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Synthesis and theoretical analysis of the structures and bonding in five new neutral square planar bis[2,4-di(aryl)-1,3,5-triazapentadienato]nickel(II) complexes

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This paper is dedicated to Professor Paul J. Taylor on the occasion of his retirement.

Abstract

Solvothermal reactions in methanol of nickel acetate tetrahydrate, $Ni(OAc)_2 \cdot 4H_2O$, with benzonitrile derivatives $NC(C_6H_4)X$, where X is one of the electron withdrawing substituents –CN, $–NO_2$, or $–CF_3$, located at the *m*- or *p*-positions relative to –CN, yield complexes of the general formula $Ni\{HN{=}C(R){–}N{=}C(R){–}NH\}_2$. More specifically, 3-nitrobenzonitrile, 4-nitrobenzonitrile, 1,3-dicyanobenzene, 1,4-dicyanobenzene, and ααα-trifluoro-*p*-toluonitrile are found to react with $Ni(OAc)_2 \cdot 4H_2O$ to yield $Ni\{HN{=}C(R){–}N{=}C(R){–}NH\}_2$, where R = $3\text{-}(NO_2)C_6H_4$, $4\text{-}(NO_2)C_6H_4$, $3\text{-}(CN)C_6H_4$, $4\text{-}(CN)C_6H_4$, or $4\text{-}(CF_3)C_6H_4$, respectively. Analogous reactions of nitriles lacking electron withdrawing groups do not occur under similar conditions. Solid-state structures have been determined for the complexes with *p*-NO_2, *p*-CN, and *p*-CF_3 substituents on the phenyl rings. In addition, we describe density functional theory (DFT) and natural bonding orbital theory (NBO) studies on a simplified analog of these compounds, aimed at understanding their molecular bonding. It is shown that the new compounds for which solid-state structures have been determined are model examples of coordination compounds containing robust ω-bonds.

Keywords: Crystal structures; Coordination compounds; Metallocycles; Condensation reactions; Density functional theory; Natural bonding orbital theory

1. Introduction

Metal-promoted reactions of nitriles have, as a whole, proven to be to be a significant tool for the synthesis of a variety of diverse compounds, and several reviews on this topic have appeared in the literature within the past decade [1–8]. Our work in this area has focused on the application of solvothermal (solventothermal) synthetic techniques to reactions of nitriles with transition metal sources as a means for preparation of both molecular and extended-structure coordination compounds. Recently, we have been studying reactions of nickel(II) acetate tetrahydrate, $Ni(OAc)_2 \cdot 4H_2O$ (**1**), with various benzonitrile derivatives in order to understand the reaction system and elucidate structural features of the resultant mononuclear metal complexes.

In 2001 Kryatov reported the solid state structure of the neutral complex $Ni\{HN{=}C(Me){–}N{=}C(Me){–}NH\}_2$ (**2**), and its synthesis from acetonitrile and nickel complex $[Ni_2(\mu{–}OH)_2(tmpa)_2]^{2+}$ {tmpa = tris(2-pyridylmethyl)amine} [9]. The formation and structural characterization of cationic (protonated) analogs of **2** by reaction of $NiCl_2 \cdot 2H_2O$ with nitriles in the presence of 2-propanone oxime has also been reported [10]. Several other structurally related nickel

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complexes have been reported [11–18]. Importantly, the latter were prepared through reactions of pre-formed ligands with metal ion sources rather than through in situ condensation of a simple molecule such as acetonitrile. As a whole, the ligands in nickel complex **2** and its analogs referred to above are representative of a common structural motif in transition metal coordination chemistry [19].

The previously reported synthesis of **2** is specific for the bimetallic nickel reagent employed by the authors, since a series of simpler (monometallic) Ni(II) starting materials failed to react with acetonitrile under analogous conditions [9]. In the reactions that produce cationic analogs of **2**, a simple monometallic nickel(II) starting material is employed, but the presence of a ketoxime is required [10]. In an extension of our earlier investigations involving reactions of simple transition metal complexes with aromatic nitriles [20,21], we have found that **1** reacts in methanol solution under mild solvothermal conditions with benzonitrile derivatives $NC(C_6H_4)X$, where X is one of the electron withdrawing substituents $–CN$, $–NO_2$, or $–CF_3$, located at either the *meta* or *para* positions relative to $–CN$, to yield neutral complexes analogous to **2**. No other reagents are added to the reaction mixture.

2. Experimental

2.1. Methods and instrumentation

Infrared spectra were recorded on a Midac Prospect-IR instrument. The MALDI mass spectrum was recorded on a Bruker Reflex II instrument, employing α-cyano-4-hydroxycinnamic acid as a matrix. All NMR spectra were recorded on a Bruker AC-300 instrument operating at 75.468 MHz for ^{13}C spectra and 300 MHz for ^{1}H spectra. Because of the limited solubility of **3**–**7** and $^{13}C–^{19}F$ coupling in **7**, large numbers of scans were needed to record useful spectra. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, USA or Desert Analytics, Tucson, AZ, USA. Methanol (anhydrous, 99.8%), ethanol (absolute, anhydrous), toluene (HPLC grade), diethyl ether (anhydrous), ethylenediamine (99%), nickel(II) acetate tetrahydrate (99.998%), 4-nitrobenzonitrile (97%), 3-nitrobenzonitrile (98%), 1,4-dicyanobenzene (98%), 1,3-dicyanobenzene (98%), 4-cyanophenol (95%), ααα-trifluoro-*p*-toluonitrile (99%), benzonitrile (99.9%), KBr, NMR solvents $\{DCON(CD_3)_2$ and $(CD_3)_2SO\}$ and silica gel (230–400 mesh) were obtained from commercial sources and used as received. Reported yields are based upon nickel starting material **1**.

