“Embroidered” Square Pyramidal Coordination Caps for Nickel(II): Mono-, Di- and Tetrafunctionalisation of a Tetrapodal Pentadentate Ligand with an NN_4 Donor Set

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 65th birthday

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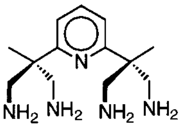
The tetrapodal pentaamine ligand 2,6-bis(1′,3′-diamino-2′-methylprop-2′-yl)pyridine **(1)**, which contains four equivalent primary amino groups, can be derivatised partly or completely by Schiff base condensation with suitable carbonyl compounds. The new ligands thus obtained are mononucleating, as shown by the X-ray crystal structures of their respective nickel(II) complexes. Reaction of **1** with 1 equiv. of salicylaldehyde and subsequent reduction allows the selective modification of one of the four sidearms. The resulting ligand **2** is hexadentate and uninegative in its nickel(II) complex {[(**2**)Ni]PF_6} **(3)** with both the secondary amine and the phenoxide functionalities coordinated to the metal centre. The unreduced Schiff base form of the ligand, **4**, does not form a complex with nickel(II) as readily, and only a small quantity of the mixed salt {[(**4**)Ni][(**1**)Ni-(H_2O)]$(Br)_2(PF_6)$} **(5)** has been obtained. While the overall coordination of **4** resembles that of **2**, there is considerably more strain in the appended chelate ring, due to the presence of the C=N double bond. Modification of one arm in **1** can also be achieved by condensation with 1 equiv. of acetylacetone, to give the new ligand **6** which, likewise, is hexadentate in its Ni^{II} complex {[(**6**)Ni]$(PF_6)_2$} **(7)**. In this case, however, the *N*/*O*-functional sidearm is not deprotonated. Rather, it is coordinated as the keto-imine tautomer, making **7** a rare example of a metal complex containing this structural fragment. Two-fold functionalisation of **1** is observed upon reaction with acetone, regardless of whether the ketone is present in stoichiometric amounts or in excess, to give the pentadentate ligand **8** with two diagonally juxtaposed isopropylidene-imine units. The complex isolated with this ligand {[(**8**)Ni]$(PF_6)_2$} **(9)** contains pentacoordinate Ni^{II}, the sixth coordination site being blocked by the rigidly positioned isopropylidene groups. When reacted with 4 equiv. of *trans*-cinnamaldehyde, all the primary amino groups in **1** condense to give the four-fold Schiff base **10**, which acts as a pentadentate podand towards nickel(II). In this complex, {[(**10**)Ni(OH_2)]Br_2} **(11)**, an aqua ligand completes the coordination octahedron. All ligands are stable towards hydrolysis when coordinated to the metal, despite the presence of *alkyl*-imine groups in some cases.

Introduction

Simple tetrapodal pentadentate ligands which act as square pyramidal coordination caps towards octahedrally coordinating transition metal ions were unknown until recently.[1−5] The ligands are required to have a donor atom in the apical position of the pyramid, whose lone pair is directed towards the centre of the octahedron, as well as four donor arms pointing toward the basal positions. This leaves a sixth site on the metal ion for the coordination of a small monodentate ligand.

A prototypical pentadentate ligand with this topology is the pyridine-derived polyamine **1**, which has been shown to be mononucleating in a series of complexes of nickel(II),[4] cobalt(III),[1,6,7] copper(II)[8] and iron(II).[9] Variation of the basal functional groups to include donors other than primary amines is possible in principle. Such ligands are of basic interest in coordination chemistry, and we have set out to study this class of compounds with a view to using them as head groups in functional metal complexes. All basal donor groups are *terminal* with respect to the ligand framework. Further derivatisation aims to append a “pocket” to the tetrapodal ligand, encircling the sixth coordination site of the metal ion. Depending on the nature of the functional groups present in this pocket, we wish to explore whether the sixth ligand can engage in a two-point interaction with the complex fragment, through a combination of dative bonding to the metal and secondary bonding interactions with the ligand periphery (e.g. hydrogen bonding or π-stacking interactions). Such interactions with the sixth ligand are expected to modulate the thermodynamics and kinetics of its binding, as well as its reactivity.



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In the case of **1**, the presence of four equivalent primary amino groups makes the molecule an attractive substrate for Schiff base condensations. The present work describes a

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series of ligands in which one, two or all four basal amino groups have been derivatised in this manner, and the full characterisation of the Ni^{II} complexes of these "embroidered" square pyramidal coordination caps. Nickel(II) was chosen as the central metal ion as it usually gives complexes that are readily purified (crystallisation, ion exchange chromatography), thus facilitating access to the pure ligands and to complexes of a wider range of metals. This contribution presents results pertaining to Schiff base derivatives of **1** that maintain a mononuclear coordination mode.

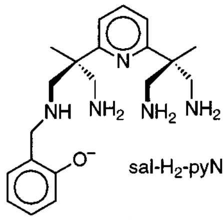
Results and Discussion

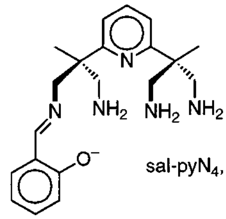
In all condensation reactions reported here, the pentaamine **1** was employed as its tetrakis(hydrobromide) salt/methanol solvate, **1**·4HBr·MeOH.[10] Methanol solutions of **1** were prepared in most cases by neutralisation of HBr with NaOMe, which was generated in situ by dissolving the appropriate amount of sodium metal. NaBr does not precipitate from methanol under the given conditions, and was not removed from solution before attempting the subsequent reactions.

