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1,3,5-Triazapentadiene Nickel(II) Complexes Derived from a Ketoxime-Mediated Single-Pot Transformation of Nitriles

Maximilian N. Kopylovich,[a] Alexander M. Kirillov,[a] Ekaterina A. Tronova,[a,b] Matti Haukka,[c] Vadim Yu. Kukushkin,[b] and Armando J. L. Pombeiro*[a]

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A series of cationic (2+) $[Ni\{HN{=}C(R)NHC(R){=}NH\}_2](X)_2$ {R = 4-(Cl)C_6H_4 (**1**), 3-(NC)C_6H_4 (**3**), 4-(NC)C_6H_4 (**4**) and Me (**7**); X = Cl^- (**1**, **3**, **4**) or $MeCOO^-{\cdot}H_2O$ (**7**)} and neutral $[Ni\{HN{=}C(R)NC(R){=}NH\}_2]$(solvate) {R = 3-(Cl)-4-py (**2**), 3-py (**5**) and 4-py (**6**); solvate = MeOH and/or H_2O; py = pyridyl} *N*,*N*-chelating bis(1,3,5-triazapentadiene/ato)nickel(II) $[Ni(tap)_2]^{2+/0}$ complexes has been easily generated by a ketoxime-mediated single-pot reaction of a nickel(II) salt [$NiCl_2{\cdot}2H_2O$ or $Ni(MeCOO)_2{\cdot}4H_2O$] with 4-chlorobenzonitrile, isophthalonitrile, terephthalonitrile, acetonitrile, 2-chloro-4-cyanopyridine, 3-cyanopyridine or 4-cyanopyridine, respectively. The obtained compounds have been characterized by IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, FAB-MS(+) or ESI-MS(+), elemental analyses and single-crystal X-ray diffraction [for **7** and solvated mono- {**1a**·$(Me_2CO)_{0.33}{\cdot}(MeOH)_{0.67}$} and bis-deprotonated (**2b**·$2Me_2CO$, **4b**·$CHCl_3$, **5b**·Me_2CO and **6b**·MeOH) products, formed upon recrystallization of **1**, **2**, **4**, **5** and **6**, respectively]. The crystal structures of all compounds bear similar monomeric $Ni(tap)_2$ units with a nearly square-planar geometry. In addition, the structure of **7** features the formation of infinite 1D zig-zag water–acetate chains $\{[(H_2O)_2(MeCOO)_2]^{2-}\}_n$, which multiply interact with the $[Ni(tap)_2]^{2+}$ cations to generate a 2D hydrogen-bonded supramolecular assembly.

Introduction

The coordination chemistry of 1,3,5-triazapentadienes (tap) is a topic of current interest,[1] as attested by the diversity of the synthesized members of this growing family of ligands and the increasing number of their structurally characterized complexes.[2] In particular, bis(1,3,5-triazapentadiene/ato) metal complexes $[M(tap)_2]$[3–6] structurally resemble phthalocyanines (compounds with a variety of uses in modern technologies)[7] and were recently applied in catalysis, photochemistry and supramolecular and materials chemistry.[5,6] However, most of the synthetic routes to tap derivatives are characterized by one or several of the following limitations: they (i) involve complicated multistep processes, (ii) require harsh reaction conditions, (iii) use expensive, uncommon and/or difficult-to-operate sensitive chemicals, (iv) show limited versatility and (v) exhibit low yields and selectivities.[3e,3f,4,5d,5e]

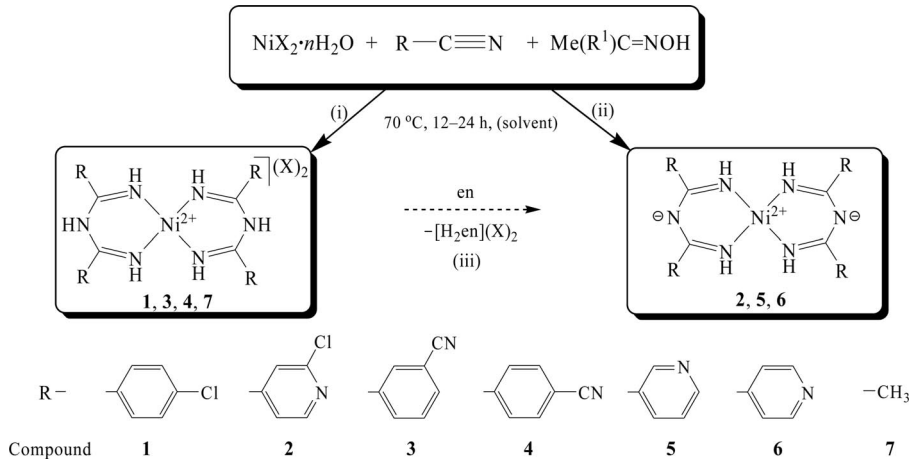
Within our general research line focused on metal-mediated transformations of nitriles,[8,9] we have reported a facile ketoxime-promoted route for symmetrical bis(1,3,5-triazapentadiene/ato) complexes of Ni^{II},[10] generated from a single-pot reaction of a nickel salt with an organonitrile. The important advantages of this method are its simplicity, use of inexpensive and commercially available chemicals, rather mild reaction conditions and good yields of products. With these features in mind, the current study aims to show the versatility and generality of such a method by extending the family of the thus prepared complexes to other examples, in particular, those functionalized with pyridyl substituents. Hence, we describe herein the easy synthesis and characterization of a series of symmetrical cationic (**1**, **3**, **4** and **7**) and neutral (**2**, **5** and **6**) *N*,*N*-chelating $[Ni(tap)_2]^{2+/0}$ complexes bearing various R substituents {R = 4-(Cl)C_6H_4, 3-(NC)C_6H_4, 4-(NC)C_6H_4, Me, 3-(Cl)-4-py, 3-py and 4-py, respectively}, derived from the corresponding organonitriles.

