1645 m, 1605 m, 1563 m, 1518 w, 1484 w, 1391 vs, 1136 vs, 721 w, 696 m cm^{-1}. LRMS (+FAB): m/z = 339 $[(C_6H_5COO)_2Ni + K]^+$. $C_{42}H_{42}N_8NiO_4$ (781.55): calcd. C 64.55, H 5.42, N 14.33; found C 64.38, H 5.50, N 14.25.

X-ray Crystallography: Crystals of $\mathbf{1}{\cdot}C_4H_8O$, $\mathbf{2}{\cdot}2C_4H_8O$, $\mathbf{3}{\cdot}2CH_3OH$, $\mathbf{4}{\cdot}2CH_3OH$ and **5** suitable for X-ray diffraction were grown by slow evaporation of a solution of **1**, **2**, **5** in THF and **3**, **4** in CH_3OH, in air. The intensity data were collected with a Bruker

Table 3. Crystal data and refinements for compounds **1**−**5**

Compound	**1**·C_4H_8O	**2**·2C_4H_8O	**3**·2CH_3OH	**4**·2CH_3OH	**5**
Empirical formula	$C_{32}H_{40}Cl_2N_8NiO$	$C_{40}H_{56}Cl_2N_8NiO_2$	$C_{26}H_{28}N_{10}NiO_2$	$C_{26}H_{28}N_{10}NiO_2$	$C_{42}H_{42}N_8NiO_4$
Molecular mass	682.33	810.54	571.29	571.29	781.55
Crystal system	monoclinic	triclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.771(3)	8.404(2)	11.638(6)	7.1659(8)	9.1260(16)
b (Å)	18.813(7)	11.635(3)	6.954(4)	8.6303(10)	14.285(3)
c (Å)	10.560(4)	12.045(3)	16.500(8)	10.6513(12)	15.834(3)
α [°]	90	85.317(5)	90	76.819(2)	94.294(3)
β [°]	94.808(8)	80.593(5)	94.410(10)	87.711(2)	106.730(4)
γ [°]	90	69.049(4)	90	88.352(2)	90.162(3)
V (Å^3)	1736.4(11)	1084.8(5)	1331.3(12)	640.72(13)	1970.6(6)
Z	2	1	2	1	2
F(000)	716	430	580	298	820
$D_{\text{calcd.}}$ [g cm^{-3}]	1.305	1.241	1.405	1.481	1.317
μ(Mo-K_α) [mm^{-1}]	0.750	0.612	0.773	0.803	0.545
Reflections collected	8569	5438	6128	3805	10743
Unique reflections	3068	3750	2322	2761	7563
$R_{\text{int.}}$	0.1093	0.0466	0.0897	0.0455	0.0391
Observed reflections	1259	1818	1957	2409	4043
GOF on F^2	0.833	0.885	1.062	1.065	0.906
$R1$, $wR2$ [$I > 2\sigma(I)$][a]	0.0558, 0.1211	0.0707, 0.1631	0.0691, 0.1858	0.0484, 0.1369	0.0513, 0.1126
$R1$, $wR2$ (all data)	0.1542, 0.1484	0.1442, 0.1956	0.0771, 0.1972	0.0542, 0.1411	0.1061, 0.1447

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

AXS SMART 1000 CCD area-detector diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 293 K. The collected frames were processed with proprietary software SAINT[26] and an absorption correction was applied (SADABS[27]) to the collected reflections. The structures of these molecules were solved by direct methods and expanded by standard difference Fourier syntheses using the software SHELXTL.[28] Structure refinements were made on F^2 using the full-matrix least-squares technique. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in their idealized positions and allowed to ride on the respective carbon atoms. Pertinent crystallographic data and other experimental details are summarized in Table 3. CCDC-200431 (**1**), -215047 (**2**), -200430 (**3**), -215048 (**4**) and -215049 (**5**) contain the supplementary crystallographic data 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, 12 Union Road, Cambridge CB2 1EW, UK [Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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