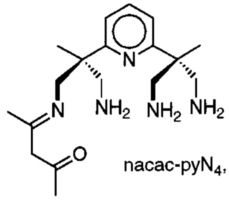
Preliminary experiments showed that the pentaamine **1** reacts readily with 4 equivalents of salicylaldehyde in methanol to give the four-fold Schiff base condensation product, and that reduction of the C=N double bonds with sodium borohydride is similarly straightforward. The Schiff base and the secondary amine derivatives are both potentially nonadentate ligands with NN_4O_4 donor sets, but the presence of four 2-hydroxy substituents in the periphery of the NN_4 pyramid is expected to induce considerable steric crowding with respect to the formation of mononuclear complexes of "small" transition metal ions such as nickel(II), utilizing only the NN_4 donor set. Indeed, we have so far not been able to isolate complexes of the type $[Ni^{II}(NN_4O_4)]$.

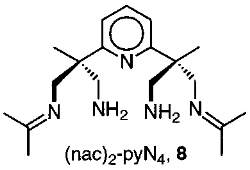
sal-H_2-pyN_4 (2), sal-pyN_4 (4) and Their Complexes With Ni^{II}

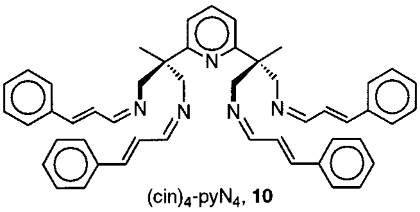
In light of the above observation we attempted the condensation of **1** with only one equivalent of salicylaldehyde, in the hope of obtaining asymmetric ligands of type **2** (after reduction) or **4**. These potentially hexadentate ligands may block all the coordination sites of the metal centre, but their synthesis appears to be a reasonable point of entry into the coordination chemistry of mononucleating derivatives of **1**. In accordance with the terminology used for monosubstituted diamines (so-called "half-units", which are of current interest for their potential in asymmetric catalysis), ligands such as **2** or **4** would represent "quarter-units".[11–13]


sal-H_2-pyN_4, **2**


sal-pyN_4, **4**


nacac-pyN_4, **6**


(nac)$_2$-pyN_4, **8**


(cin)$_4$-pyN_4, **10**

For the preparation of sal-H_2-pyN_4 (formula **2** shows its deprotonated form), one equivalent each of **1** and salicylaldehyde are reacted in methanolic solution at room temperature. The reaction is rapid, as judged by the appearance of a yellow colour which is characteristic of the Schiff base. Reduction of the condensation product in situ with sodium borohydride gives a solution containing the ligand sal-H_2-pyN_4 (cf. **2**). After workup and addition of a suitable nickel(II) salt, followed by hexafluorophosphate anion, the desired mononuclear metal complex **3** precipitates as a purple crystalline material, in which the ligand is deprotonated and carries a negative charge. No attempt has as yet been made to optimise the yield (30% after recrystallisation). While the 1:1 condensation may not go to completion (see **4** and **5**, below), it is possibly not fully specific either, so that more highly substituted side products (sal:pyN_4 > 1:1) may form which, upon reduction, do not give the respective metal complexes as readily. In any case, nickel complexation should provide a convenient means of isolating pure **2**.

The spectroscopic characteristics of **3** (see Experimental Section) resemble those determined for a series of octahedral nickel(II) complexes of the polyamine ligand **1**, in which a monodentate ligand occupies the sixth coordination site.[4] In the UV/Vis spectrum, an absorption attributable to a d–d transition occurs at λ = 509 nm and thus at higher energy than in the aqua complex $[(\mathbf{1})Ni(H_2O)]I_2$ (λ = 543 nm),[4] indicating that the NN_4O ligand **2** generates a stronger ligand field than the parent NN_4 ligand **1**. The compound is paramagnetic, with shifted and broadened resonances in the ^1H NMR spectrum, as expected for a complex of octahedrally coordinated high-spin nickel(II).

Compound **3** crystallises with one molecule of water and one molecule of methanol per formula unit. The molecular structure of the cation, which has C_1 symmetry, is shown in Figure 1. The nickel(II) ion is coordinated by the NN_4 part of the ligand donor set in a pyramidal fashion, and the phenoxide oxygen atom of the peripheral arm occupies the coordination site remaining on the metal centre, the overall coordination geometry of Ni^{II} thus being octahedral. All chelate rings are six-membered. The nickel atom is displaced by 0.0397(5) Å towards the phenoxide oxygen atom, relative to the plane defined by the four equatorial amino nitrogen atoms. While the arrangement of donor atoms along the main axes of the octahedron is close to linear {176.4(1) − 177.8(1)°, see Table 1}, the NN_4 donor cap shows a slight distortion similar to that observed for a series of complexes of the type $[(\mathbf{1})Ni(X)]^{n+}$, where X is a neutral or anionic monodentate ligand.[4] The pyridine ring, itself a regular hexagon, is tilted to one side of the NN_4Ni pyramid so that the heterocycle and the aliphatic carbon atoms C18, C19, C22 and C23 are no longer coplanar {interplanar angle = 17.0(2)°}. The acute angle subtended by the lines N11−C13 and N11−Ni1 at N11 is 11.9(1)° (instead of 0°). At the same time, the nonbonded distance C16···C21 is lengthened to 5.370(5) Å, while the corresponding distance C17···C20 is shortened to 4.752(5) Å. As a consequence, the least-squares planes defined by the four methylene carbon atoms C16, C17, C20, and C21, and the four equatorial amino nitrogen atoms N12, N13, N14, and N15, are not parallel but at an angle of 8.0(1)° (Table 2). Since this kind of distortion is also observed in the parent complexes $[(\mathbf{1})Ni(X)]^{n+}$, where it has been attributed to crystal packing effects,[4] it is not necessarily caused by the presence of an additional chelating group in the ligand periphery, viz. the salicylaldehyde-derived side-arm. The accommodation of the latter into the ligand framework does not induce significant changes in any of the $Ni^{II}-N$ bond lengths ($Ni1-N_{eq}$: 2.080(3)−2.129(3) Å; $Ni1-N_{py}$: 2.075(2) Å), as compared to the range of values observed in $[(\mathbf{1})Ni(X)]^{n+}$. In particular, the bond length between Ni1 and the secondary amino nitrogen atom N15 does not differ markedly from the other values for d(Ni−N) in this structure.[14] Apparently, the only structural effect of the chelating sidearm on the NN_4 coordination cap in **3** when compared to that in $[(\mathbf{1})Ni(X)]^{n+}$ is that there are no longer matching pairs of opposite bite angles in the equatorial plane, these angles all being different and spanning the range 85.2(1)−95.3(1)° (Table 1).

