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# Structural studies of nickel complexes of the unsymmetrical tridentate ligand *N*-phenyl-*N*-(2-pyridyl)formamidinate

F. Albert Cotton *, Peng Lei, Carlos A. Murillo *

*Department of Chemistry and Laboratory for Molecular Structure and Bonding, P.O. Box 30012, Texas A&M University, College Station, TX 77842-3012, USA*

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## Abstract

We describe the preparation and structural characterization of six nickel complexes with the unsymmetrical formamidine HPhPyF (*N*,*N*′-phenylpyridylformamidine). These six compounds include one dinuclear species $Ni_2(PhPyF)_4$ (**1**), two mononuclear complexes: *cis*-$[Ni(HPhPyF)_2(MeCN)_2][BF_4]_2$ (**3**) and $Ni(HPhPyF)Br_2$ (**6**), and three trinuclear compounds: $Ni_3(PhPyF)_4(MeCN)_2(BF_4)_2$ (**2**), $[Ni_3(PhPyF)_4Cl]Cl$ (**4**), and $Ni_3(PhPyF)_4Cl_2$ (**5**). In the dinuclear species **1**, the two nickel atoms are surrounded by four formamidinate ligands. Each is pseudo-octahedral and there is long separation ( ≈ 3.41 Å) between them. One mononuclear compound, *cis*-$[Ni(HPhPyF)_2(MeCN)_2][BF_4]_2$ (**3**) has a distorted octahedral geometry, the other $Ni(HPhPyF)Br_2$ (**6**) contains a Ni atom in a pseudo-tetrahedral environment. All three trinuclear compounds contain a linear chain of three $Ni^{II}$ atoms wrapped by four PhPyF anions, but each has a different axial environment. There are two axially coordinated MeCN in **2**, only one axial Cl anion for **4** and two axial Cl anions for **5**. In **2**, **4**, and **5**, the $Ni_3^{6+}$ chains are symmetrical with relatively long Ni···Ni separations in the range 2.44–2.51 Å.

*Keywords:* Nickel compounds; Linear trinickel compounds; Unsymmetrical formamidine; Crystal structures

## 1. Introduction

Metal–metal interactions in dinuclear paddlewheel compounds have been intensively investigated and are well understood [1]. Recently, increasing attention has been given to the chemistry of the metal complexes with larger numbers of metal atoms in linear arrays [2]. Thus, a large number of complexes with linear trimetal units have been synthesized [2–7]. The majority of these complexes characterized to date are supported by the anion of dipyridylamine (dpa) and have the formula $M_3(dpa)_4X_2$ (M = Cr [3], Co [4], Ni [5], Cu [6], Rh [7], Ru [7]), where X is usually an anion, such as $Cl^-$, occupying axial positions. The typical structure of a $M_3(dpa)_4X_2$, molecule is shown in Scheme 1. Some other anionic nitrogen based ligands, such as DPhIP (the anion of 2,6-di(phenylimino)piperidine) [8] and BPAP (the dianion of bisphenylaminopyridine) [9], shown in Scheme 2, have also been used to support linear trimetal units.

A very detailed study of $Ni_3(dpa)_4Cl_2$ [5b] from this laboratory led to the conclusion that there is no metal–metal bonding even though the nickel–nickel separations are relatively short ( ≈ 2.43 Å). Instead, there is antiferromagnetic coupling between the terminal five-coordinated nickel atoms, each of which has two unpaired electrons. The central nickel atom is $d^8$, square-planar and diamagnetic. Peng and coworkers [10] have done extensive work on the preparation of multinuclear nickel compounds with five, seven, nine nickel atoms in a linear array using oligo-pyridyl amino ligands. Their results indicate that antiferromagnetic interactions are similar to those in the trinickel unit and they decrease as might be expected with increasing chain length.

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* Corresponding authors.
*E-mail addresses:* cotton@tamu.edu (F. Albert Cotton), murillo@tamu.edu (C.A. Murillo).

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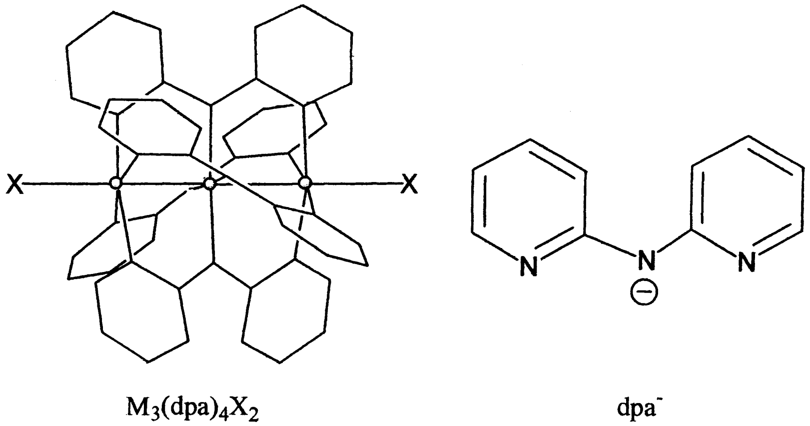
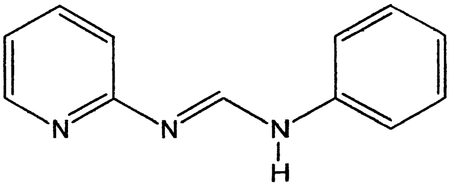


Scheme 1.