[a] Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, TU Lisbon,
Av. Rovisco Pais, 1049-001 Lisbon, Portugal
Fax: +351-218464455
E-mail: pombeiro@ist.utl.pt
[b] Department of Chemistry, St.Petersburg State University, 198504 Stary Petergof, Russian Federation
[c] University of Joensuu, Department of Chemistry, P. O. Box 111, 80101 Joensuu, Finland

Results and Discussion

Synthesis and Spectroscopic Characterization

A particular feature of our previously described Ni^{II}-ketoxime-mediated syntheses of tap ligands consisted of the use of excess liquid nitrile[10a] or liquid oxime[10b] as a reagent and solvent. However, in some cases, such a synthetic procedure failed. Hence, we searched for other solvents and found that acetone could be an appropriate choice. Thus, the reactions of nickel chloride dihydrate, in acetone at reflux, with 4 equiv. each of 2-propanone oxime and 4-chlorobenzonitrile (for **1**), isophthalonitrile (for **3**) or terephth-



Scheme 1. Ni-ketoxime-mediated synthesis of cationic and neutral bis(1,3,5-triazapentadiene/ato)nickel(II) complexes (crystallization solvent molecules are omitted and protolytic equilibria involving pyridyl N atoms are not shown for simplicity); en = $H_2NCH_2CH_2NH_2$.

alonitrile (for **4**) gave rise to a single-pot formation of the cationic (2+) bis(1,3,5-triazapentadiene)nickel(II) complexes with the general formula $[Ni\{HN{=}C(R)NHC(R){=}NH\}_2](Cl)_2$ [R = 4-(Cl)C_6H_4 (**1**), 3-(NC)C_6H_4 (**3**) and 4-(NC)C_6H_4 (**4**)] [reaction (i), Scheme 1].

A similar reaction but with nickel acetate tetrahydrate and acetonitrile as both solvent and reagent led to the formation of an analogous water-soluble complex $\{Ni[HN{=}C(Me)NHC(Me){=}NH]_2\}(MeCOO)_2{\cdot}2H_2O$ (**7**). However, if $Ni(MeCOO)_2{\cdot}4H_2O$ is treated, in 2-butanone oxime solution at 70 °C, with 2-chloro-4-cyanopyridine (for **2**), 3-cyanopyridine (for **5**) or 4-cyanopyridine (for **6**), the neutral bis(1,3,5-triazapentadienato)nickel(II) complexes $[Ni\{HN{=}C(R)NC(R){=}NH\}_2]$(solvate) [R = 3-(Cl)-4-py (**2**), 3-py (**5**) and 4-py (**6**); py = pyridyl; solvate = MeOH and/or H_2O] were isolated [reaction (ii), Scheme 1] after recrystallization in the presence of ethylenediamine; the latter base is needed for complete deprotonation of the central tap N atom and/or the pyridyl groups.

Although some related $Ni(tap)_2$ compounds with various symmetrical R substituents have already been reported, their synthetic procedures are different and more complicated (involving expensive chemicals, several reaction steps or rather harsh reaction conditions)[4,5d] than those reported here for compounds **1**–**7**. All the products obtained were isolated as air-stable solids in ca. 81–47% yield (on the basis of the Ni salt) and characterized by IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, FAB-MS(+) or ESI-MS(+), elemental analyses and single-crystal X-ray diffraction {for **7** and solvated mono- [**1a**·$(Me_2CO)_{0.33}$·$(MeOH)_{0.67}$] and bis-deprotonated (**2b**·$2Me_2CO$, **4b**·$CHCl_3$, **5b**·Me_2CO and **6b**·MeOH) products derived upon recrystallization of the corresponding complexes **1**, **2**, **4**, **5** and **6**, respectively}.

The complexes initially isolated in the cationic form (**1**, **3**, **4** and **7**) can be transformed to the corresponding neutral species if treated (recrystallized) with ethylenediamine [reaction (iii), Scheme 1]. In general, 1,3,5-triazapetadienato complexes are easier to dissolve and recrystallize, and, therefore, the majority of X-ray analyses were undertaken for the bis-deprotonated (**2b**·$2Me_2CO$, **4b**·$CHCl_3$, **5b**·Me_2CO and **6b**·MeOH) or monodeprotonated [**1a**·$(Me_2CO)_{0.33}$·$(MeOH)_{0.67}$] derivatives (see below).

The ketoxime (propanone oxime or butanone oxime) plays an important role in the synthesis of compounds **1**–**7**, since the reactions between the nickel(II) salts and the organonitriles do not occur in the absence of ketoxime. Furthermore, nitriles do not react with a ketoxime in the absence of a nickel(II) salt. Most probably, upon nucleophilic addition to the nitrile (NCR), the ketoxime facilitates its hydrolytic conversion into ammonia and the amidine $RC(=NH)NH_2$ (the latter formed upon coupling of NH_3 and NCR).[4b,9b] The thus generated amidine further reacts with a ligated nitrile to give rise to the 1,3,5-triazapentadiene/ato products.[4d,5d] Such a transformation can take place through the formation of an intermediate nickel(II) complex derived from the double addition of the ketoxime to the nitrile ligand, as proposed earlier by some of us for the ketoxime-mediated conversion of phthalonitriles into phthalocyanines and for related Ni^{II}-ketoxime-mediated processes.[6,9a,10]

The IR spectra of **1**–**7** show typical[4,10] ν(NH), ν(C=N) and δ(NH) vibrations with maxima in the ranges of 3295–3125, 1690–1650 and 1565–1460 cm^{-1}, respectively, while strong and broad ν(OH) bands [3480–3350 cm^{-1}] of the crystallization MeOH and/or H_2O molecules also appear in the spectra of compounds **5**, **6** and **7**. In addition, complexes **3** and **4** feature characteristic ν(C≡N) vibrations at ca. 2230 cm^{-1}. The monoprotonated molecular ions $[M + H]^+$ are detected with the expected isotopic distribution patterns in the positive mass spectra of the neutral complexes **2**, **5** and **6**. However, the $[M - 2Cl - H]^+$ or $[M - 2MeCOO - H]^+$ are the heaviest fragments detected in the spectra of **1**, **3**, **4** or **7**. The ^1H and $^{13}C\{^1H\}$ NMR spectra reveal the expected resonances at typical chemical shifts for the tap ligands and show features that are common for this type of complexes.[4,6,10] The elemental analyses are consistent with the proposed formulations, which are also supported by X-ray crystallography.