The chelate ring formed by the phenoxide sidearm is a folded hexagon, the fold being along the vector O1···C30. Defining the side of the benzene ring facing the equatorial nitrogen atoms as positive, the phenoxide oxygen and methylene carbon atoms (O1 and C30) are displaced from this plane by +0.061(3) Å and −0.139(4) Å, respectively. The secondary amino nitrogen atom N15 is outside the benzene ring plane by +1.026(6) Å. The latter observation supports the notion that free rotation around the bond N15−C30 (i.e. reduction of the imine precursor) greatly facilitates the phenoxide sidearm to become a chelating group (cf. the related discussion for the Schiff base complex **5**, below). The value for d(Ni1−O1) is 2.066(2) Å and thus lies in the range observed for this type of bond in other octahedral Ni^{II} complexes.[15][16]

A nickel(II) complex of the salicylaldimine ligand **4** does not form as readily. Condensation of **1** and salicylaldehyde as described above, followed by addition of suitable Ni^{II} salts, has so far yielded only a small amount of the mixed salt $\{[(\mathbf{4})Ni][(\mathbf{1})Ni(H_2O)](Br)_2(PF_6)\}$ **(5)** the composition of which shows incomplete condensation (cf. the discussion of **2** and **3**, above.) Ligand **4** may be sluggish to form a complex with Ni^{II} because of the unfavourable conformation of the incipient chelate ring due to the presence of a C=N double bond. This ring is expected to be planar (conjugation of the aldimine and aromatic systems) and hence considerably strained. Alternatively, the phenol oxygen atom may remain an uncoordinated spectator group in the ligand periphery (see Introduction). For clarification, **5** has been characterised by X-ray crystallography.

The molecular structure of the cation $[(\mathbf{4})Ni]^+$, in which the ligand is deprotonated to the phenoxide, is shown in Figure 1. The overall coordination of **4** resembles that of **2** (see Figure 1; note the labelling schemes for $[(\mathbf{4})Ni]^+$ and $[(\mathbf{2})Ni]^+$, which reflect similar tilts of the pyridine rings, leading to different labels for the substituted equatorial nitrogen atoms). Some relevant structural parameters of the NN_4 part of the ligand are as follows; while the bond lengths $Ni-N_{py}$ and $Ni-N_{primary}$ are similar in the structures of **3** and **5** (Table 1), the Ni−N bond to the nitrogen atom carrying the appended chelate arm is significantly shorter in **5** {2.018(7) Å} than in **3** {2.119(3) Å}, as expected for an sp^2-hybridised nitrogen atom in the case of **5**. In contrast, the nickel−phenoxide bond is longer in **5** {2.115(5) Å} than in **3** {2.066(2) Å}, which is probably a manifestation of the strain imposed by the C=N double bond. The distortion of the ligand cap is of the same degree as in **3** (Table 2).

The chelate ring formed by the phenoxide sidearm is essentially planar. The maximum deviation from the best plane defined by all six ring atoms is 0.207(4) Å for O1. Selected angles in the ring are C30−N14−Ni1 127.8(7)°, C31−C30−N14 125.2(9)° and Ni1−O1−C32 123.9(5)°. The deviations from the ideal values of 120° and 109.5°, respectively, further attest to the strain in the ring. As manifest in the molecular structure of **3**, this strain is considerably relieved upon reduction of the C=N double bond. It may thus be concluded that, if the incipient chelate ring is six-membered, unsaturation does not altogether prevent its formation. For a donor group appended to the NN_4 cap to remain uncoordinated, and thus set up for interactions with a substrate coordinated to the metal (see Introduction), the donor atom should be attached to the β-, not the γ-carbon atom of the sidearm. The other cation in the structure, $[(\mathbf{1})Ni(H_2O)]^{2+}$, has parameters similar to those previously described for $[(\mathbf{1})Ni(H_2O)]I_2$.[4]