2.2. Synthesis

2.2.1. General synthetic methods

Unless otherwise stated, all manipulations were performed under aerobic conditions. Syntheses were carried out by combining the reactants with 5.0 mL of methanol in glass vials, stirring, and then placing the vials in PTFE-lined autoclaves and heating at 110 °C. Reaction times were five days unless otherwise stated. Unless otherwise indicated, products were isolated by filtration on fritted glass discs and washed with methanol, toluene, and diethyl ether then dried.

2.2.2. Preparation of bis[2,4-di(m-nitrophenyl)-1,3,5-triazapentadienato]nickel(II) (3)

In a typical reaction, **1** (25.6 mg, 0.103 mmol) and 3-nitrobenzonitrile (91.0 mg, 0.614 mmol) reacted to produce thin yellow crystals, unsuitable for X-ray crystallography. Attempts to obtain diffraction-quality crystals via a variety of recrystallization techniques and manipulation of reaction conditions were unsuccessful. Yield: 19.7 mg, 28.0%. *Anal.* Calc. for $C_{28}H_{20}N_{10}O_8Ni$: C, 49.22; H, 2.95; N, 20.50. Found: C, 49.24; H, 2.87; N, 20.33%. IR (KBr): 3349(w), 3328(w), 3092(w), 2922(w), 2859(w), 1982(w), 1913(w), 1847(w), 1737(w), 1591(m), 1544(sh), 1525(vs), 1508(vs), 1480(vs), 1466(sh), 1422(s), 1347(vs), 1299(vs), 1274(sh), 1176(m), 1097(m), 1078(sh), 1044(m), 1000(w), 958(w), 913(m), 872(m), 810(m), 803(m), 749(s), 722(s), 703(vs), 670(w), 637(w) cm^{-1}. ^{1}H NMR $(DCON(CD_3)_2)$: 7.84 [t, 4H, H(Ar), $J_{HH} =$ 8 Hz overlapping with s(br), 4H, NH], 8.41 [m, 4H, H(Ar)], 8.60 [m, 4H, H(Ar)], 8.91 [t, 4H, H(Ar), $J_{HH} = 1.9$ Hz] ppm. ^{13}C NMR $(DCON(CD_3)_2)$: 163.3, 149.2, 140.7, 134.9, 130.9, 125.7, 123.1 ppm.

2.2.3. Preparation of bis[2,4-di(p-nitrophenyl)-1,3,5-triazapentadienato]nickel(II) (4)

In a typical reaction, **1** (34.0 mg, 0.137 mmol) and 4-nitrobenzonitrile (121.3 mg, 0.819 mmol) reacted to produce well formed red needle-shaped crystals suitable for single crystal X-ray analysis. The crystals were collected by filtration on a fritted glass disc, washed with copious quantities of methanol, ethanol, toluene, and diethyl ether and dried to afford **4** (36.1 mg, 38.7%). *Anal.* Calc. for $C_{28}H_{20}N_{10}O_8Ni$: C, 49.22; H, 2.95; N, 20.50. Found: C, 48.88; H, 3.13; N, 20.26%. IR (KBr): 3361(w), 3347(w), 3335(m), 3113(w), 3094(w), 3077(w), 2935(w), 2840(w), 2446(w), 1597(m), 1549(vs), 1524(vs), 1480(vs), 1431(s), 1397(m), 1344(vs), 1297(s), 1237(w), 1185(w), 1158(w), 1109(s), 1040(m), 1011(s), 944(w), 865(s), 853(s), 813(s), 779(w), 768(w), 743(w), 707(vs), 665(m), 651(w), 628(w) cm^{-1}. ^{1}H NMR $(DCON(CD_3)_2)$: 7.72 [s(br), 4H, NH], 16.45 [s, 16H, H(Ar)] ppm. ^{13}C NMR $(DCON(CD_3)_2)$: 163.3, 149.6, 145.0, 129.9, 124.4 ppm.