More recently, the one-electron oxidation of $Ni_3(dpa)_4Cl_2$was reported [11]. The Ni–Ni distances in the oxidized compound $Ni_3(dpa)_4(PF_6)_3$ (~2.28 Å) are much shorter than those in the unoxidized species (~2.43 Å), and are consistent with three-center metal–metal bonding and a formal bond order of 0.5.

In this work, we report syntheses and structural studies of a series of nickel complexes including mononickel, dinickel and trinickel complexes supported by the anion of the unsymmetrical *N*,*N′*-phenylpyridylformamidine HPhPyF. A schematic drawing of the formamidine is shown in Scheme 3.



**N,N'—phenylpyridylformamidine (HPhPyF)**

Scheme 3.

## 2. Experimental

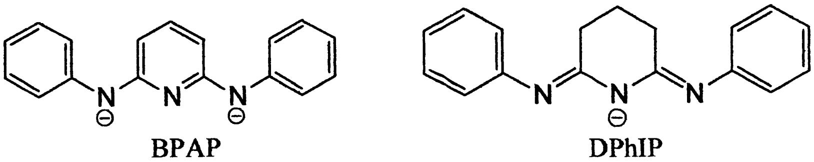
### 2.1. General procedures

All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were purified prior to use by distillation over appropriate drying agents in a nitrogen atmosphere. The compounds HPhPyF [12], $Ni(py)_4Cl_2$ [13] and $Ni(PPh_3)_2Br_2$ [14] were synthesized as previously described. Anhydrous $NiCl_2$, $NiBr_2$ and $AgBF_4$ were purchased from Strem. The former was refluxed in thionyl chloride prior to use. Methyllithium (1.6 M in ether) was obtained from Acros. Magnetic measurements were done at room temperature on a magnetic susceptibility balance (Johnson Matthey Chemicals Limited).

### 2.2. Preparations

#### 2.2.1. Preparation of $Ni_2(PhPyF)_4$ (**1**)

A flask was charged with HPhPyF (396 mg, 2.00 mmol) dissolved in 30 ml of THF. The solution was cooled to −78 °C, and 1 equiv. of MeLi was added slowly. The solution was removed from the cold bath, stirred until it reached room temperature. The mixture was then added via cannula to a flask containing anhydrous $Ni(py)_4Cl_2$ (670 mg, 1.50 mmol). The reaction mixture was refluxed for 12 h. The volume was then reduced to approximately 10 ml, and upon addition of 40 ml of hexanes a deep-brown precipitate formed. The solid was collected by filtration, and washed thoroughly with ether. After drying, the solid was dissolved in 15 ml of $CH_2Cl_2$, and then 40 ml of hexanes was added to precipitate the product. The mixture was filtered, and the solid was briefly dried under vacuum. Finally, the product was dissolved in 15 ml of $CH_2Cl_2$, and layered with 40 ml of hexanes. Large, dark-blue crystals of $Ni_2(PhPyF)_4$ formed in a week. Yield: 52%.



Scheme 2.

### 2.2.2. Preparation of $Ni_3(PhPyF)_4(MeCN)_2(BF_4)_2$ (**2**) and $[Ni(HPhPyF)_2(MeCN)_2](BF_4)_2$ (**3**)

The ligand HPhPyF (396 mg, 2.00 mmol) was dissolved in 15 ml of THF and deprotonated with 1 equiv. of MeLi at −78 °C. After the temperature of the solution had slowly risen to room temperature, the THF was removed under vacuum. Then, 40 ml of MeCN was used to dissolve the residue and the solution was transferred to a flask containing $NiBr_2$ (378 mg, 1.50 mmol). The yellow mixture was stirred for 3 h at room temperature. To this mixture $AgBF_4$ (584 mg, 3.00 mmol) was added, and the mixture was refluxed for 12 h, and then filtered. The filtrate was reduced to half of its original volume and 60 ml of $Et_2O$ was added. A black–brown solid formed. This was collected by filtration, washed twice with 20 ml of $Et_2O$, and then dried briefly under vacuum. Finally, the solid was dissolved in 20 ml of MeCN, and the solution was layered with ether (40 ml). Three-weeks later, several dark-red, block-shaped crystals of $Ni_3(PhPyF)_4(MeCN)_2(BF_4)_2$ (**2**) were obtained along with some blue needle-like crystals of $[Ni(HPhPyF)_2(MeCN)_2](BF_4)_2$ (**3**). The crystals were separated manually. The yield for compound **2** was about 2% and that of **3** was 40%.

### 2.2.3. Preparation of $[Ni_3(PhPyF)_4Cl]Cl$ (**4**)

To the ligand HPhPyF (396 mg, 2.00 mmol) in 40 ml of THF was added 1 equiv. of MeLi at −78 °C. The deprotonation was essentially complete when the temperature of the mixture rose to room temperature. The THF solution was transferred to a flask containing $Ni(py)_4Cl_2$ (1.34 g, 3.00 mmol). The reaction mixture was refluxed for 15 h and then filtered. The volume of the resulting solution was reduced to approximately 10 ml. Ether (50 ml) was added to this mixture. The solid was collected by filtration, washed with copious amounts of ether, and then dissolved in 15 ml of THF. Addition of hexanes produced a precipitate which was isolated by filtration. Finally, the solid was dissolved in 15 ml of $CH_2Cl_2$, and layered with 40 ml of hexanes. Black–red crystals of $Ni_3(PhPyF)_4Cl]Cl$ formed within 2 weeks along with a lot of dark-blue crystals of **1**. The yield of the trinuclear compound **4** was ~8%. Magnetic susceptibility at room temperature: 3.08 $\mu_B$.