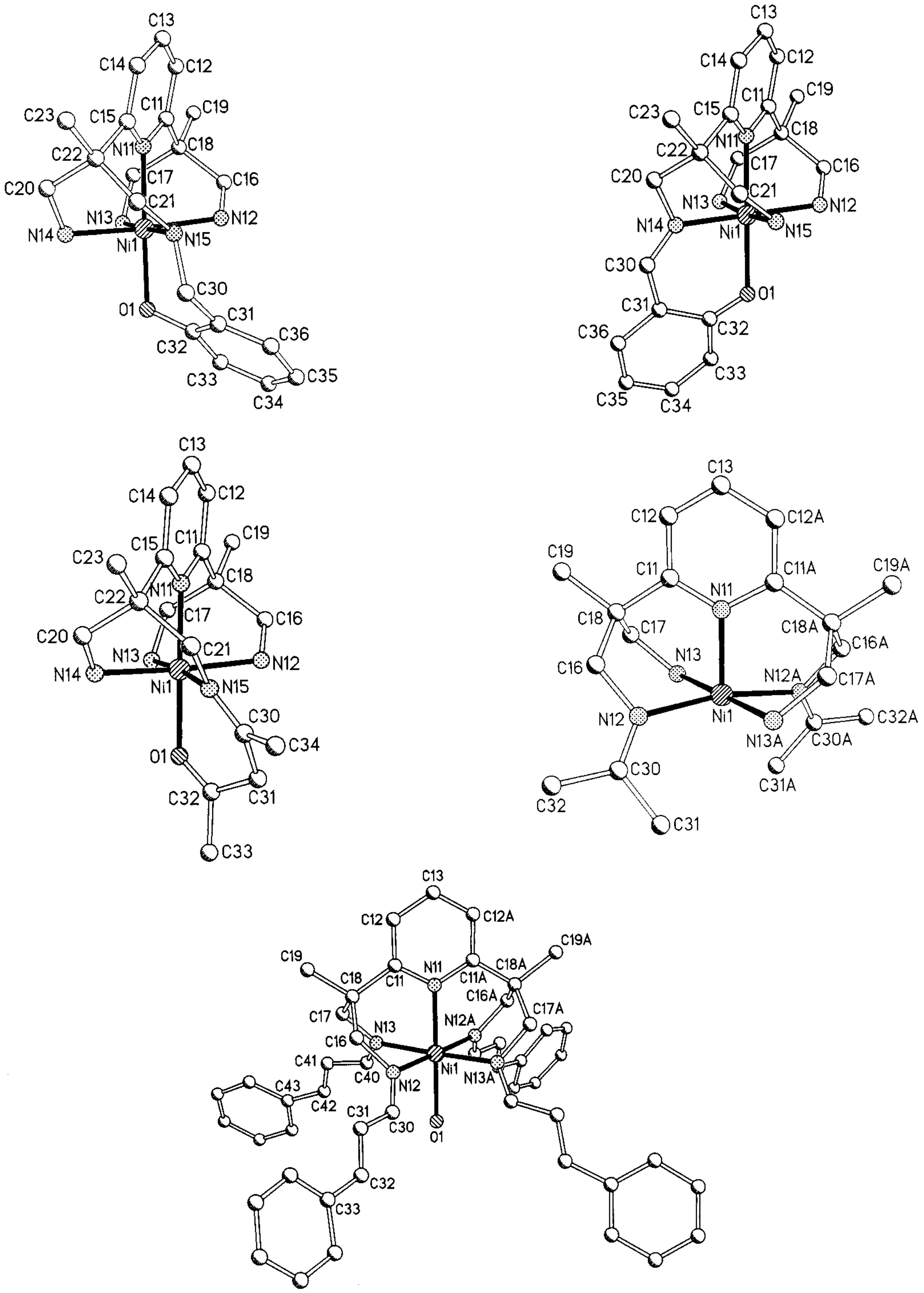


Figure 1. Molecular structures of the cations in **3** (top left), **5** (top right), **7** (middle left), **9** (middle right), and **11** (bottom); for clarity, ball-and-stick representations have been chosen, and hydrogen atoms have been omitted, the atom labelling is based on like orientations of the distortion of the NN_4 ligand cap, where applicable (see text)

nacac-pyN_4 (6), and [(6)Ni](PF_6)$_2$ (7)

The difficulties in isolating a complex of the salicylaldimine quarter-unit **4** led us to study the condensation reaction of **1** with 1 equiv. of a related carbonyl substrate, acetylacetone (2,4-pentanedione). The expected condensation product is a β-ketoamine. While Schiff bases of salicylaldehyde can only exist as the phenol-imine tautomers, three distinct tautomeric forms are possible for β-ketoamines (enol-imine **A**, keto-enamine **B**, and keto-imine **C**).[17][18] Therefore, whereas salicylaldimines usually lose a proton upon metal complexation to become uninegative ligands, β-ketoamines may be either uninegative or neutral in their complexes, depending on whether the "central" carbon

Table 1. Selected bond lengths [Å] and angles [°] for **3**, **5**, **7**, **9** and **11** with estimated standard deviations in parentheses; the atom numbering is dictated by the tilt of the pyridine ring (see Figures and text)