X-ray Crystal Structures

The single-crystal X-ray analyses show that all the characterized compounds possess rather similar cationic (**1a**, **7**) or neutral (**2b**, **4b**, **5b**, **6b**) monomeric bis(1,3,5-triazapentadiene/ato) units with an almost square-planar coordination environment around the central nickel(II) atom. The ellipsoid plots for the structures of **1a**, **2b**, **5b** and **7** are depicted in Figure 1, while their selected bond parameters are summarized in Table 1. Figures 2 and 3 represent the water–acetate chain and a 2D hydrogen-bonded supramolecular layer identified in the structure of **7**. As representative examples, the structures of **2b** and **7** are discussed below in detail.

The molecular structure of **2b**·2Me_2CO is composed of the neutral [Ni{HN=C[3-(Cl)-4-py]NC[3-(Cl)-4-py]=NH}$_2$] units (Figure 1b) with two acetone molecules of crystallization per formula unit. The centrosymmetric tetracoordinate Ni1 atom possesses an almost square-planar coordination geometry that is filled by two symmetry equivalent 1,3,5-triazapentadienato(1–) ligands acting as bidentate *N*,*N*-chelators. Their binding through the almost similar Ni1–N1 [1.8472(16) Å] and Ni1–N3 [1.8551(17) Å] bonds involves the six-membered Ni1–N1–C1–N2–C7–N3 ring with the almost right-angled N1–Ni1–N3 bite angle [89.66(7)°]. Other bond angles within the Ni(tap) core (Table 1) vary from 119.02(17) [C1–N2–C7] to 129.34(14)° [Ni1–N3–C7]. The N1–C1 [1.312(3) Å] and N3–C7 [1.304(3) Å] bonds are shorter (by ca. 0.03 Å) than N2–C1 [1.342(3) Å] and N2–C7 [1.347(2) Å], which thus reveals a lack of significant delocalization within the 1,3,5-triazapentadienatonickel(II) cores. Interestingly, the two symmetry non-equivalent 3-(Cl)-4-py rings exhibit different spatial orientations. While one ring (with the N5 py atom) is coplanar with the Ni1–N1–C1–N2–C7–N3 fragment (Figure 1b), the second 3-(Cl)-4-py ring (with the N4 py atom) is significantly bent out of the NiN_4 core plane. In general, most of the bonding parameters in **2b** (Table 1) do not significantly differ from the values found in related Ni(tap)$_2$ complexes.[4,6a,10]

The crystal structure of **7** bears the [Ni{HN=C(Me)-NHC(Me)=NH}$_2$]$^{2+}$ cation (Figure 1d), two acetate anions and two water molecules of crystallization. The cation features two symmetry-equivalent neutral tap ligands in which the central N2 atoms are protonated. The ligands adopt an essentially square-planar coordination environment around the centrosymmetric Ni1 centre, where the methyl protons are the only atoms lying out of the main plane. The lengths of the N1–C1 [1.288(3) Å] and N3–C3 [1.289(3) Å] bonds are indicative of their double-bond character and are

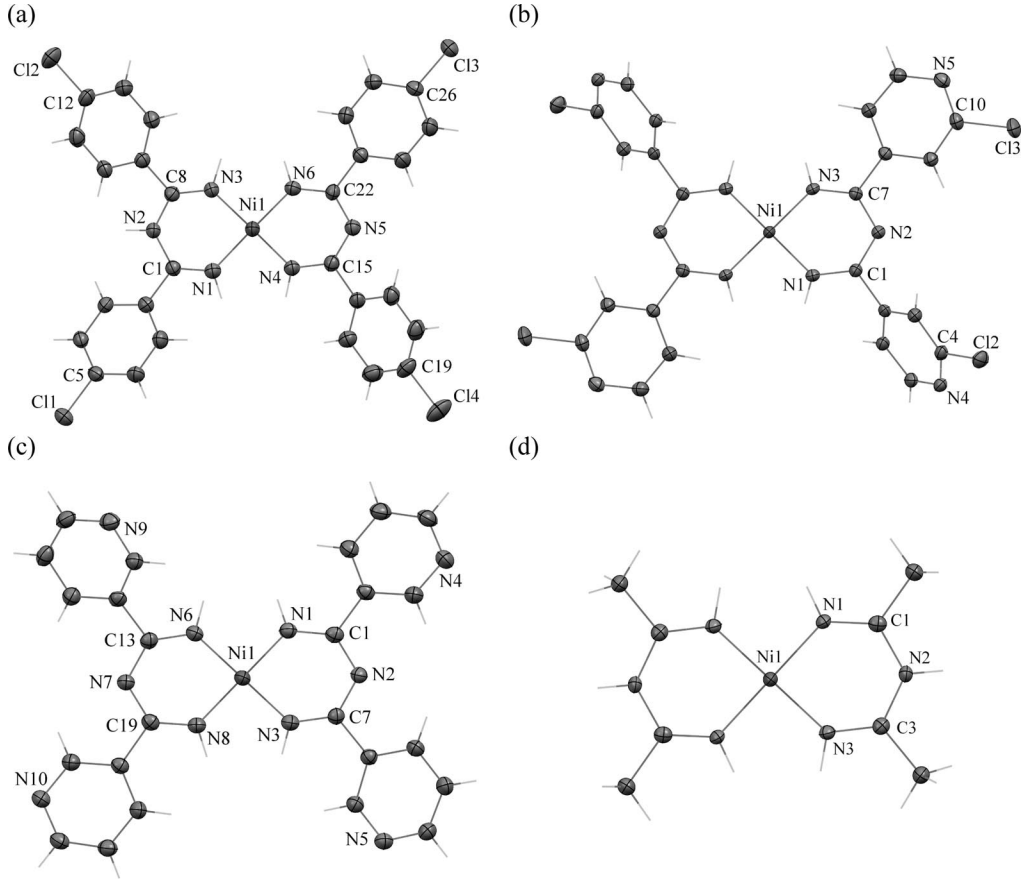


Figure 1. Crystal structures of (a) **1a**, (b) **2b**, (c) **5b** and (d) **7** with a partial atom labelling scheme Thermal ellipsoids are drawn at the 50% probability level. Counterions and crystallization solvent molecules are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for **1a**, **2b**, **5b** and **7**.[a]