2.2.4. Preparation of bis[2,4-di(m-cyanophenyl)-1,3,5-triazapentadienato]nickel(II) (5)

In a typical reaction, **1** (34.0 mg, 0.136 mmol) and 1,3-dicyanobenzene (104.9 mg, 0.819 mmol) reacted to produce extremely thin orange crystals, unsuitable for X-ray crystallography. Attempts to obtain diffraction-quality crystals via a variety of recrystallization techniques and manipulation of reaction conditions were unsuccessful. Elemental analysis and ^{1}H NMR both indicated that the crystals consisted of **5** co-crystallized with one molecule of methanol per molecule of the nickel complex. Yield of **5** · CH_3OH: (27.5 mg, 31.8% based upon starting **1**). *Anal.* Calc. for $C_{33}H_{24}N_{10}ONi$: C, 62.38; H, 3.81; N, 22.05. Found: C, 62.50; H, 3.49; N, 22.28%. IR (KBr): 3439(br), 3330(s), 3073(w), 3039(w), 2851(w), 2226(s), 1971(w), 1907(w), 1838(w), 1808(w), 1720(m), 1603(m), 1558(m), 1547(vs), 1488(sh), 1476(vs), 1441(sh), 1404(vs), 1320(sh), 1300(s), 1259(w), 1216(w), 1199(w), 1173(m), 1131(w), 1093(m), 1054(m), 1000(w), 980(w), 956(w), 905(m), 805(s), 782(w), 730(vs), 679(s), 622(m) cm^{-1}. ^1H NMR $((CD_3)_2SO)$: 7.36 [s(br), 4H, NH], 7.72 [t, 4H, H(Ar), $J_{HH} = 8$ Hz], 7.99 [m, 4H, H(Ar)], 8.34 [m, 4H, H(Ar)], 8.42 [t, 4H, H(Ar), $J_{HH} = 1.5$ Hz] ppm. ^{13}C NMR $((CD_3)_2SO)$: 161.6, 138.7, 133.5, 132.3, 130.9, 129.6, 118.7, 111.3 ppm. MALDI-MS $m/z = 603.0$ (calc. 603.1), $C_{32}H_{21}N_{10}Ni^+$.

2.2.5. Preparation of bis[2,4-di(p-cyanophenyl)-1,3,5-triazapentadienato]nickel(II) (6)

In a typical reaction, **1** (8.6 mg, 0.035 mmol) and 1,4-dicyanobenzene (26.1 mg, 0.204 mmol) reacted to produce **6** as an orange-yellow solid. Yield: 3.0 mg, 14%. The very small scale was employed in order to minimize the presence of solid byproducts and unreacted 1,4-dicyanobenzene that otherwise complicate the purification process for **6**. *Anal.* Calc. for $C_{32}H_{20}N_{10}Ni$: C, 63.71; H, 3.34; N, 23.22. Found: C, 63.76; H, 2.93; N, 22.68%. IR (KBr): 3329(m), 3076(w), 2951(w), 2229(s), 1931(w), 1807(w), 1716(m), 1607(m), 1580(s), 1536(vs), 1489(s), 1457(vs), 1397(s), 1306(s), 1288(sh), 1248(w), 1199(m), 1161(w), 1115(m), 1042(m), 1017(m), 973(w), 945(m), 854(s), 832(w), 798(w), 761(s), 699(m), 645(w) cm^{-1}. ^1H NMR $((CD_3)_2SO)$: 7.47 [s(br), 4H, NH], 7.96 [d, 8H, H(Ar), $J_{HH} = 9$ Hz], 8.15 [d, 8H, H(Ar), $J_{HH} = 9$ Hz] ppm. ^{13}C NMR $((CD_3)_2SO)$: 161.9, 141.7, 132.2, 128.2, 118.7, 112.3 ppm. Layering of diethyl ether above an ethylenediamine solution of **6**, prepared by heating a mixture of ethylenediamine and **6** to reflux under argon, resulted over the course of several days in the formation of single crystals suitable for X-ray analysis.

2.2.6. Preparation of bis[2,4-di(p-trifluoromethylphenyl)-1,3,5-triazapentadienato]nickel(II) (7)

In a typical reaction, **1** (25.9 mg, 0.104 mmol) and ααα-trifluoro-*p*-toluonitrile (104.7 mg, 0.6119 mmol) reacted over the course of two weeks to produce yellow needle-shaped crystals of **7**, co-crystallized with two molar equivalents of the starting nitrile and three molar equivalents of methanol as established by X-ray analysis. These crystals were re-dissolved in diethyl ether and the resulting solution was loaded onto a 2.54 × 20 cm silica gel column. A broad pale yellow band eluted in diethyl ether and contained **7** along with some of the nitrile starting material. Removal of all traces of ααα-trifluoro-*p*-toluonitrile was accomplished by heating at approximately 110 °C under dynamic vacuum over the course of two days to afford **7** (14.7 mg, 18.2%) as a pale yellow powder. *Anal.* Calc. for $C_{32}H_{20}F_{12}N_6Ni$: C, 49.58; H, 2.60; N, 10.84. Found: C, 49.53; H, 2.59; N, 10.78%. IR (KBr): 3348(m), 3075(w), 2963(w), 2937(w), 1618(m), 1594(m), 1541(s), 1523(sh), 1491(sh), 1474(s), 1435(sh), 1403(m), 1327(vs), 1313(sh), 1287(sh), 1261(w), 1238(w), 1170(s), 1124(s), 1111(s), 1069(s), 1038(m), 1015(s), 980(sh), 945(w), 856(s), 830(m), 773(m), 745(m), 693(s), 634(w), 626(w) cm^{-1}. ^1H NMR $((CD_3)_2SO)$: 7.46 [s(br), 4H, NH], 7.85 [d, 8H, H(Ar), $J_{HH} = 8$ Hz], 8.16 [d, 8H, H(Ar), $J_{HH} = 8$ Hz] ppm. ^{13}C NMR $((CD_3)_2SO)$ 162.4, 141.7 [q, $J_{FC} = 1$ Hz], 129.9 [q, $J_{FC} = 32$ Hz], 128.2, 125.1 [q, $J_{FC} = 5$ Hz], 124.2 [q, $J_{FC} = 272$ Hz] ppm. The quartet at 141.7 ppm was partially resolved.