Bond or Angle	**3**·H_2O·MeOH	**5**·H_2O	**7**	**9**	**11**·2MeOH
Ni1−N11	2.075(2)	2.074(7)	2.043(5)	1.991(4)	2.076(7)
Ni1−N12	2.129(3)	2.106(6)	2.114(5)	2.041(3)	2.106(6)
Ni1−N13	2.084(3)	2.086(6)	2.082(5)	2.080(3)	2.085(5)
Ni1−N14	2.080(3)	2.018(7)	2.100(5)	−	−
Ni1−N15	2.119(3)	2.127(6)	2.049(5)	−	−
Ni1−O1	2.066(2)	2.115(5)	2.105(4)	−	2.167(6)
N12−C30	−	−	−	1.266(4)	1.283(8)
N14−C30	−	1.26(1)	−	−	−
N15−C30	1.489(4)	−	1.276(7)	−	−
C30−C31	1.517(5)	1.48(1)	1.521(9)	1.486(6)	1.45(1)
C31−C32	1.407(5)	1.44(1)	1.506(10)	−	1.34(1)
C32−O1	1.320(4)	1.237(9)	1.208(8)	−	−
C32−C33	1.412(5)	1.44(1)	1.499(9)	−	1.48(1)
C30−C32	−	−	−	1.497(6)	−
N11−Ni1−N12	85.8(1)	86.0(3)	86.5(2)	95.89(9)	89.8(2)
N11−Ni1−N13	91.8(1)	88.2(3)	92.5(2)	90.4(1)	88.9(2)
N11−Ni1−N14	90.6(1)	92.9(3)	89.5(2)	−	−
N11−Ni1−N15	87.2(1)	85.5(2)	93.0(2)	−	−
N12−Ni1−N13	85.2(1)	89.9(2)	87.3(2)	84.8(1)	84.3(2)
N14−Ni1−N15	87.9(1)	84.9(3)	85.1(2)	−	−
N13−Ni1−N14	95.3(1)	94.2(3)	94.5(2)	−	−
N12−Ni1−N15	91.5(1)	90.9(2)	93.5(2)	−	−
N12−Ni1−N13A	−	−	−	95.1(1)	95.7(2)
N12−Ni1−N14	176.4(1)	175.8(3)	175.7(2)	−	−
N13−Ni1−N15	176.6(1)	173.5(3)	174.4(2)	−	−
N12−Ni1−N12A	−	−	−	168.2(2)	179.6(3)
N13−Ni1−N13A	−	−	−	179.3(2)	177.9(3)
N11−Ni1−O1	177.75(10)	178.7(3)	178.7(2)	−	180
Ni1−N12−C16	116.1(2)	116.2(5)	115.5(4)	114.5(2)	116.9(4)
Ni1−N13−C17	114.3(2)	116.0(5)	114.3(4)	113.8(3)	118.2(4)
Ni1−N14−C20	114.8(2)	116.2(6)	115.0(4)	−	−
Ni1−N15−C21	113.6(2)	115.0(4)	116.4(3)	−	−
N12−C16−C18	114.5(3)	115.6(7)	115.0(5)	114.6(3)	114.9(6)
N13−C17−C18	114.5(3)	115.3(7)	115.0(6)	116.3(3)	114.5(6)
N14−C20−C22	114.3(3)	110.5(6)	115.5(5)	−	−
N15−C21−C22	115.9(3)	112.4(6)	114.3(5)	−	−
Ni1−N12−C30	−	−	−	126.9(3)	126.6(5)
Ni1−N14−C30	−	127.8(7)	−	−	−
Ni1−N15−C30	113.9(2)	−	125.3(4)	−	−
C16−N12−C30	−	−	−	118.6(3)	116.4(6)
C20−N14−C30	−	115.8(8)	−	−	−
C21−N15−C30	110.0(3)	−	118.3(5)	−	−
Ni1−O1−C32	114.4(2)	123.9(5)	125.0(5)	−	−
N12−C30−C31	−	−	−	119.2(4)	128.0(7)
N14−C30−C31	−	125.2(9)	−	−	−
N15−C30−C31	112.7(3)	−	121.0(6)	−	−
N12−C30−C32	−	−	−	124.0(4)	−
C31−C30−C32	−	−	−	116.8(4)	−
C30−C31−C32	119.0(4)	121.6(8)	118.8(5)	−	120.2(7)
C31−C32−O1	121.0(4)	125.6(8)	123.0(7)	−	−
C31−C32−C33	116.8(4)	112.4(8)	116.5(7)	−	125.9(8)
C32−C33−C34	120.7(5)	124.4(8)	−	−	116.4(10)
C32−C33−C38	−	−	−	−	124.4(9)

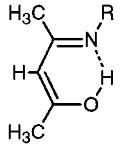
atom is part of a methine or methylene group. The keto-imine tautomer **C** is expected to be a more flexible chelating ligand than **A** and **B**, since the central carbon atom is incorporated into the chain by two single bonds. At the same time, this coordination mode is expected to be disfavoured, and hence occur rarely, owing to the loss of double bond conjugation.

The ligand nacac-pyN_4 (**6**) is obtained from an equimolar mixture of **1** and acetylacetone in refluxing methanol. Addition of nickel(II) chloride, followed by hexafluorophosphate anion, yields a purple, microcrystalline precipitate which may be recrystallised from water. Its elemental analysis fits the formula [(nacac-pyN_4)Ni]$(PF_6)_2$ (**7**) in which the pyN_4 ligand has a single acetylacetone-derived sidearm. By analogy with the syntheses of **3** and **5**, compound **7** is expected to contain divalent nickel. The sidearm is thus required to be neutral, which suggests the keto-imine tautomeric form **C**. The IR spectrum is characterised by two strong bands at 1697 cm^{-1} and 1605 cm^{-1}, which may be assigned to the C=N and C=O stretching vibrations, respectively. This finding is compatible with tautomer **C**, since the C=N stretching vibration in a conjugated cyclic system occurs

Table 2. Intramolecular angles [°] and distances [Å] illustrating the distortion of the ligand cap in complexes **3**, **5** and **7** (with estimated standard deviations in parentheses); compounds **9** and **11** do not show these distortions due to crystallographically imposed symmetry; see footnote and text for definitions of angles

Bond or Angle	**3**	**5**	**7**
ε[a]	17.0(2)	16.0(7)	3.9(4)
ζ[b]	8.0(1)	7.3(4)	2.9(1)
η[c]	11.9(1)	11.4(4)	4.5(2)
d(C16···C21)	5.370(5)	5.36(1)	5.16(1)
d(C17···C20)	4.752(5)	4.81(1)	5.02(1)

[a] Angle ε between the least-squares planes defined by the pyridine ring (N11, C11, C12, C13, C14, C15) and the quaternary and methyl carbon atoms C18/C19/C22/C23. – [b] Angle ζ between the least-squares planes defined by the equatorial nitrogen atoms N12/N13/N14/N15 and the methylene carbon atoms C16/C17/C20/C21. – [c] Angle η subtended by the lines N11···C13 and N11–Ni1 at N11



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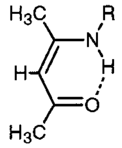

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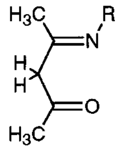

C

at lower frequency (1660–1480 cm^{-1}).[19] By the same token, complexes involving ketones are expected to show especially low C=O stretching frequencies, when compared with the free ligand.[19]