1a			
Ni1–N1	1.866(3)	N5–C15	1.346(5)
Ni1–N3	1.871(3)	N5–C22	1.340(5)
Ni1–N4	1.838(3)	N6–C22	1.320(5)
Ni1–N6	1.848(3)	N1–Ni1–N3	89.98(14)
N1–C1	1.284(5)	N4–Ni1–N1	89.05(15)
N2–C1	1.378(5)	N4–Ni1–N3	178.80(15)
N2–C8	1.377(5)	N4–Ni1–N6	89.58(15)
N3–C8	1.287(5)	N6–Ni1–N1	178.41(15)
N4–C15	1.307(5)	N6–Ni1–N3	91.38(14)
2b			
Ni1–N1	1.8472(16)	N3–C7	1.304(3)
Ni1–N3	1.8551(17)	N1–Ni1–N3	89.66(7)
N1–C1	1.312(3)	N1–Ni1–N1^{i}	180.0
N2–C1	1.342(3)	N1–Ni1–N3^{i}	90.34(7)
N2–C7	1.347(2)		
5b			
Ni1–N1	1.866(2)	N7–C13	1.351(3)
Ni1–N3	1.869(2)	N7–C19	1.352(3)
Ni1–N6	1.861(2)	N8–C19	1.323(3)
Ni1–N8	1.8616(19)	N1–Ni1–N3	89.94(9)
N1–C1	1.319(3)	N8–Ni1–N1	178.34(9)
N2–C1	1.349(3)	N6–Ni1–N8	89.56(9)
N2–C7	1.350(3)	N6–Ni1–N3	178.74(9)
N3–C7	1.311(3)	N8–Ni1–N3	90.24(9)
N6–C13	1.313(3)	N6–Ni1–N1	90.30(9)
7			
Ni1–N1	1.8601(16)	N3–C3	1.289(3)
Ni1–N3	1.8537(16)	N1–Ni1–N3	90.42(7)
N1–C1	1.288(3)	N1–Ni1–N3^{ii}	89.58(7)
N2–C3	1.366(2)	N1–Ni1–N1^{ii}	180.0
N2–C1	1.368(3)		

[a] Symmetry codes: (i) $-x$, $-y$, $-z$; (ii) $-x+1$, $-y$, $-z+1$.

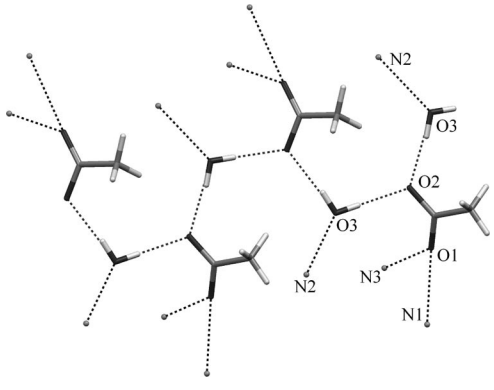


Figure 2. Perspective representation (arbitrary view) of infinite 1D water–acetate hydrogen-bonded chains $\{[(H_2O)_2(MeCOO)_2]^{2-}\}_n$ identified in the crystal structure of **7**. Hydrogen bonds D–H···A [d(D···A) (Å), D–H–A (°)]: within water–acetate chain, O3–H3A···O2^{i} [2.763(2), 176.5], O3–H3B···O2^{ii} [2.716(2), 168.1]; between water–acetate chain and $[Ni\{HN{=}C(Me)NHC(Me){=}NH\}_2]^{2+}$ units, N1–H1N···O1^{iii} [2.876(2), 174.6], N2–H2N···O3 [2.730(2), 175.0], N3–H3N···O1^{iv} [2.875(2), 157.3]. Symmetry codes: (i) x, y, $z-1$; (ii) x, $-y+1$, $z-1/2$; (iii) x, $-y$, $z-1/2$; (iv) $-x+1$, y, $-z+3/2$.

shorter (by ca. 0.06 Å) than those of N2–C1 [1.368(3) Å] and N2–C3 [1.366(2) Å] (Table 1). All the above bond lengths in **7** are similar to the corresponding bond lengths [1.296(3) and 1.360(3) Å] found in the related bis-deprotonated complex $[Ni\{HN{=}C(Me)NC(Me){=}NH\}_2]\cdot 2H_2O$.[4b]

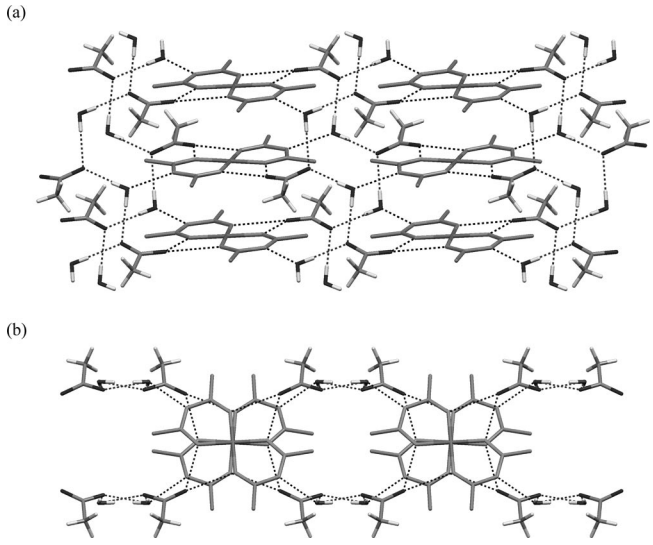


Figure 3. Fragments of the crystal packing diagram of **7** showing (a) front and (b) side views of a 2D supramolecular layer, generated by multiple interlinkages of six neighbouring $[Ni\{HN{=}C(Me)NHC(Me){=}NH\}_2]^{2+}$ units (H atoms omitted) with six water–acetate $\{[(H_2O)_2(MeCOO)_2]^{2-}\}$ chains through extensive hydrogen bonding. Representations (a) and (b) correspond to the rotated views along the *a* and *c* axis, respectively. For an atom labelling scheme and H-bonding parameters, see Figure 2.