2.3. X-ray crystallography

2.3.1. General methods for data collection, structure solution, and refinement

Evaluation of crystals and data collection were performed on a Bruker CCD-1000 diffractometer with Mo Kα ($\lambda = 0.71073$ Å) radiation and a diffractometer to crystal distance of 4.9 cm. Crystals were selected under oil under ambient conditions, attached to nylon loops, and mounted in a stream of cold nitrogen at 100(2) K, then centered in the X-ray beam. Data were collected to survey the reciprocal space to the extent of a full sphere to a resolution of 0.80 Å. The resulting highly redundant datasets were corrected for Lorentz and polarization effects. Absorption corrections were based upon fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [22]. Successful solutions for all structures by the direct methods provided most non-hydrogen atoms from the *E*-maps. The remaining non-hydrogen atoms were located in alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculations at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Further details regarding the determination of structures for **4, 6**, and **7** are given in the following sections and in Table 1.

2.3.2. Determination of the structure of 4

A red crystal with approximate dimensions 0.46 × 0.38 × 0.16 mm^3 was selected. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3° in a 6° range about ω with an exposure time of 30 s per frame. A total of 53 reflections were obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 6160 strong reflections from the actual data collection. A total of 10430 data were harvested by collecting three sets of frames with 0.25° scans in ω with an exposure time of 90 s per frame.

Table 1
Crystal data and structure refinement [22] for **4**, **6**, and **7**

Compound	**4**	**6** (plus co-crystallized solvent)	**7** (plus co-crystallized nitrile and solvent)
Empirical formula	$C_{28}H_{20}N_{10}NiO_8$	$C_{32}H_{20}N_{10}Ni \cdot$ solvent	$C_{50}H_{36}F_{18}N_8NiO_2$
Formula weight	683.25	603.29	1181.58
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2/n$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	5.3646(7)	7.1236(14)	8.2162(6)
b (Å)	11.4362(15)	11.398(2)	10.8864(7)
c (Å)	21.972(3)	11.659(2)	14.5746(10)
α (°)	90	69.297(3)	83.4660(10)
β (°)	91.781(2)	82.724(4)	83.4320(10)
γ (°)	90	85.182(3)	70.4900(10)
Volume (Å^3)	1347.4(3)	877.6(3)	877.6(3)
Z	2	1	1
D_{calc} (Mg/m^3)	1.684	1.142	1.613
Absorption coefficient (mm^{-1})	0.796	0.586	0.519
$F(000)$	700	310	598
Crystal size (mm^3)	$0.46 \times 0.38 \times 0.16$	$0.43 \times 0.32 \times 0.20$	$0.46 \times 0.35 \times 0.31$
θ Range for data collection (°)	2.57–26.39	1.88–26.38°	1.99–26.38
Index ranges	$-6 \leqslant h \leqslant 6$, $-14 \leqslant k \leqslant 14$, $-27 \leqslant l \leqslant 27$	$-7 \leqslant h \leqslant 8$, $-14 \leqslant k \leqslant 14$, $-14 \leqslant l \leqslant 14$	$-10 \leqslant h \leqslant 10$, $-13 \leqslant k \leqslant 13$, $-18 \leqslant l \leqslant 18$
Reflections collected	10430	5510	12539
Independent reflections [R_{int}]	2716 [0.04381]	3369 [0.0326]	4944 [0.0223]
Completeness to $\theta =$ 26.38 (%)	98.2	93.8	99.2
Absorption correction	multiscan with SADABS	multiscan with SADABS	multiscan with SADABS
Maximum and minimum transmission	0.8832 and 0.7110	0.8917 and 0.7866	0.8556 and 0.7962
Refinement method	full-matrix least-squares on F_2	full-matrix least-squares on F_2	full-matrix least-squares on F_2
Data/restraints/parameters	2716/0/214	3369/0/197	4944/73/369
Goodness-of-fit on F_2	1.123	1.097	1.047
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0559$, $wR_2 = 0.1261$	$R_1 = 0.0462$, $wR_2 = 0.1214$	$R_1 = 0.0486$, $wR_2 = 0.1200$
R indices (all data)	$R_1 = 0.0703$, $wR_2 = 0.1310$	$R_1 = 0.0500$, $wR_2 = 0.1239$	$R_1 = 0.0568$, $wR_2 = 0.1264$
Largest difference peak and hole (e Å^{-3})	0.660 and −0.380	1.014 and −0.378	0.945 and −0.942

The systematic absences in the diffraction data for **4** were uniquely consistent for the space group $P2_1/n$ that yielded chemically reasonable and computationally stable results of refinement [22]. The complex occupies a crystallographic inversion center.

2.3.3. Determination of the structure of 6

A red crystal with approximate dimensions $0.43 \times 0.32 \times 0.20$ mm^3 was selected. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3° in a 6° range about ω with an exposure time of 10 s per frame. A total of 44 reflections were obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 4508 strong reflections from the actual data collection. A total of 5510 data were harvested by collecting three sets of frames with 0.3° scans in ω with an exposure time of 30 s per frame.