### 2.2.4. Preparation of $Ni_3(PhPyF)_4Cl_2$ (**5**)

The method of preparation was similar to that of **4**, except that a threefold excess of $Ni(py)_4Cl_2$ was used. After 3 weeks, very dark red (almost black) crystals of $Ni_3(PhPyF)_4Cl_2$ formed along with the some dark-blue crystals of **1**. The yield for the trinickel compound **5** was ~5%.

### 2.2.5. Preparation of $Ni(HPhPyF)Br_2$ (**6**)

To a flask charged with HPhPyF (396 mg, 2.00 mmol) and $Ni(PPh_3)_2Br_2$, 10 g of naphthalene was added. The mixture was quickly heated to 145 °C with gently stirring. A dark-purple, crystalline precipitate formed. After 10 min of stirring at 145 °C, the reaction mixture was allowed to cool to room temperature. The solid was washed with copious amounts of ether, then 2 × 10 ml of benzene.

The remaining solid was dissolved in 20 ml of acetone, and an insoluble portion was removed by filtration. The resulting acetone solution was layered with 40 ml of hexanes. Dark-purple crystals formed in a week. Yield: 58%.

## 2.3. Crystallographic studies

Data were collected on a Bruker SMART 1000 CCD area detector system. In each case, a suitable crystal was attached to the tip of a quartz fiber with a small amount of grease and transferred to a goniometer, where the crystal was kept in a stream of cold nitrogen. Cell parameters were obtained using SMART software [15]. Data were corrected for Lorentz and polarization effects using the program SAINTPLUS [16]. Absorption corrections were applied using SADABS [17].

The positions of heavy atoms were found by the direct methods programmed in SHELXS-97 [18]. Subsequent cycles of least-square refinement followed by difference Fourier syntheses revealed the positions of the non-hydrogen atoms. All hydrogen atoms were placed in idealized positions.

Crystallographic data and structure refinement details for all the structures reported in this work are listed in Table 1. All space groups were uniquely determined by systematic absences, and refinements proceeded straightforwardly.

# 3. Results and discussion

## 3.1. Synthetic considerations

We were surprised to encounter a great deal of difficulty in preparing trinickel compounds with the PhPyF ligand. From a purely preparative point of view, here our report is far from satisfactory, but the existence of these compounds of structural interest has been established.

A simple and commonly-used method to prepare linear trimetal chain complexes is to react the lithium salt of the ligand with a stoichiometric amount of the anhydrous metal halides [2–6]. However, we found anhydrous nickel halides (chloride and bromide) to be very unreactive toward the lithium salt of HPhPyF. No reaction takes place when LiPhPyF and $NiX_2$ (X = Cl,

Table 1
Crystallographic data and refinement details

| | **1** | **2** | **3** | **4** | **5**·$CH_2Cl_2$ | **6** |
|---|---|---|---|---|---|---|
| Empirical formula | $C_{48}H_{40}N_{12}Ni_2$ | $C_{52}H_{46}B_2F_8N_{14}Ni_3$ | $C_{28}H_{28}B_2F_8N_8Ni$ | $C_{48}N_{40}Cl_2N_{12}Ni_3$ | $C_{49}H_{42}Cl_4N_{12}Ni_3$ | $C_{12}H_{11}Br_2N_3Ni$ |
| Formula weight | 902.34 | 1216.78 | 708.91 | 1031.95 | 1116.88 | 415.77 |
| Space group | $P2_1/n$ | $I4_1/a$ | $Pbcn$ | $P4/ncc$ | $P4_32_12$ | $P2_1/c$ |
| $a$ (Å) | 13.5762(7) | 18.7409(7) | 20.911(2) | 13.461(2) | 14.8822(6) | 133441(11) |
| $b$ (Å) | 10.4773(5) | 18.7409(7) | 10.5688(4) | 13.461(2) | 14.8822(6) | 13.3396(11) |
| $c$ (Å) | 29.800(2) | 29.8937(15) | 14.0333(11) | 24.334(7) | 43.382(4) | 8.1227(6) A |
| $\beta$ (°) | 96526(1) | | | | | 96.556(2) |
| $V$ (Å$^3$) | 4211.4(4) | 10499.3(8) | 3101.4(4) | 4409.5(16) | 9608.4(9) | 41436.4(2) |
| $D_{calc}$ (g cm$^{-3}$) | 1.423 | 1540 | 1.518 | 1.554 | 1.544 | 1.923 |
| $Z$ | 4 | 8 | 4 | 4 | 8 | 4 |
| $T$ (K) | 213(2) | 213(2) | 213(2) | 213(2) | 213(2) | 213(2) |
| $R_1$ [a], $wR_2$ [b] [$I > 2\sigma(I)$] | 0.0276, 0.0693 | 0.0539, 0.1294 | 0.0464, 0.1299 | 0.0706, 0.1544 | 0.0639, 0.1539 | 0.0273, 0.0658 |
| $R_1$ [a], $wR_2$ [b] (all data) | 0.0338, 0.0727 | 0.0683, 0.1411 | 0.0552, 0.1441 | 0.1513, 0.2006 | 0.0766, 0.1636 | 0.0416, 0.0775 |
| Quality of fit [c] | 1.034 | 1.177 | 1.065 | 1.094 | 1.152 | 1.009 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

[c] Quality of fit $= [\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{parameters})]$ based on all data.