Following our interest in the identification and analysis of different water clusters[5a,10b,11] and supramolecular assemblies driven by water molecules,[12] within the matrices of metal complexes, we have analyzed the extensive hydrogen-bonding interactions in the structure of **7**. It has been found that the two symmetry-equivalent acetate anions and two water molecules of crystallization (per formula unit) present in the structure of **7** generate infinite 1D zig-zag water–acetate chains (Figure 2) through repeating O–H···O hydrogen bonds. Hence, each O3 atom of a water molecule acts as a double H-bond donor simultaneously bridging with two neighbouring acetate anions through the O3–H3A···O2^{i} [2.763(2) Å, 176.5°] and O3–H3B···O2^{ii} [2.716(2) Å, 168.1°] hydrogen bonds (hereinafter all the symmetry codes are those defined in the caption of Figure 2). In addition, the thus generated anionic water–acetate chains extensively interact with the $[Ni\{HN{=}C(Me)NHC(Me){=}NH\}_2]^{2+}$ cations, by accepting all the NH protons of $[Ni(tap)_2]^{2+}$ through strong repeating N2–H2N···O3 [2.730(2) Å, 175.0°], N1–H1N···O1^{iii} [2.876(2), 174.6] and N3–H3N···O1^{iv} [2.875(2), 157.3] hydrogen bonds (Figure 2). These multiple interactions give rise to the formation of a 2D supramolecular layer, as represented in Figure 3. In this layer, the Ni1···Ni1 separations between neighbouring cations (Figure 3a) are 3.869(3) and 11.619(3) Å, which are equal to the 1/2*c* and *b* unit cell parameters, respectively (Table 2).

Table 2. Crystal data for compounds **1a**, **2b**, **4b**, **5b**, **6b** and **7**.

	1a·$(Me_2CO)_{0.33}$·$(MeOH)_{0.67}$	**2b**·$2Me_2CO$	**4b**·$CHCl_3$	**5b**·Me_2CO	**6b**·MeOH	**7**
Empirical formula	$C_{29.67}H_{25.67}Cl_5N_6NiO$	$C_{30}H_{28}Cl_4N_{10}NiO_2$	$C_{33}H_{21}Cl_3N_{10}Ni$	$C_{27}H_{26}N_{10}NiO$	$C_{26}H_{28}N_{10}NiO_2$	$C_{12}H_{28}N_6NiO_6$
Formula mass	718.20	761.13	722.66	565.29	571.29	411.11
Temperature [K]	110(2)	120(2)	110(2)	120(2)	120(2)	120(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$C2/c$
a [Å]	15.3578(5)	12.4661(3)	7.1312(6)	14.8509(19)	11.5810(5)	21.3175(13)
b [Å]	13.6747(6)	6.62390(10)	11.4789(11)	10.4411(15)	6.8970(2)	11.6190(7)
c [Å]	15.7276(6)	20.4146(6)	11.5562(13)	16.665(3)	16.3240(7)	7.7378(3)
α [°]	90	90	68.261(4)	90	90	90
β [°]	99.528(2)	104.569(2)	82.678(5)	98.541(3)	94.694(2)	107.214(3)
γ [°]	90	90	84.247(7)	90	90	90
V [Å^3]	3257.4(2)	1631.52(7)	870.08(15)	2555.4(7)	1299.49(9)	1830.71(17)
Z	4	2	1	4	2	4
$\rho_{calcd.}$ [Mg m^{-3}]	1.464	1.549	1.379	1.469	1.460	1.492
μ (Mo-K_a) [mm]$^{-1}$	1.040	0.969	0.827	0.802	0.792	1.101
No. of collected reflections	31719	25944	5466	40008	20920	14712
No. of independent reflections	6352	3730	2848	5871	2968	2476
$R_{int.}$	0.0657	0.0425	0.0680	0.0747	0.0514	0.0665
GOF	1.066	1.069	1.044	1.054	1.100	1.037
Final R_1,[a] wR_2[b] ($I \geq 2\sigma$)	0.0553, 0.1348	0.0327, 0.0750	0.0919, 0.2203	0.0421, 0.0968	0.0415, 0.0925	0.0395, 0.0709

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Conclusion

In this study, we have further extended the versatility of our previously described Ni^{II}-ketoxime-mediated system[10] towards the single-pot transformations of various organonitriles, thus opening up an easy entry to a series of cationic and neutral bis(1,3,5-triazapentadiene/ato)nickel(II) complexes **1**–**7**. The advantages of this synthetic procedure with respect to prior work[3e,3f,4,5d,5e] include the simplicity, commercial availability and relatively low cost of the chemicals involved, rather mild reaction conditions and high yields and selectivities. Further, compounds **2**–**6** can be considered as a novel type of metalloligands capable of forming new heteropolynuclear metal species upon further complexation. We also anticipate that some metal-mediated reactions of the pendant CN groups of **3** and **4** might lead to further assembly of the nickel species.

The present work also widens the family of structurally characterized examples[2,4,5d,6a,10] of $Ni(tap)_2$ complexes. The analysis of the crystal structure of **7** led to the identification of infinite 1D water–acetate chains $\{[(H_2O)_2(MeCOO)_2]^{2-}\}_n$ that play an important role in the formation of a 2D supramolecular assembly through extensive hydrogen-bonding interactions. In this regard, one should mention that the investigation and analysis of water–acetate clusters and polymeric assemblies remains poorly explored,[13] in spite of their widespread presence in various environments.[2,13] Moreover, the present type of $\{[(H_2O)_2(MeCOO)_2]^{2-}\}_n$ chain also extends to other examples of the growing number and diversity of water-containing associates identified[10b] in the crystal matrices of $Ni(tap)_2$ complexes.