The systematic absences in the diffraction data for **6** were consistent for the space groups $P\bar{1}$ and $P1$. The E-statistics strongly suggested the centrosymmetric space group $P\bar{1}$ that yielded chemically reasonable and computationally stable results of refinement [22]. The complex occupies a crystallographic inversion center.

There was one solvate molecule present in the asymmetric unit. A significant amount of time was invested in attempting to identify and refine the disordered molecule. Bond length restraints were applied to model this molecule but the resulting isotropic displacement coefficients suggested that the molecule was mobile. In addition, the refinement was computationally unstable. Option SQUEEZE of program PLATON [23,24] was used to correct the diffraction data for diffuse scattering effects and to identify the solvate molecule. PLATON calculated the upper limit of volume that can be occupied by the solvent molecule to be 263.4 Å^3, or 30.0% of the unit cell volume. The program calculated 57 electrons in the unit cell for the diffuse species.

2.3.4. Determination of the structure of 7

A yellow crystal with approximate dimensions $0.46 \times 0.35 \times 0.31$ mm^3 was selected. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3° in a 6° range about ω with the exposure time of 10 s per frame. A total of 54 reflections were obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 5820 strong reflections from the actual data collection. A total of 12 539 data were harvested by collecting four sets of frames with 0.25° scans in ω with an exposure time of 103 s per frame.

The systematic absences in the diffraction data were consistent for the space groups $P\bar{1}$ and $P1$. The E-statistics strongly suggested the centrosymmetric space group $P\bar{1}$ that yielded chemically reasonable and computationally stable results of refinement [22]. The metal complex occupies a crystallographic inversion center. There are also two molecules of methanol and two molecules of ααα-trifluoro-*p*-toluonitrile per molecule of the Ni complex in the unit cell. The trifluoromethyl group on C(8) is disordered over three positions in a 44:43:13 ratio and was refined with an idealized geometry.

3. Results and discussion

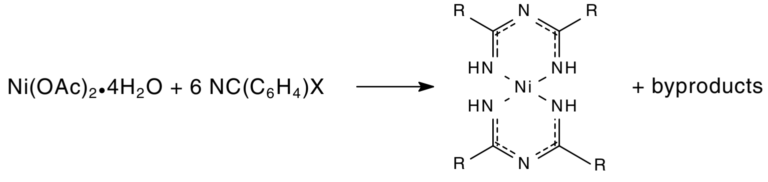
3.1. Preparation of compounds 3–7

Five neutral metallocyclic complexes have been prepared in "one-pot" syntheses employing reactions of **1** with six molar equivalents of benzonitrile derivatives substituted with the strong electron withdrawing groups –CN, $-NO_2$, or $-CF_3$ at the *meta* or *para* positions relative to the reacting cyano groups in the starting nitrile. The reaction and generalized structure for the products are shown in Scheme 1.

The formation of these compounds represents a generalization of the acetonitrile condensation reaction involving nickel reported in the literature [9] in that a simple monometallic nickel precursor is employed, rather than the (bimetallic) $[Ni_2(\mu\text{-}OH)_2(tmpa)_2]^{2+}$. Further, five new nitriles are observed to undergo reactions analogous to that observed for acetonitrile in the previous work. In contrast to the original report, solvothermal synthesis in an (apparently) non-reactive solvent is employed in the formation of **3**–**7**, rather than a solvolysis reaction occurring at ambient or slightly elevated temperature. An additional and perhaps more important factor contributing to our results is the use of aromatic nitriles (benzonitrile derivatives) bearing strongly electron-withdrawing substituents at *meta* or *para* positions relative to the reacting nitrile functional group. It appears that the presence of these electron withdrawing groups is required for the reaction represented in Scheme 1 to occur under the conditions we employ. The reaction was not observed (as judged by the lack of any solids or observable color change in the product mixture following treatment under conditions similar to those under which **3**–**7** were synthesized) for unsubstituted benzonitrile or 4-cyanophenol, a benzonitrile derivative bearing an electron-donating –OH group at the *para* position relative to –CN. This provides some further support for generalization of the mechanism described by the authors of the original report [9] to the present work. This mechanism was proposed to involve ligand formation via condensation of an acetamidine molecule, generated in situ, with either the acetonitrile solvent, acetamide, or another acetamidine molecule. All three of these possibilities are reasonable, and the proposed mechanism is indeed based upon solid literature precedent [18,25–31]. Regardless of the identity of the species reacting with acetamidine, attack at the C═N carbon by nitrogen is required for the ultimate formation of the ligand. Clearly, this step of the overall process would be facilitated by any group that decreases the electron density at the carbon atom under attack.