Br) are mixed in THF even during an extended period of reflux. It seemed clear that either some other source of nickel(II) was required, or more forcing conditions were needed if an anhydrous nickel halide had been used as a starting material. When 2 equiv. of $AgBF_4$ were added to precipitate the bromide ions from $NiBr_2$ in an attempt to make the nickel(II) ion more readily accessible to LiPhPyF, the trinuclear complex, $Ni_3$(PhPyF)$_4$(MeCN)$_2$(BF$_4$)$_2$ (**2**) was obtained but the isolated yield was minute. The major product of this reaction, **3**, was a mononuclear nickel complex of octahedral structure[1] containing the neutral ligand, with the formula of [Ni(HPhPyF)$_2$(MeCN)$_2$][BF$_4$]$_2$.

In a search for other suitable Ni(II) sources to prepare trinickel complexes by reaction with the anion of HPhPyF, Ni(py)$_4$Cl$_2$ was examined. The reaction was carried out with Ni(py)$_4$Cl$_2$ and LiPhPyF in the stoichiometric ratio of 3:4 necessary to form a trinuclear compound. However, under such conditions only the dinuclear species $Ni_2$(PhPyF)$_4$ (**1**) was obtained. This compound appears to be thermodynamically very stable. Since **1** is deficient in Ni, relative to the $Ni_3^{6+}$ species, twice as much Ni(py)$_4$Cl$_2$ was used. In this way, a small amount of the trinickel complex [$Ni_3$(PhPyF)$_4$Cl]Cl (**4**) was isolated, but a significant amount of the dinuclear compound **1** was again obtained. When a larger excess of Ni(py)$_4$Cl$_2$ (approximately threefold) was used, a different trinickel species, $Ni_3$(PhPyF)$_4$Cl$_2$ (**5**), was isolated, but, again, **1** was present as the major product. The reactions of LiPhPyF and Ni(py)$_4$Cl$_2$ are summarized in Scheme 4.

Naphthalene has been proven to be a good reaction medium for the preparation of multinuclear metal chain complexes with the number of metal atoms extending from 3 to 9 as shown by Peng and coworkers [10]. In those reactions, naphthalene allows the reaction temperature to rise as high as about 185 °C, which is critical to generate the target compounds having many metal atoms in a linear array. However, the naphthalene reaction medium could not be used for the preparation of trinickel compounds with the anion PhPyF since a thermogravimetric analysis of HPhPyF showed that the ligand decomposes at approximately 153 °C. The reaction of HPhPyF with $NiCl_2$, Ni(py)$_4$Cl$_2$ and Ni(PPh$_3$)$_2$Br$_2$ in naphthalene using KOBu$^t$ as a base at 145 °C did not yield isolable products. When no base was added, the reaction of HPhPyF with Ni(PPh$_3$)$_2$Br$_2$ in naphthalene gave a mononickel species, Ni(HPhPyF)Br$_2$, in which a neutral ligand HPhPyF is found to be chelating the nickel atom, with the two bromide atoms filling the remaining two positions of a distorted tetrahedron.

The difficulty in preparing the $Ni_3^{6+}$ chain compounds described here contrasts with the ease of preparing the $Cr_3^{6+}$ analogs. Those have been synthesized relatively straightforwardly by reaction of $CrCl_2$ and unsymmetrical formamidinates [19].

### 3.2. Structural studies

The molecular structure of the dinuclear compound $Ni_2$(PhPyF)$_4$ is shown in Fig. 1. It crystallizes in the space group $P2_1/n$ with all atoms of the molecule occupying general positions. Each ligand uses two nitrogen atoms to chelate one nickel atom while the third nitrogen atom spans to the other nickel atom. Each nickel atom has a very distorted octahedral

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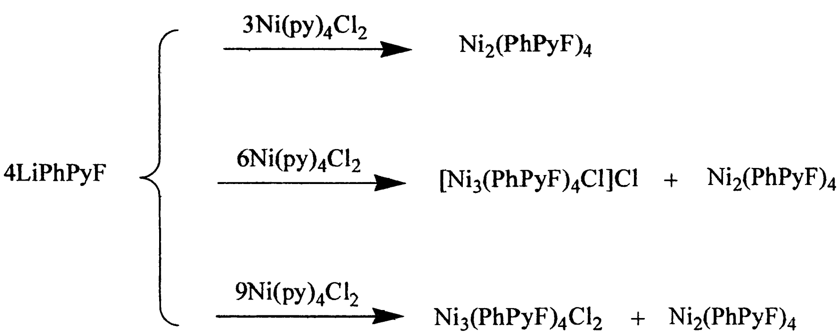
[1] The crystal structure of this compound showed an octahedral arrangement with two neutral HPhPyF ligands chelating to the nickel atom and two MeCN molecules *cis* to each other.



Scheme 4.

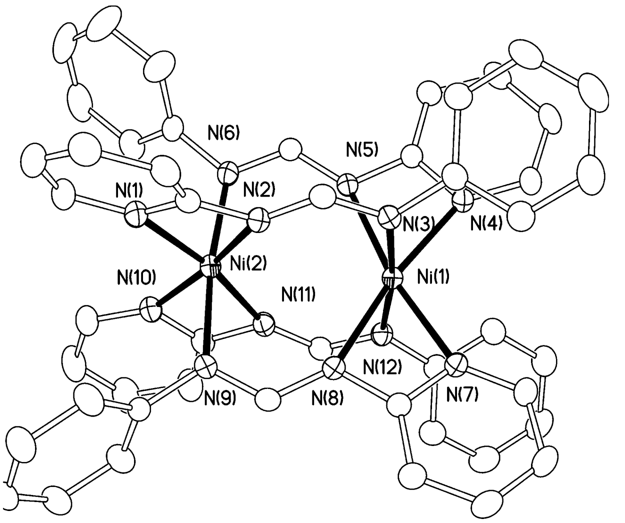


Fig. 1. The molecular structure of $Ni_2(PhPyF)_4$ (**1**) with ellipsoids shown at the 45% probability level. Hydrogen atoms are omitted for clarity. Selected bond distance (Å): Ni(1)–N(3), 2.091(1); Ni(1)–N(4), 2.116(1); Ni(1)–N(5), 2.181(1); Ni(1)–N(7), 2.097(1); Ni(1)–N(8), 2.185(1); Ni(1)–N(12), 2.094(1).