Future research towards the application of the obtained compounds in catalysis and crystal engineering, as well as the extension of the present ketoxime-mediated transformations to other metal centres and functionalized nitrile substrates, will be pursued.

Experimental Section

General Materials and Procedures: All synthetic work was performed in air. The reagents and solvents were obtained from commercial sources and used as received, i.e. without further purification or drying. $NiCl_2·2H_2O$ was prepared according to a previously described procedure.[10a] C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico, TU Lisbon. Melting points were determined with a Leica Gallen III instrument. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (*m*-NBA) matrices of the samples with 8 keV (ca. 1.18×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved by using CsI. Electrospray mass spectra were carried out with an ion-trap Varian 500-MS LC ion trap mass spectrometer equipped with an electrospray (ESI) ion source. The solutions in methanol were continuously introduced into the mass spectrometer source with a syringe pump at a flow rate of 10 μL/min. The drying gas temperature was maintained at 350 °C and dinitrogen was used as a nebulizer gas at a pressure of 35 psi. The scan was performed from m/z = 50 to 1500. Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX or a Jasco FT/IR–430 instrument in KBr pellets, and all the wavenumbers are given in cm^{-1}. ^{1}H and ^{13}C{^{1}H} NMR spectra were measured on a Varian UNITY 300 or a Bruker Avance II 300 (UltraShield™ Magnet) spectrometer at ambient temperature. ^{1}H and ^{13}C chemical shifts (δ) are expressed in ppm relative to Me_4Si, and J values are given in Hz.

$[Ni\{HN{=}C\{4\text{-}(Cl)C_6H_4\}NHC\{4\text{-}(Cl)C_6H_4\}{=}NH\}_2](Cl)_2$ (1): $NiCl_2·2H_2O$ (166 mg, 1.00 mmol) was stirred in acetone (10 mL), whereupon 4-chlorobenzonitrile (550 mg, 4.00 mmol) and 2-propanone oxime (0.32 mL, 4.00 mmol) were added, and the obtained mixture

was heated at reflux for 1 d. Homogenization of the reaction mixture was observed over 1 h, followed by a change in colour and gradual release (after several hours) of a yellow powder, which, after the completion of the reaction (24 h), was separated by filtration. It was washed by acetone (3 × 5 mL) and dried under reduced pressure to furnish compound **1** as a yellow solid. Yield: 47% (336 mg), on the basis of nickel chloride. M.p. 247 °C (dec.) (sublimation at 150 °C). $C_{28}H_{22}Cl_6N_6Ni$ (713.9): calcd. C 47.11, H 3.11, N 11.77; found C 47.09, H 3.16, N 11.91. FAB-MS (+) (*m*-NBA): *m*/*z* = 641 [M – 2Cl – H]$^+$, 347 [Ni{N=C(4-ClC_6H_4)NHC(4-ClC_6H_4)=N}]$^+$. IR (KBr): $\tilde{\nu}$ = 3128 [vs br., *ν*(NH)], 1651 [s, *ν*(C=N)], 1538 [s, *δ*(NH)] cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO, Me_4Si): *δ* = 7.50 (d, *J* = 8.0 Hz, 8 H, 2-C*H*), 8.00 (d, *J* = 8.0 Hz, 8 H, 3-C*H*) ppm, N*H* were not detected. ^{13}C{^{1}H} NMR (75.4 MHz, [D$_6$]DMSO, Me_4Si): *δ* = 162.0 (*C*=N), 136.6 and 134.5 [4-*C*(Cl) and 1-*C*], 129.2 and 127.9 (3-*C*H and 2-*C*H) ppm. Slow evaporation in air at ca. 25 °C of an methanol/acetone/chloroform (1:1:1, v/v) solution of **1** resulted in its partial dehydrochlorination, which led to X-ray quality crystals of [Ni{HN=C{4-(Cl)-C_6H_4}N(H)$_{0.5}$C{4-(Cl)C_6H_4}=NH}$_2$]Cl·$(Me_2CO)_{0.33}$·$(MeOH)_{0.67}$ {**1a**·$(Me_2CO)_{0.33}$·$(MeOH)_{0.67}$}.

[Ni{HN=C{3-(Cl)-4-py}NC{3-(Cl)-4-py}=NH}$_2$] (2): $Ni(MeCOO)_2$·$4H_2O$ (248 mg, 1.00 mmol) was stirred in 2-butanone oxime (5 mL) for 30 min at 70 °C to give a homogeneous light-green solution (solution A). 2-Chloro-4-cyanopyridine (554 mg, 4.00 mmol) was stirred separately in 2-butanone oxime (5 mL) for 30 min at 70 °C and then added to the above-mentioned solution A. The resulting reaction mixture was heated for 12 h at 70 °C, which led to the transformation of the clear green solution to a brownish–orange suspension. This suspension was left to cool to room temperature to yield a dark-orange product that was separated by filtration, washed with acetone (15 mL) and diethyl ether (10 mL) and then dried in air at room temperature. Recrystallization of the product from a hot MeOH/$CHCl_3$ mixture (1:1, v/v) in the presence of ethylenediamine (1.00 mmol) gave a bright-yellow crystalline precipitate of **2**. Yield: 77% (497 mg), on the basis of nickel acetate. The compound does not have a characteristic melting point and decomposes upon heating above 300 °C. $C_{24}H_{16}Cl_4N_{10}Ni$ (645.0): calcd. C 44.69, H 2.50, N 21.72; found C 44.74, H 2.58, N 21.30. FAB-MS(+) (*m*-NBA): *m*/*z* = 645 [M + H]$^+$. IR (KBr): $\tilde{\nu}$ = 3279 [vs br., *ν*(NH)], 1593 [m–w, *ν*(C=N)], 1525 [s, *δ*(NH)] cm^{-1}. ^{1}H NMR [300 MHz, $CDCl_3$(90%)+CD_3OD(10%), Me_4Si]: *δ* = 8.36 (d, *J* = 3.9 Hz, 4 H, 5-C*H*), 7.81 (s, 4 H, 2-C*H*), 7.70 (d, *J* = 3.9 Hz, 4 H, 6-C*H*) ppm, N*H* were not detected. ^{13}C{^{1}H} NMR [7.4 MHz, $CDCl_3$(90%)+CD_3OD(10%), Me_4Si]: *δ* = 171.7 (*C*=N), 156.5, 143.7, 133.5, 122.5 and 119.2 (py*C*) ppm. X-ray quality crystals of [Ni{HN=C{3-(Cl)-4-py}NC{3-(Cl)-4-py}=NH}$_2$]·$2Me_2CO$ (**2b**·$2Me_2CO$) were grown by slow evaporation in air at ca. 25 °C of a methanol/acetone solution (1:1, v/v) of **2**.