The X-ray structure analysis of **7** confirms the single derivatisation of the ligand cap and the presence of a keto-imine tautomeric acetylacetone-derived sidearm (Figure 1), making **7** a rare if not the only example of a transition metal complex where this coordination mode is observed.[20] The overall coordination geometry of nickel(II) resembles that in **3**, but the NN$_4$ coordination cap shows a lesser distortion of the carbon backbone, as quantified by means of the parameters listed in Table 2 (cf. the structures of **3** and **5**). The bond Ni1–N15 involving the ketimine nitrogen atom {2.049(5) Å} is shorter than the other equatorial Ni–N bonds, and has the same length as the Ni–N$_{py}$ bond (Table 1). The nickel and equatorial nitrogen atoms are not coplanar; rather, N15 is below and N14 above the plane defined by the other three equatorial atoms (Ni1, N12, N13) by 0.198(5) Å and 0.144(5) Å, respectively. The N–O chelate ring is six-membered and adopts a boat conformation, the methylene carbon atom C31 (at the "bow") and Ni1 (at the "stern") being above the best plane containing N15, C30, C32, and O1 by 0.384(8) Å and 0.635(1) Å, respectively. The bond between Ni1 and the keto oxygen atom {Ni1–O1, 2.105(4) Å} is intermediate between the corresponding axial bonds in **3** and **5** (Table 1). The coplanarity of all bonds at the imine nitrogen atom N15, the lack of planarity of the N–O chelate ring, and the differences in bond lengths within this ring (Table 1) make the assignment of the keto-imine tautomer **C** conclusive. Apparently, the geometric requirements imposed by the central nickel atom on the derivatised coordination cap are such that the ligand sidearm is best accommodated as a chelating group when in the keto-imine form, thus favouring this unusual coordination mode. The presence of the keto-imine form may also explain the remarkable hydrolytic stability of **7**. By contrast, nickel(II) complexes containing the chelating tautomers **A** or **B** (with R = alkyl) are reported to be extremely sensitive to traces of water in solution, and hence are accessible only under anhydrous conditions.[17][18]

(nac)$_2$-pyN$_4$ (8), and [(8)Ni](PF$_6$)$_2$ (9)

Initial experiments aimed at the synthesis of complex **7** yielded a crystalline by-product which analysed too high for carbon to be the acetylacetone derivative. An excess of sodium methoxide had been used for the deprotonation of **1**·4HBr·MeOH, making the solution sufficiently basic for acetylacetone to undergo a retro-aldol reaction, thereby liberating acetone. The elemental analysis data of the by-product were compatible with the nickel(II) complex of a bis(acetoneimine) derivative of the pentaamine ligand **1**, which we subsequently sought to synthesise in a directed manner.

Complex **9**, containing the ligand (nac)$_2$-pyN$_4$ (**8**), forms as the only isolated product in high yield as a purple, microcrystalline material when treating a methanolic solution of **1** with 4 equivalents of acetone at room temperature, followed by addition of nickel(II) acetate and ammonium hexafluorophosphate. The complex, while containing aliphatic Schiff base units, is remarkably stable towards hydrolysis. No special precautions need to be taken to exclude water from the reaction mixture, which is in fact the optimal solvent for recrystallisation. More forcing reaction conditions (reflux and/or a much larger excess of acetone) do not lead to more highly condensed products, two primary amino groups in the molecule remaining unaffected. The latter observation is in agreement with results reported by Curtis and co-workers,[21] who studied the reactivity of tris(1,3-propanediamine)-nickel(II) perchlorate in dry acetone and obtained a square-planar derivative of bis(1,3-propanediamine)-nickel(II) as an isolable intermediate, in which one acetone molecule had condensed with each of the two diamine ligands. A *trans* arrangement of the coordinated *N*-isopropylidene groups was suggested for this complex. Its hydrolytic instability, however, prevented structural charaterisation. From this intermediate Curtis and co-workers obtained, upon prolonged reaction, a square planar nickel(II) complex of a 16-membered macrocycle containing diacetone-amine-imine linkages.[22] We have so far not observed similar reactivity for complex **9**.

The IR spectrum of **9** has a strong absorption at 1663 cm^{-1} assigned to the C=N stretching vibration, whereas the ^{1}H NMR spectrum is of little diagnostic value as it shows paramagnetically broadened and shifted signals (solvent: CD_3OD/D_2O). The UV/Vis spectrum of an aqueous or a methanolic solution of **9** reveals a band at 509 nm, which we assign to a d−d transition. The elemental analysis data suggest **9** to be a pentacoordinate complex, hexafluorophosphate being a very weakly coordinating ion at best. The solid-state UV/Vis spectrum (diffuse reflectance) is identical within experimental error to the solution spectrum (200−800 nm), the d−d band being recorded at 504 nm. Since the spectra of d^8 complexes are very sensitive to changes in the axial ligand positions,[23] these findings indicate the cation in **9** to be pentacoordinate both in aqueous or methanolic solution and in the solid state. The magnetic moment determined for **9** (Gouy balance) is 3.12 BM (spin only), corresponding to two unpaired electrons (theoretical value: 2.83 BM). By contrast, a diamagnetic ground state is predicted, to a first approximation, for Ni^{2+} (d^8) in a regular square pyramidal coordination environment.[24]

Compound **9** was studied by cyclic voltammetry to determine the redox potential of the $Ni^{II/III}$ couple in this less than usual coordination geometry. The cyclic voltammogram of **9** at room temperature between +1.24 and −2.36 V (Figure 2) shows a reversible redox wave in the anodic region ($E_{1/2}$ = +0.88 V) and an irreversible redox wave in the cathodic region (−1.67 V). The anodic process is assigned to the $Ni^{II/III}$ couple, whereas the cathodic process may involve irreversible reduction of the ligand, or generation of Ni^{I} and subsequent fast decomposition of the complex.