3.2. Characterization of products and X-ray structural determinations on 4, 6 and 7

We were successful in obtaining diffraction-quality single crystals of **4**, **6**, and **7** and determining their structures via single crystal X-ray methods. Molecular drawings of **4**, **6**, and **7** are shown in Figs. 1–3, respectively. Selected bond distances and angles are presented in Table 2. The compositions of **3** and **5**, which do not crystallize well, are inferred by comparison of their infrared and NMR spectra to those of **4**, **6**, and **7**, and by elemental analysis. We also acquired a MALDI (matrix assisted laser desorption/ionization) mass spectrum for **5**, which co-crystallizes with one molecule of methanol per molecule of **5**, that clearly showed a peak corresponding to the molecular ion



3: $NC(C_6H_4)X$ = 3-nitrobenzonitrile, R = $3\text{-}(NO_2)C_6H_4$
4: $NC(C_6H_4)X$ = 4-nitrobenzonitrile, R = $4\text{-}(NO_2)C_6H_4$
5: $NC(C_6H_4)X$ = 1,3-dicyanobenzene, R = $3\text{-}(CN)C_6H_4$
6: $NC(C_6H_4)X$ = 1,4-dicyanobenzene, R = $4\text{-}(CN)C_6H_4$
7: $NC(C_6H_4)X$ = α,α,α-trifluoro-p-toluonitrile, R = $4\text{-}(CF_3)C_6H_4$

Scheme 1.

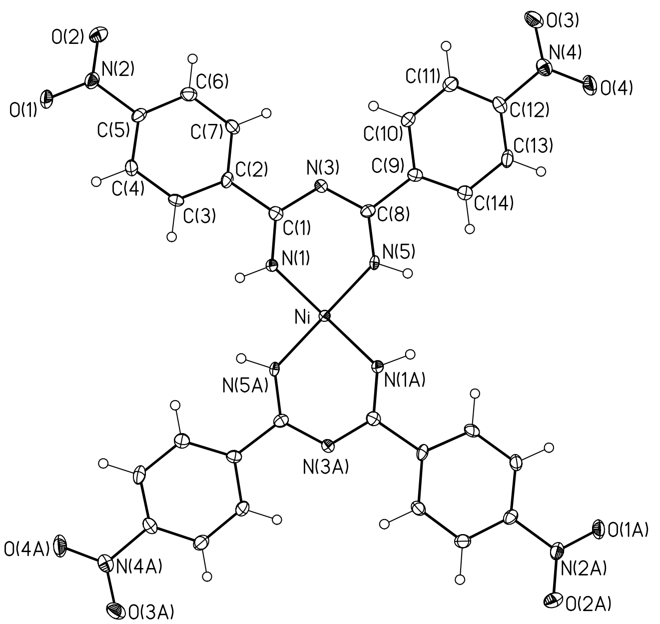


Fig. 1. A molecular drawing of **4** shown with 50% probability ellipsoids. Selected dihedral angles: N(1)–C(1)–C(2)–C(3) = 14.7(4)°, N(5)–C(8)–C(9)–C(14) = 16.6(4)°.

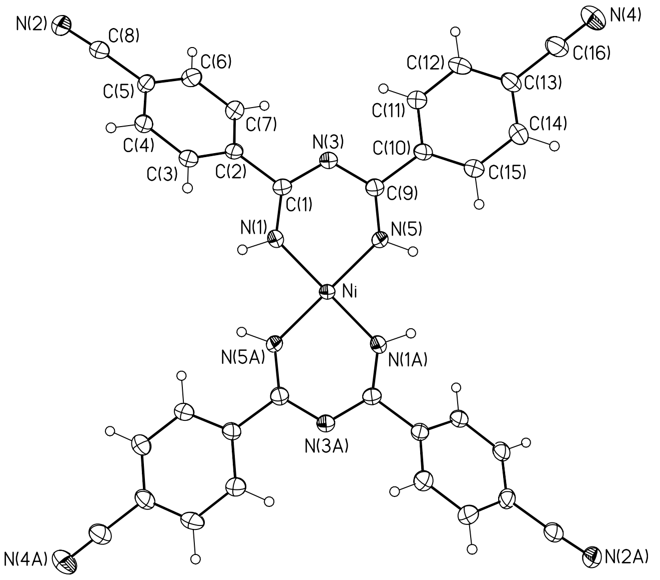


Fig. 2. A molecular drawing of **6** shown with 50% probability ellipsoids. Selected dihedral angles: N(1)–C(1)–C(2)–C(3) = 41.6(3)°, N(5)–C(9)–C(10)–C(15) = −19.0(3)°.

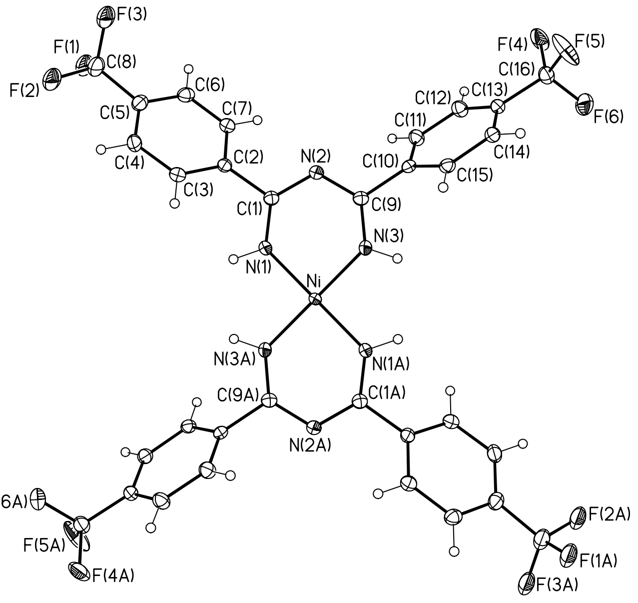


Fig. 3. A molecular drawing of **7** shown with 50% probability ellipsoids. Only the preferred orientation of the disordered CF_3 group at C(8) is shown. Selected dihedral angles: N(1)–C(1)–C(2)–C(3) = 37.0(3)°, N(3)–C(9)–C(10)–C(15) = −51.4(3)°.

plus one proton. The observed isotopic pattern closely matched a calculated isotopic pattern, providing further support for the formulation of **5**.