[Ni{HN=C{3-(NC)C_6H_4}NHC{3-(NC)C_6H_4}=NH}$_2$](Cl)$_2$ (3): This compound was prepared by following the procedure described for **1** but by using isophthalonitrile (513 mg, 4.00 mmol) instead of 4-chlorobenzonitrile. Yield: 48% (325 mg), on the basis of nickel chloride. The compound does not have a characteristic melting point and decomposes upon heating above 300 °C. $C_{32}H_{22}Cl_2N_{10}Ni$ (676.2): calcd. C 56.84, H 3.28, N 20.71; found C 57.18, H 3.33, N 20.46. FAB-MS(+) (*m*-NBA): *m*/*z* = 603 [M – 2Cl – H]$^+$. IR (KBr): $\tilde{\nu}$ = 3294 [br. s, *ν*(NH)], 2229 [m–w, *ν*(C≡N)], 1660 [s, *ν*(C=N)], 1545 [s, *δ*(NH)] cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]-DMSO, Me_4Si): *δ* = 9.58 and 9.27 (br. s, 4H + 2 H, N*H*), 8.41 (s, 4 H, 2-C*H*), 8.28 (d, *J* = 7.2 Hz, 4 H, 4-C*H*), 8.01 (d, *J* = 7.3 Hz, 4 H, 6-C*H*), 7.74 (t, *J* = 7.2 Hz, 4 H, 5-C*H*) ppm. No reliable ^{13}C{^{1}H} NMR spectrum could be recorded because of the poor solubility of **3**.

[Ni{HN=C{4-(NC)C_6H_4}NHC{4-(NC)C_6H_4}=NH}$_2$](Cl)$_2$ (4): This compound was prepared by following the procedure described for **1** but by using terephthalonitrile (513 mg, 4.00 mmol) instead of 4-chlorobenzonitrile. Yield: 59% (399 mg), on the basis of nickel chloride. M.p. 194 °C (dec.). $C_{32}H_{22}Cl_2N_{10}Ni$ (676.2): calcd. C 56.84, H 3.28, N 20.71; found C 57.09, H 3.16, N 20.91. FAB-MS(+) (*m*-NBA): *m*/*z* = 640 [M – Cl]$^+$, 604 [M – 2Cl – H]$^+$. IR (KBr): $\tilde{\nu}$ = 3364 (vs br.), 3219 [vs br., *ν*(NH)], 2232 [m–w, *ν*(C≡N)], 1668 [vs, *ν*(C=N)], 1533 [s, *δ*(NH)] cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]-DMSO, Me_4Si): *δ* = 7.92 (d, *J* = 7.5 Hz, 8 H, 3-C*H*), 8.07 (d, *J* = 7.5 Hz, 8 H, 2-C*H*), 10.2 (br. s, 4 H, N*H*) ppm. ^{13}C{^{1}H} NMR (75.4 MHz, [D$_6$]DMSO, Me_4Si): *δ* = 127.8 (2-*C*H), 131.9 (3-*C*H), 169.6 [*C*=N(–N)] ppm, poor solubility of the compound prevented the collection of all NMR spectroscopic data. Slow evaporation in air at ca. 25 °C of a methanol/chloroform (1:1, v/v) solution of **4** (in the presence of an equimolar amount of ethylenediamine) resulted in its dehydrochlorination, which led to X-ray quality crystals of [Ni{HN=C{4-(NC)C_6H_4}NC{4-(NC)C_6H_4}=NH}$_2$]·$CHCl_3$ (**4b**·$CHCl_3$).

[Ni{HN=C(3-py)NC(3-py)=NH}$_2$]·MeOH (5): This compound was prepared by following the procedure described for **2** but by using 3-cyanopyridine (416 mg, 4.00 mmol) instead of 2-chloro-4-cyanopyridine. Yield: 63% (340 mg), on the basis of nickel acetate. The compound does not have a characteristic melting point and decomposes upon heating above 300 °C. $C_{25}H_{24}N_{10}NiO$ (539.2): calcd. C 55.69, H 4.48, N 25.98; found C 55.77, H 4.77, N 26.03. ESI-MS(+) (in MeOH): *m*/*z* = 507 [M + H]$^+$. IR (KBr): $\tilde{\nu}$ = 3369 [s br., *ν*(OH+NH)], 1591 [s, *ν*(C=N)], 1547 [s, *δ*(NH)] cm^{-1}. ^{1}H NMR [300 MHz, $CDCl_3$(90%)+CD_3OD(10%), Me_4Si]: *δ* = 8.98 [s, 4 H, 2-C*H*(3-py)], 8.53 [d, *J* = 4.4 Hz, 4 H, 4-C*H*(3-py)], 8.27 [d, *J* = 7.8 Hz, 4 H, 6-C*H*(3-py)], 7.35 [dd, *J* = 7.8 and 7.8 Hz, 4 H, 5-C*H*(3-py)] ppm, NH and methanol protons were not observed because of proton exchange with the solvent. ^{13}C{^{1}H} NMR [7.4 MHz, $CDCl_3$(90%)+CD_3OD(10%), Me_4Si]: *δ* = 123.5 [5-*C*H(3-py)], 134.4 [1-*C*H(3-py)], 135.6 [6-*C*H(3-py)], 147.7 [2-*C*H(3-py)], 149.9 [4-*C*H(3-py)], 50.9 (CH_3OH), 162.7 [*C*=N(–N)] ppm. X-ray quality crystals of [Ni{HN=C(3-py)NC(3-py)=NH}$_2$]·Me_2CO (**5b**·Me_2CO) were grown by slow evaporation, in air at ca. 25 °C, of an acetone solution of **5**.