An x-ray crystallographic analysis confirms the assumed pentacoordination of the cation in **9** in the solid state. The structure of $[(\mathbf{8})Ni]^{2+}$ is shown in Figure 1. The pyridine, primary amine, and acetone-imine nitrogen atoms define a square pyramid. The molecule lies on a twofold rotation axis which contains Ni1, the pyridine nitrogen atom N11, and the *para* carbon atom of the pyridine ring, C13. As a consequence of the crystallographic symmetry, a distortion of the ligand cap as described for **3**, **5** and **7** is not observed. The primary amine nitrogen atoms (N13, N13A) and the nickel atom are on a straight line {N13−Ni1−N13A 179.3(2)°}, while the bonds connecting Ni1 with the acetone-imine nitrogen atoms N12 and N12A are at an angle of 168.2(2)° (N12−Ni1−N12A). Of the bonds involving Ni1, the axial bond Ni1−N11 to the pyridine nitrogen atom is the shortest at 1.991(4) Å, the basal bonds being somewhat longer, with bond lengths reflecting the sp^2 and sp^3 character of the nitrogen atoms, respectively {Ni1−N12: 2.041(3) Å; Ni1−N13: 2.080(3) Å}. All bonds radiating from the isopropylidene-imine nitrogen atom N12 are coplanar, as expected, and the rigidity in this donor group is accommodated by deviations of the angles at N12 and Ni1 from the expected values of 120° and 90°, respectively (see Table 1). As a consequence of this rigidity, the “inside” methyl groups (C31, C31A) approach each other to within 2.59(6) Å (C31−H···H−C31A), thereby shielding the nickel atom and blocking access to the sixth coordination site.

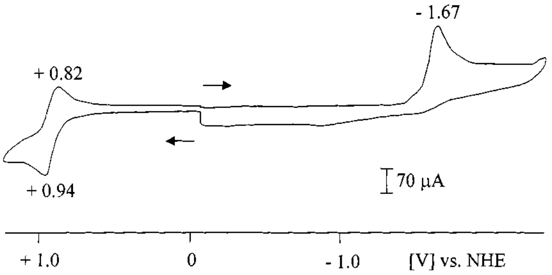

Figure 2. Cyclic voltammogram of **9** at room temperature (solvent: DMF; scan rate: 50 mVs^{-1})

$(cin)_4$-pyN_4 (10), and $[(10)Ni(OH_2)](Br)_2$ (11)

The ligand concluding the present series is a derivative of **1** in which all four primary amino groups are condensed with a suitable carbonyl compound, namely *trans*- cinnamaldehyde (*trans*-3-phenyl-2-propenal). We expected this readily available α,β-unsaturated aromatic aldehyde to show high reactivity in the transformation at hand, as condensation would result in the formation of conjugated double bond systems in the four sidearms.[25] These would be relatively rigid, and the aromatic rings would be sufficiently removed from the metal centre for unfavourable steric interactions to prevent podand-like coordination of the ligand.

Fourfold condensation of cinnamaldehyde with the polyamine ligand is achieved by reacting the correct molar ratio of materials in refluxing methanol. Workup gives a yellow crude product which shows poorly resolved ^{1}H NMR spectra (see Experimental Section). In the IR spectrum, a strong band is observed at 1635 cm^{-1}, which is assigned to the C=N stretching vibration. When a methanolic solution of this product is treated with solid nickel(II) acetate, complexation is spontaneous, as jugdged by the colour change to orange. Workup of this solution gives an orange-brown microcrystalline solid whose IR and mass spectroscopic data indicate a complex containing the cation $[(\mathbf{10})Ni(ac)]^{+}$.

Single crystals of the aqua complex **11**, containing two molecules of methanol per formula unit, were obtained by repeated recrystallisation of the presumed acetato complex from methanol. The structure of the cation is shown in Figure 1, and relevant distances and angles are listed in Table 1. The molecule has C_2 symmetry, with Ni1, the aqua oxygen atom O1, and the pyridine nitrogen and *para* carbon atoms N11 and C13 lying on the two-fold rotational axis. The crystallographically imposed symmetry implies a regular conformation of the ligand cap; similar to the situation in compound **9**, all carbon atoms in the 2,6-diethylpyridine ligand backbone are coplanar, and the nonbonded distance between pairs of methylene carbon atoms (C16···C17A, C17···C16A) is the same {5.14(1) Å}. In contrast to the structure of **9**, the equatorial nitrogen atoms in **11** are coplanar with the central metal, with angles N12−Ni1−N12A and N13−Ni1−N13A of 179.6(3)° and 177.9(3)°, respectively. The bond lengths Ni−N are all rather similar and lie in the range 2.076(7)−2.107(6) Å. As a consequence of the conjugated systems of double bonds, the atoms in the ligand sidearms (from the methylene carbon via the imine nitrogen atoms out to the phenyl rings) are virtually coplanar, with bonds and angles not deviating greatly from the normal values (Table 1). The aqua oxygen atom is coordinated to Ni1 at a distance of 2.148(7) Å, which is the same as in the parent complex $[(\mathbf{1})Ni(OH_2)]I_2$ {2.133(3) Å}.[4] The methanol molecules in this structure are situated between pairs of sidearm phenyl rings and are engaged in what seem to be weak hydrogen-bonded interactions with the bromide counterions, which are at a distance of 3.27(1) Å from the methanol oxygen atoms (sum of the van der Waals radii of O and Br: 3.37 Å[26]).

Conclusion

The series of ligands presented here may be obtained by selective or exhaustive condensation of the tetrapodal pentaamine **1** with a choice of carbonyl compounds, to give the respective Schiff bases. Derivatives obtained from **1** by introduction of *one* additional donor group into the ligand periphery are potentially hexadentate. They readily form mononuclear complexes with nickel(II) if an additional chelate ring can arise that is six-membered and sufficiently flexible (**2** and **6**). In the case of the salicylaldimine derivative **4**, this requires reduction of the C=N double bond. The derivative obtained from **1** by modification of *two* amino groups (having two diagonally juxtaposed isopropylideneimine units, **8**) forms a mononuclear complex in which these rigidly positioned substituents, while preventing the coordination of a sixth ligand, are sufficiently removed from one another so as not to prevent complexation as such. The condensation of all *four* primary amino groups in **1** with cinnamaldehyde leads to a derivative whose podand-like behaviour towards nickel(II) is facilitated by the limited steric demand of the phenylpropenylidene substituents. In all cases, nickel(II) complexation allows the isolation of pure, crystalline materials, which should make these ligands available for complexation studies with other transition metals. Also, the remaining primary amino groups of the singly derivatised square-pyramidal coordination caps make these ligands attractive subjects for further derivatisations.