Complexes **4**, **6**, and **7** occupy crystallographic inversion centers in their respective lattices, thus idealized molecular symmetry (D_{2h}) exceeds crystallographic symmetry (C_i) in these cases. While the coordination environment of each Ni atom is square planar, the entire complexes deviate from planarity as the phenyl substituents are tilted relative to the six-membered heterocycles Ni–N–C–N–C–N. Interestingly, in the three complexes the phenyl rings are tilted in two different ways; in **4**, atoms C(3) and C(14) are on the opposite sides of the nickel heterocycle Ni–N–C–N–C–N, Fig. 1, whereas in **6** and **7** the corresponding atoms (C(3) and C(15) in **6**, C(3) and C(15) in **7**) are on the same side of the nickel coordination plane. The Ni–N bond distances and N–Ni–N angles are in good agreement with those reported for three relevant Ni(II) complexes, Table 2. The N–Ni–N bite angles are slightly smaller than the interligand N–Ni–N angles in all cases, but all angles are close to 90°.

3.3. Density functional theory and natural bonding orbital studies

In order to understand the molecular bonding in the complexes described here we performed density functional theory (DFT) studies of a simplified analog of **3**–**7**, bis[1,3,5-triazapentadienato]nickel(II) (**8**), Fig. 4 at the PBE1PBE/6-311+G* level of theory [32]. The geometrical parameters of the optimized structure are in excellent agreement with experimental data from this work and other selected papers, Table 2. Calculated metal–ligand distances can exceed the experimental values by over 0.1 Å, however in the case of **4**, **6**, and **7** the DFT distances differ from the observed parameters only by an average of 0.009 Å, emphasizing a good choice of the level of theory.

The metal–ligand donor–acceptor interactions in **8** were studied with the natural bonding orbital theory analysis [33]. In the 16-electron complex **8** the central Ni metal is sd-hybridized with the hybridized orbitals oriented at 90° to each other. The two pairs of opposite Ni–N bonds are best described as 3-center 4-electron *hyper*valent ω-bonds.

Table 2
Literature, experimental, and theoretical parameters for selected square-planar complexes of Ni(II)

	Ni–N (Å)	N–Ni–N(bite) (°)	N–Ni–N (interligand) (°)	Reference
Bis[2,4-di(dimethylamino)-1,3,5-triazapentadienato]nickel(II)	1.848 1.854	88.81	91.19	[11]
Bis[2,4-dimethyl-1,3,5-triazapentadienato]nickel(II)	1.850 1.851	89.31	90.69	[9]
Bis[2,4-diamino-1,3,5-triazapentadienato]nickel(II)	1.852 1.859	88.62	91.38	[15]
4	1.846(2) 1.853(2)	89.37(11)	90.63(11)	This work
6	1.8570(17) 1.8650(17)	89.60(7)	90.40(7)	This work
7	1.847(2) 1.856(2)	89.14(9)	90.86(9)	This work
8	1.862[a]	88.80[a]	91.20[a]	This work

[a] Calculated values for **8** with D_{2h} geometry.

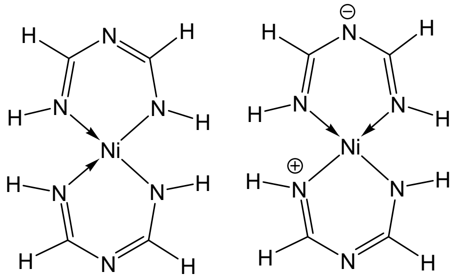


Fig. 4. Two possible resonance structures of **8**. Both structures show pairs of 3-center, 4-electron *ω*-bonds. A routine natural resonance theory analysis of **8** failed due to a very high number of energetically similar possible resonance structures.

The ω-bonds are usually highly ionic, collinear, and characterized by very strong $n_{\mathrm{L}} \rightarrow \sigma^{*}_{\mathrm{M-L}}$ donor–acceptor interactions. All of these criteria are met in **8**. The Ni–N bonds are strongly polarized toward the nitrogen atoms, consistent with the natural charge of +0.95 on the nickel and −0.78 on each of the four nitrogen atoms. The N–Ni–N triads are perfectly linear, which is also observed experimentally in **4**, **6**, and **7**, where the Ni atoms occupy crystallographic inversion centers. The donor–acceptor interaction between the sp^2 nitrogen lone pair and the antibonding orbital of the opposite Ni–N σ-bond is an enormous 103.3 kcal/mol for each N–Ni–N triad. Thus, complexes **4**, **6**, and **7** are model examples of coordination compounds containing robust ω-bonds.