geometry, and the nickel–nickel separation is long, about 3.41 Å, indicating there is no metal–metal bonding. There are two kinds of structural motifs commonly expected for dimetal complexes with four tridentate ligands and the general formula $M_2L_4$. In one type the two metal atoms form a direct bond and thus there is a short separation while the third donor atom on each L ligand is dangling as in $Cr_2(dpa)_4$ [2a]. The addition of a third metal atom to the dimetal unit is then possible by taking advantage of the third dangling nitrogen donor. In the second type, the structural motif for $M_2L_4$ is that seen here in the structure of $Ni_2(PhPyF)_4$. There is no dangling nitrogen donor as all of 12 nitrogen atoms in the four ligands coordinate to the metal atoms and two distorted octahedra are formed. Such a compound is thermodynamically very stable, and, it is very difficult to introduce an additional metal atom. This accounts for the low yield of trinickel complexes and the common presence of dinickel species in these reactions. This structural motif has been seen before in the compounds $V_2(dpa)_4$ [20b] $Mo_2(D\text{-}PhIP)_4(BF_4)_2$.

For the following discussion of trinickel complexes, it is important to compare some previously determined trinickel chain, $Ni_3^{6+}$, structures with those being reported here. For this purpose, critical dimensions for two such molecules are listed in Table 2 along with those for the new compounds **2**, **4**, and **5**.

The molecular structure of $Ni_3(PhPyF)_4(MeCN)_2(BF_4)_2$ (**2**) is shown in Fig. 2. The compound crystallizes in the $I4_1/a$ space group with a $C_2$ axis perpendicular to the linear trinickel chain and going through the central nickel atom. The chain is wrapped by four ligands in a *transoid* relationship and two MeCN molecules occupying the axial positions. The counterions are $BF_4^-$. The distance from the terminal nickel atom to the nitrogen atom of MeCN is 2.028(4) Å. This is relatively short compared to the $Ni-N_{MeCN}$ distance ($\approx 2.11$ Å) in the mononuclear compound *cis*-$Ni(PhPyF)_2(MeCN)_2(BF_4)_2$ (**3**), and is indicative of a strong metal–ligand interaction. The nickel–nickel separation is slightly longer (0.04 Å) than that in $Ni_3(dpa)_4Cl_2$, but the Ni–N distances follow the same trend as those in $Ni_3(dpa)_4Cl_2$, The Ni–N distances for the central nickel atoms arc considerably shorter than those for the terminal ones with average values in $Ni_3(PhPyF)_4(MeCN)_2^{2+}$ being 1.888[3] and 2.089[3] Å, respectively. These values are almost identical to those in $Ni_3(dpa)_4Cl_2$. This strongly suggests that they may have a similar electronic structure. Based on the earlier results for $Ni_3(dpa)_4Cl_2$, the trinickel chain in $Ni_3(PhPyF)_4(MeCN)_2^{2+}$ can be interpreted as having two five-coordinate terminal nickel atoms, each possessing two unpaired electrons while the central nickel atom is $d^8$, square-planar, and diamagnetic. There is probably antiferromagnetic coupling between the terminal magnetic centers, but this has not been investigated because of the low yield of compound **2**.

The core structure of $[Ni_3(PhPyF)_4Cl]Cl$ (**4**) (Fig. 3) reveals a linear $Ni_3^{6+}$ chain supported by a set of four PhPyF anions. The compound crystallizes in the space group $P4/ncc$ with a $C_4$ axis passing through the trinickel chain. There is only one Cl anion in an axial

Table 2
Comparison of important parameters in the neutral linear trinickel compounds

| Mean values [a] | $Ni_3(dpa)_4Cl_2$ | $(TBA)_2Ni_3(BPAP)_4$ | $Ni_3(PhPyF)_4Cl_2$ (**5**) | $[Ni_3(PhPyF)_4Cl]Cl$ (**4**) | $Ni_3(PhPyF)_4(MeCN)_2(BF_4)_2$ (**2**) |
|---|---|---|---|---|---|
| Ni· · ·Ni (Å) | 2.43[8] | 2.368[1] | 2.5075(10), 2.5027(10) | 2.443(3), 2.454(3) | 2.469(5) |
| Ni–X axial (Å) | 2.34[6] | – | 2.317[2] | 2.331(5) | 2.0284(4) |
| Ni–N, central (Å) | 1.88[9] | 1.906[7] | 1.893[5] | 1.911(7) | 1.889[3] |
| Ni–N outer, (Å) | 2.10[7] | 1.917[5] | 2.100[5] | 1.921(6) 2.129(7) | 2.090[3] |
| Overall torsion angle (°) | 51.0 | 30 | 40.4 | 30 | 40.5 |
| Ref. | [5c] | [9] | this work | this work | this work |

[a] Numbers within square brackets are e.s.d.s. of average values.