[Ni{HN=C(4-py)NC(4-py)=NH}$_2$]·MeOH·H_2O (6): This compound was prepared by following the procedure described for **2** but by using 4-cyanopyridine (416 mg, 4.00 mmol) instead of 2-chloro-4-cyanopyridine. Yield: 75% (418 mg), on the basis of nickel acetate. The compound does not have a characteristic melting point and decomposes upon heating above 300 °C. $C_{25}H_{26}N_{10}NiO_2$ (557.2): calcd. C 53.89, H 4.70, N 25.14; found C 53.47, H 4.50, N 25.00. ESI-MS(+) (in MeOH): *m*/*z* = 507 [M + H]$^+$. IR (KBr): $\tilde{\nu}$ = 3355 [s br., *ν*(OH+NH)], 1689 [m–w, *ν*(C=N)], 1462 [s, *δ*(NH)] cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO, Me_4Si): *δ* = 8.71 [d, *J* = 6.0 Hz, 4 H, 3-C*H*(4-py)], 7.92 [d, *J* = 6.0 Hz, 4 H, 2-C*H*(3-py)], 7.53 (br. s, 2 H, N*H*), 4.10 (s, 1 H, CH_3OH), 3.35 (H_2O), 3.20 (s, 3 H, CH_3OH) ppm. ^{13}C{^{1}H} NMR (75.4 MHz, [D$_6$]DMSO, Me_4Si): *δ* = 48.5 (CH_3OH) 121.4 [2-*C*H(4-py)], 144.3 [1-*C*H(3-py)], 149.8 [3-*C*H(3-py)], 161.7 [*C*=N(–N)] ppm. X-ray quality crystals of [Ni{HN=C(4-py)NC(4-py)=NH}$_2$]·MeOH (**6b**·MeOH) were grown by slow evaporation, in air at ca. 25 °C, of a methanol solution of **6** in the presence of an equimolar amount of ethylenediamine.

[Ni{HN=C(Me)NHC(Me)=NH}$_2$](MeCOO)$_2$·$2H_2O$ (7): This compound was prepared by following the procedure described for **1** but

by using $Ni(MeCO_2)_2{\cdot}4H_2O$ (249 mg, 1.00 mmol) and acetonitrile (10 mL) as both solvent and reagent instead of $NiCl_2{\cdot}2H_2O$ and acetone and 4-chlorobenzonitrile, respectively. Recrystallization of the product from hot water gave pale-yellow crystals (of X-ray quality) of **7**. Yield: 81% (333 mg), on the basis of nickel acetate. The compound does not have a characteristic melting point and decomposes upon heating above 300 °C. $C_{12}H_{28}N_6NiO_6$ (411.1): calcd. C 35.06, H 6.87, N 20.44; found C 34.79, H 6.88, N 20.39. FAB-MS(+) (*m*-NBA): *m*/*z* = 256 [M – 2MeCOO – H]$^+$. IR (KBr): $\tilde{\nu}$ = 3477 [s br., *ν*(OH)], 3165 [s br., *ν*(NH)], 1666 [s, *ν*(C=N)], 1556 [s, *δ*(NH)] cm^{-1}. ^{1}H NMR (300 MHz, D_2O, Me_4Si): *δ* = 2.06 (br. s, CH_3+CH_3COO) ppm, NH protons were not observed. $^{13}C\{^1H\}$ NMR (75.4 MHz, D_2O, Me_4Si): *δ* = 20.0 (CH_3), 21.5 (CH_3COO), 163.2 [*C*=N(–N)], 178.0 [*C*=O(–O)] ppm.

X-ray Crystal Structure Determination: The X-ray quality single crystals of **1a**·$(Me_2CO)_{0.33}$·$(MeOH)_{0.67}$, **2b**·$2Me_2CO$, **4b**·$CHCl_3$, **5b**·Me_2CO, **6b**·MeOH and **7** were mounted in inert oil within the cold gas stream of the diffractometer. The X-ray diffraction data were collected with a Nonius Kappa CCD diffractometer at 120 (**2b**, **5b**, **6b**, **7**) or 110 K (**1a**, **4b**). The Denzo–Scalepack[14] program package was used for cell refinements and data reduction. Structures were solved by direct methods by using the SIR-97 (**2b**, **6b**), SIR-2002 (**1a**, **4b**), SIR-2004 (**7**) or SHELXS-97 (**5b**) programs.[15] A multiscan absorption correction based on equivalent reflections (XPREP in SHELXTL or SADABS)[16] was applied to all data. The structures were refined with SHELXL-97[17a] and the WinGX graphical user interface.[17b] In **1a**, the acetone and methanol solvent molecules were disordered and mixed with each other. The disordered acetone and methanol molecules were refined with occupancies of 0.33 and 0.66, respectively. Furthermore, the C–O distance in the MeOH molecule was constrained. In addition, the carbon atom (C98) was restrained so that its U_{ij} components approximate isotropic behaviour. In **4b**, the chloroform of crystallization was partially lost and was refined with an occupancy of 0.5. In addition, all the C–Cl and Cl···Cl distances were set to be similar. Because of partial solvent loss, the crystal of **4b** was only weakly diffracting. In **1a**, **4b**, **5b**, **6b** and **7**, the NH and OH hydrogen atoms were located from the difference Fourier map but were constrained to ride on their parent atom, with U_{iso} = 1.5 or 0.25. In **2b**, the NH hydrogen atoms were located from the difference Fourier map and refined isotropically. The main crystallographic data for all measured structures are summarized in Table 2. A search in the Cambridge Structural Database (CSD)[2] revealed that structures similar to those of **4b**[4a] and **6b**[4c] were reported by others, albeit as an unknown solvate and measured at 298 K, respectively. Hence, our structures **4b** (with solvated chloroform molecule) and **6b** (determined at 120 K) are not discussed in the present work. CCDC-757194, -757195, -757196, -757197, -757198, -757199 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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