4. Conclusions

Five new neutral substituted [1,3,5-triazapentadienato]nickel(II) complexes have been prepared via one-pot solvothermal reactions and characterized. The preparation of these compounds generalizes the previously reported acetonitrile condensation reaction [9] and suggests that the synthetic procedures discussed here may be useful in the simple preparation of a variety of similar neutral 1,3,5-triazapentadienato complexes substituted with electron withdrawing groups. It has also been shown here that the new compounds for which solid-state structures have been determined are model examples of coordination compounds containing robust ω-bonds.

5. Supplementary material

Crystallographic data for the structures of compounds **4**, **6**, and **7** have been deposited with the Cambridge Crystallographic Data Centre as CCDC271166, CCDC271167, and CCDC271168, respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: int. code +44 1223 336 033, e-mail: data_request@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk.

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References

[1] R.A. Michelin, M. Mozzon, R. Bertani, Coord. Chem. Rev. 147 (1996) 299.
[2] A.W. Parkins, Platinum Met. Rev. 40 (1996) 169.
[3] Z.N. da Rocha, G. Chiericato Jr., E. Tfouni, Adv. Chem. Ser. (1997) 297.
[4] M. Hvastijová, J. Kohout, J.W. Buchler, R. Boča, J. Kožíšek, L. Jäger, Coord. Chem. Rev. 175 (1998) 17.
[5] T. Ghaffar, A.W. Parkins, J. Mol. Catal. A 160 (2000) 249.
[6] V.Yu. Kukushkin, A.J.L. Pombeiro, Chem. Rev. 102 (2002) 1771.
[7] J.L. Eglin, Comments Inorg. Chem. 23 (2002) 23.
[8] M.L. Kuznetsov, Russ. Chem. Rev. 71 (2002) 265.
[9] S.V. Kryatov, A.Y. Nazarenko, M.B. Smith, E.V. Rybak-Akimova, J. Chem. Soc., Chem. Commun. (2001) 1174.

[10] M.N. Kopylovich, A.J.L. Pombeiro, A. Fischer, L. Kloo, V.Yu. Kukushkin, Inorg. Chem. 42 (2003) 7239.

[11] M. Zhu, L. Lu, P. Yang, X. Jin, Acta Crystallogr., Sect. E 58 (2002) m272.

[12] M.M. Bishop, L.F. Lindoy, P. Turner, Supramol. Chem. 14 (2002) 179.

[13] M.M. Bishop, L.F. Lindoy, B.W. Skelton, A. White, Supramol. Chem. 13 (2001) 293.

[14] M.M. Bishop, A.H.W. Lee, L.F. Lindoy, P. Turner, Polyhedron 22 (2003) 735.

[15] M.M. Bishop, L.F. Lindoy, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (2002) 377.

[16] J. Guo, W.-K. Wong, W.-Y. Wong, Eur. J. Inorg. Chem. (2004) 267.

[17] H. Kitamura, T. Ozawa, K. Jitsukawa, H. Masuda, H. Einaga, Mol. Cryst. Liq. Cryst. Sci. Technol. A 285 (1996) 281.

[18] R. Norrestam, Acta Crystallogr., Sect. C 40 (1984) 955.

[19] F.H. Allen, Acta Crystallogr., Sect. B 58 (2002) 380.

[20] K.J. Nelson, R.W. McGaff, D.R. Powell, Inorg. Chim. Acta 304 (2000) 130.

[21] C.D. Molek, J.A. Halfen, J.C. Loe, R.W. McGaff, J. Chem. Soc., Chem. Commun. (2001) 2644.

[22] Bruker-AXS. SADABS V.2.05, SAINT V.6.22, SHELXTL V.6.10 and SMART 5.622 Software Reference Manuals, Bruker-AXS, Madison, WI, USA, 2000–2003.

[23] A.L. Spek, Acta Crystallogr., Sect. A 46 (1990) C34.

[24] A.L. Spek, PLATON – A Multipurpose Tool, Utrecht University, Utrecht, 2003.

[25] M.G.B. Drew, P.C. Yates, J. Trocha-Grimshaw, K.P. McKillop, S.M. Nelson, J. Chem. Soc., Chem. Commun. (1985) 262.

[26] M. Ito, K. Sakai, T. Tsubomura, Y. Takita, Bull. Chem. Soc. Jpn. 72 (1999) 239.

[27] M. Ito, H. Kawano, T. Takeuchi, Y. Takita, Chem. Lett. (2000) 372.

[28] N.C. Stephenson, J. Inorg. Nucl. Chem. 24 (1962) 801.

[29] J.H. Forsberg, V.T. Spaziano, T.M. Balasubramanian, G.K. Liu, S.A. Kinsley, C.A. Duckworth, J.J. Poteruca, P.S. Brown, J.L. Miller, J. Org. Chem. 52 (1987) 1017.

[30] V. Robinson, G.E. Taylor, P. Woodward, M.I. Bruce, R.C. Wallis, J. Chem. Soc., Dalton Trans. (1981) 1169.

[31] K. Suematsu, Chem. Pharm. Bull. 32 (1984) 291.

[32] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN 03, Revision C.02, Gaussian Inc., Wallingford, CT, 2004.

[33] F. Weinhold, C.R. Landis, Valency and Bonding: A Natural Bond and Orbital Donor–Acceptor Perspective, Cambridge University Press, New York, 2005.