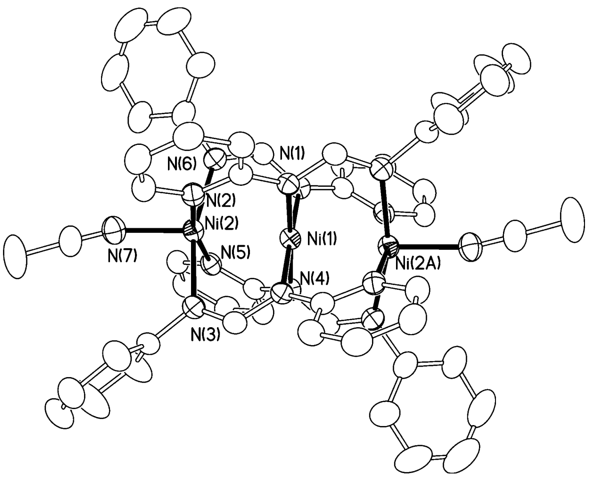


Fig. 2. Perspective view of $Ni_3(PhPyF)_4(MeCN)_2^{2+}$ in **2**. Atoms are drawn at 45% probability level and hydrogen atoms are omitted for clarity.

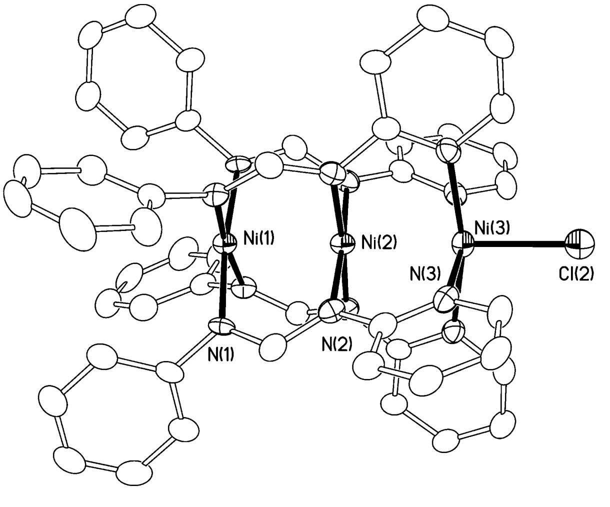


Fig. 3. A drawing of the cation $Ni_3(PhPyF)_4Cl^+$ in **4** showing a vacant axial site. Ellipsoids are drawn at the 45% probability level and hydrogen atoms are omitted.

position with the distance of 2.331(5) Å to the nickel atom; the other Cl anion, required to balance the charge, is not coordinated. The ligand arrangement is quite different from that in **2**, with all the ligands pointing in the same direction. Thus, all the pyridine rings are at one end of the molecule while all the phenyl groups are at other end. Despite this, the Ni–Ni distances of 2.443(3) A and 2.454(3) A are not significantly different and comparable to those in **2** and $Ni_3(dpa)_4Cl_2$, suggesting an absence of direct bonding between nickel atoms. Space-filling models of the two ends of $[Ni_3(PhPyF)_4Cl]^+$ are shown in Fig. 4. It is clear that the axial Cl anion fits on the end having pyridyl ring while there is not enough space for a Cl anion at the other end because of α hydrogen atoms on the phenyl rings.

The pattern of Ni–N distances in **4** is quite different from that in $Ni_3(dpa)_4Cl_2$, $Ni_3(PhPyF)_4Cl_2$ (**5**) and $[Ni_3(PhPyF)_4(CH_3CN)_2](BF_4)_2$ (**2**). In **4** there is only one outer nickel atom that is five-coordinate, and for that one the Ni–N distances are 2.129(7) Å. The Ni–N distances for the other four-coordinated outer nickel atom are 1.921(6) Å, and for the center four-coordinated nickel atom the Ni–N distance are all 1.911(7) Å. The central and the outer nickel atom devoid of axial ligation are $d^8$ and square-planar, and would be expected to be diamagnetic while the other outer nickel atom attached to a Cl anion should possess two unpaired electrons. This is consistent with magnetic measurement of compound **4** at room temperature, which shows a magnetic moment of 3.08 $\mu_B$.

Compound **5**, $Ni_3(PhPyF)_4Cl_2$, crystallizes in the space group $P4_32_12$ with the entire molecule on a general position. The structure (Fig. 5) consists of two

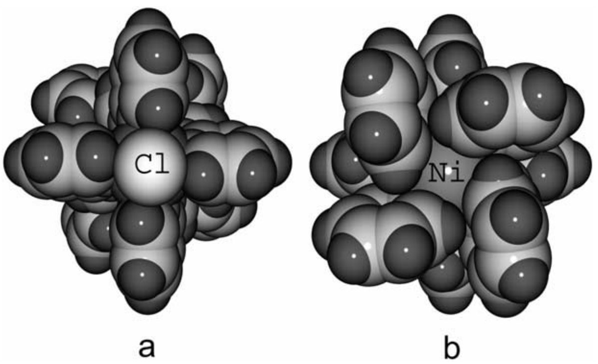


Fig. 4. Space-filling models showing the two ends of $[Ni_3(PhPyF)_4Cl]^+$ in **4**. Note that the α-hydrogen atoms of the phenyl rings in **b** obstruct the possible approach of a Cl anion forcing an empty axial site.

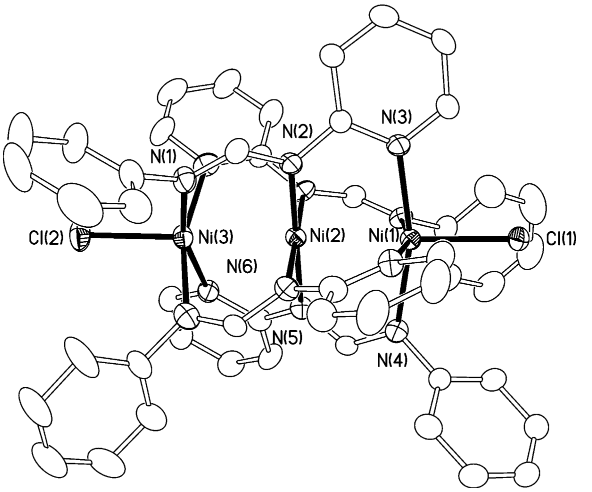


Fig. 5. A drawing of the molecular structure of $Ni_3(PhPyF)_4Cl_2$ (**5**). Ellipsoids are drawn at 45% probability level with hydrogen atoms omitted for clarity.

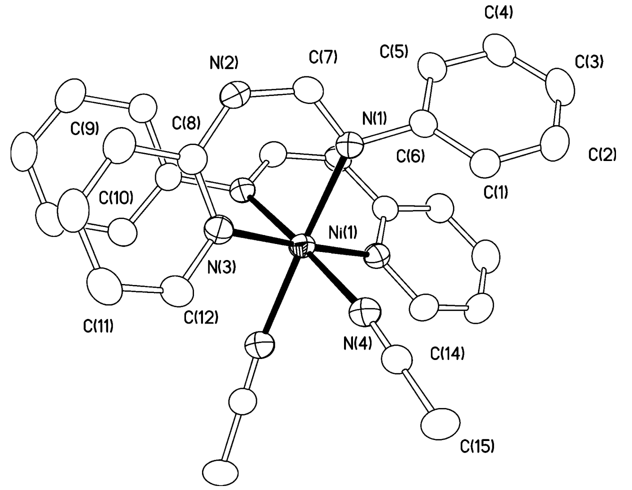


Fig. 6. A drawing of the cation in **3** with ellipsoids drawn at the 45% probability level. Hydrogen atoms are omitted. Selected bond distance (Å): Ni(1)–N(1), 2.113(2); Ni(1)–N(3): 2.099(2); Ni(1)–N(4), 2.113(2).

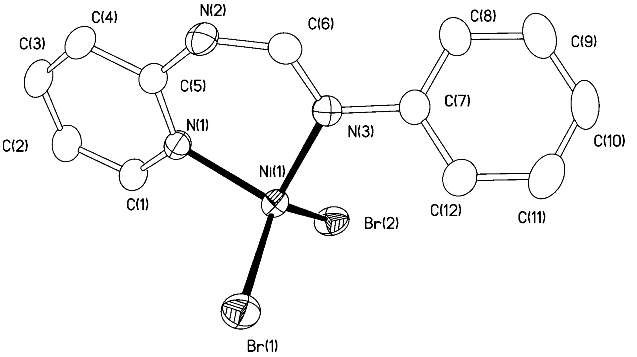


Fig. 7. The molecular structure of $Ni(HPhPyF)Br_2$ (**6**) showing the pseudo-tetrahedral environment. Ellipsoids are drawn at the 45% probability level with hydrogen atoms omitted. Selected bond distances (Å): Ni(1)–N(1), 1.982(2); Ni(1)–N(3), 1.959(2); Ni(1)–Br(1), 2.3402(5); Ni(1)–Br(2), 2.3719(5).

square pyramidal Ni(II) atoms at each end of the trinickel chain and one square-planar, central Ni(II) atom. The ligands are *cisoid* to each other, whereas in **2** they are *transoid*. The Ni···Ni distances are 2.5075(10) and 2.5027(10) Å. These values are 0.07 Å longer than those in the $Ni_3(dpa)_4Cl_2$ analogue. The Ni–N distances are similar to those in $Ni_3(PhPyF)_4(MeCN)_2^{2+}$ and $Ni_3(dpa)_4Cl_2$. Once again, the central nickel atom can be regarded as having a low-spin, square-planar geometry; while the two outer nickel atoms are in a triplet state, but because of the low yield magnetic measurements have not been made.

In all three new trinickel compounds, the PhPyF ligands are twisted. The torsion angles from one terminal nickel atom to the other terminal nickel atom range from 30 to 40.5°. Individual values are given in Table 2. The compounds with the smaller torsion angles of 30° are $(TBA)_2Ni_3(BPAP)_4$ 9 and **4**. The former does not show axial coordination while the latter has only one axial coordination site occupied. The others have two axially coordinated ligands. This is consistent with observations made on $Cr_3^{6+}$ compounds [19].

The structures of the mononuclear compounds **3** and **6** are given in Figs. 6 and 7, respectively. In the former, there are two neutral formamidines chelating the Ni atom which is also coordinated by two *cis* acetonitrile molecules. Compound **6** possesses one chelating formamidine and two Br anions creating a roughly tetrahedral environment around the nickel atom. This structure is reminiscent of that of $Co(Hdpa)Cl_2$ [21].

## 4. Supplementary material

Crystallographic data in CIF format for compounds **1**–**6** have been deposited at the Cambridge Crystallographic Data Center, CCDC Nos. CCDC 201 042–201 047, respectively. Copies of CIFs are available free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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## References

[1] F.A. Cotton, R.A. Walton, Multiple Bonds Between Metal Atoms, second ed., Oxford University Press, Oxford, 1993.

[2] See for example: (a) F.A. Cotton, L.M. Daniels, C.A. Murillo, X. Wang, Chem. Commun. (1998) 39;
(b) R. Clérac, F.A. Cotton, L.M. Daniels, K.R. Dunbar, C.A. Murillo, I. Pascual, Inorg. Chem. 39 (2000) 752;
(c) R. Clérac, F.A. Cotton, L.M. Daniels, K.R. Dunbar, T. Lu, C.A. Murillo, X. Wang, J. Am. Chem. Soc. 122 (2000) 2272;
(d) R. Clérac, F.A. Cotton, L.M. Daniels, K.R. Dunbar, C.A. Murillo, X. Wang, J. Chem. Soc., Dalton Trans. (2001) 386;
(e) S.-J. Shieh, C.-C. Chou, G.H. Lee, C.-C. Wang, S.-M. Peng, Angew. Chem., Int. Ed. Engl. 36 (1997) 56;
(f) S.-Y. Lai, W.-T. Lin, Y.-H. Chen, C.-C. Wang, G.-H. Lee, M.-H. Yang, M.-K. Leung, S.-M. Peng, J. Am. Chem. Soc. 121 (1999) 250.

[3] (a) F.A. Cotton, L.M. Daniels, C.A. Murillo, I. Pascual, J. Am. Chem. Soc. 119 (1997) 10223;
(b) R. Clérac, F.A. Cotton, K.R. Dunbar, C.A. Murillo, I. Pascual, Inorg. Chem. 39 (2000) 748.

[4] (a) E.-C. Yang, M.-C. Cheng, M. Tsai, S.-M. Peng, J. Chem. Soc., Chem. Commun. (1994) 2377;
(b) F.A. Cotton, L.M. Daniels, G.T. Jordan, IV, C.A. Murillo, J. Am. Chem. Soc. 119 (1997) 10377;
(c) R. Clérac, F.A. Cotton, L.M. Daniels, K.R. Dunbar, K. Kirschbaum, C.A. Murillo, A.A. Pinkerton, A.J. Schultz, X. Wang, J. Am. Chem. Soc. 122 (2000) 6226.

[5] (a) T.J. Hurley, M.A. Robinson, Inorg. Chem. 7 (1968) 33;
(b) S. Adulchecha, B.J. Hathaway, J. Chem. Soc., Dalton Trans. (1991) 993;
(c) R. Clérac, F.A. Cotton, L.M. Daniels, K.R. Dunbar, C.A. Murillo, I. Pascual, X. Wang, Inorg. Chem. 38 (1999) 2655.

[6] (a) L.-P. Wu, P. Field, T. Morrissey, C. Murphy, P. Nagle, B. Hathaway, C. Simmons, P.J. Thornton, J. Chem. Soc., Dalton Trans. (1990) 3835;
(b) J.F. Berry, F.A. Cotton, P. Lei, C.A. Murillo, Inorg. Chem. 42 (2003) 377.

[7] J.-T. Sheu, C.-C. Lin, I. Chao, C.-C. Wang, S.-M. Peng, Chem. Commun. (1996) 315.

[8] R. Clérac, F.A. Cotton, L.M. Daniels, K.R. Dunbar, C.A. Murillo, H. Zhou, Inorg. Chem. 39 (2000) 3414.

[9] F.A. Cotton, L.M. Daniels, P. Lei, C.A. Murillo, X. Wang, Inorg. Chem. 40 (2001) 2778.

[10] (a) C.-C. Wang, W.-C. Lo, C.-C. Chou, G.H. Lee, J.-M. Chen, S.-M. Peng, Inorg. Chem. 37 (1998) 4059;
(b) S.-Y. Lai, C.-C. Wang, Y.H. Chen, C.-C. Lee, Y.-H. Liu, S.-M. Peng, J. Chin. Chem. Soc. (Taipei) 46 (1999) 477;
(c) S.-M. Peng, C.-C. Wang, Y.-L. Jang, Y.-H. Chen, F.-Y. Li, C.-Y. Mou, M.-K. Leung, J. Magn. Magn. Mater. 209 (2000) 80.

[11] (a) J.F. Berry, F.A. Cotton, L.M. Daniels, C.A. Murillo, J. Am. Chem. Soc. 124 (2002) 3212;
(b) J.F. Berry, F.A. Cotton, L.M. Daniels, C.A. Murillo, X. Wang, Inorg. Chem., in press.

[12] F.A. Cotton, P. Lei, C.A. Murillo, L.-S. Wang, Inorg. Chim. Acta 349 (2003) 165.

[13] G.T. Long, P.J. Clarke, Inorg. Chem. 17 (1978) 1394.

[14] J.A.J. Jarris, R.H.B. Mais, P.G. Owston, J. Chem. Soc. (1968) 1473.

[15] SMART V5.05, Software for the CCD Detector System, Bruker Analytical X-ray Systems, Madison, WI, 1998.

[16] SAINTPLUS V5.05, Software for the CCD Detector System, Bruker Analytical X-ray Systems, Madison, WI, 1998.

[17] SADABS, Program for absorption correction using SMART CCD based on the method of Blessing: R.H. Blessing. Acta Crystallogr., A, 51 (1995) 33.

[18] G.M. Sheldrick, Acta Crystallogr., A 46 (1990) 467.

[19] F.A. Cotton, P. Lei, C.A. Murillo, Inorg. Chim. Acta 349 (2003) 173.

[20] (a) F.A. Cotton, L.M. Daniels, C.A. Murillo, H.-C. Zhou, Inorg. Chim. Acta 305 (2000) 69;
(b) F.A. Cotton, C.A. Murillo, H.-C. Zhou, Inorg. Chem. 39 (2000) 3261.

[21] F.A. Cotton, L.M. Daniels, G.T. Jordan, IV, C.A. Murillo, Polyhedron 17 (1998) 589.