Experimental Section

Materials and Instrumentation: All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques, unless indicated otherwise. Solvents were dried and distilled before use. Reagents were AR grade or better and were purchased from Merck, Fluka, or Aldrich. $2,6\text{-}C_5H_3N\{CMe(CH_2NH_2)_2\}_2\cdot4HBr\cdot MeOH$ ($\mathbf{1}\cdot4HBr\cdot MeOH$) was prepared as described elsewhere.[10] IR (KBr discs) and UV/Vis spectra (solvent: water or methanol; solid state: diffuse reflectance) were recorded on Perkin−Elmer 16PC FT-IR or Shimadzu UV-3101 PC instruments. The cyclic voltammogram of **9** was recorded under an atmosphere of nitrogen using an EG & G PAR 246 A potentiostat equipped with a ROTEL A three-electrode cell, having a glassy carbon working electrode, a Pt counter electrode and Ag/AgCl/KCl (sat. in H_2O) as the reference electrode. The solvent was dimethylformamide, the conducting electrolyte $N^nBu_4PF_6$ (10^{-1} mol/l), scan rate 50 mV/s. Ferrocene was used as internal standard, with a potential of +0.40 V vs. NHE.[27] NMR spectra were measured on a JEOL JNM-EX 270 spectrometer, and mass spectra were obtained on JEOL MSTATION 700 and Micromass ZABSpecE spectrometers. Elemental analyses were performed using Carlo Erba Elemental Analysers 1106 (CHN) and 1108 (CHNS).

X-ray Crystallography: Crystal data for compounds **3**, **5**, **7**, **9**, and **11** are presented in Table 3, and selected distances and angles are listed in Table 1. The structures of the cations are shown in Figure 1. All structures were solved by direct methods and refined using the programme package SHELXTL 5.03.[28] All non-hydrogen atoms were refined anisotropically (full-matrix least-squares on F^2).

In the case of **3** and **9**, all hydrogen atoms were located in a difference Fourier synthesis and refined with a fixed common isotropic displacement parameter (exception for **3**: the hydrogen atoms in the methanol molecule were calculated in geometrically optimised positions). For **5**, **7** and **11**, all hydrogen atoms were positioned geometrically (exception for **5**: the hydrogen atoms of the aqua ligand in $[(\mathbf{1})Ni(H_2O)]^{2+}$ and of solvate water were located in a difference Fourier synthesis and not refined; exception for **11**: the hydrogen atoms in the aqua ligand were not included in the calculations). In the structure of **3**, the PF_6^- counterion is disordered, and two preferred orientations could be refined (occupancy factors 0.68(1) and 0.32(1), respectively). In **7**, one of the two PF_6^- anions shows rotational disorder, which was resolved with refined occupancy factors 0.61(2) and 0.39(2), respectively, for alternative sets of the four equatorial F atom sites. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-129 628 (**3**) to CCDC-129 632 (**11**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]

$[(\mathbf{2})Ni]PF_6$ (3): To a stirred suspension of $pyN_4\cdot4HBr\cdot MeOH$ (0.48 g, 0.79 mmol) in methanol (50 mL) was added sodium metal (0.07 g, 3.16 mmol), which dissolved within ca. 5 minutes to give a clear solution. To this solution was added dropwise over 2 h a solution of salicylaldehyde (0.10 g, 0.79 mmol) in methanol (20 mL). The resulting yellow solution was taken to dryness, and the remaining oil taken up in ethanol (20 mL). To this mixture was added $NaBH_4$ (0.24 g, 6.32 mmol) in small portions, and the mixture heated to reflux for 1 h. Excess $NaBH_4$ was then hydrolysed by careful addition of water (10 mL). Addition of $Ni(ac)_2\cdot4H_2O$ (0.23 g, 0.79 mmol) gave a purple solution, from which a purple solid crystallised upon dissolution of NH_4PF_6 (0.13 g, 0.79 mmol). The solid was separated by filtration. Recrystallisation from water/methanol (50:50 v/v) yielded crystals suitable for an X-ray structural analysis (0.15 g, 0.24 mmol, 30% relative to **1**). − IR (KBr): ṽ = 3375m, 2926m, 1594s, 1477s, 1456s, 1296s, 1086m, 1019s, 850s (PF_6), 558s cm^{-1}. − UV/Vis (water): λ_{max} (ε) = 509 nm (22 $dm^3\cdot mol^{-1}\cdot cm^{-1}$). − MS (FAB); *m/z* (%): 414 (100) [M^+]. − $C_{20}H_{30}N_5F_6NiOP\cdot CH_3OH\cdot H_2O$ (610.23): calcd. C 41.33, H 5.94, N 11.47; found C 40.89, H 6.22, N 11.11.

$[(\mathbf{4})Ni][(\mathbf{1})Ni(H_2O)](Br)_2(PF_6)$ (5): To a solution prepared as described above for **3** (50 mL MeOH; $pyN_4\cdot4HBr\cdot MeOH$: 0.58 g,

Table 3. Crystallographic data for compounds **3**, **5**, **7**, **9** and **11**

	3·H_2O·MeOH	**5**·H_2O	**7**	**9**	**11**·2 MeOH
Empirical Formula	$C_{21}H_{36}F_6N_5NiO_3P$	$C_{33}H_{57}Br_2F_6N_{10}Ni_2O_3P$	$C_{18}H_{31}F_{12}N_5NiOP_2$	$C_{19}H_{33}F_{12}N_5NiP_2$	$C_{51}H_{59}Br_2N_5NiO_3$
Formula Weight	610.23	1064.10	682.13	680.15	1008.56
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space Group (no.)	$P2_1/c$ (no. 14)	$P2_1$ (no. 4)	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)	*P*bcn (no. 60)
a [Å]	12.109(3)	8.638(3)	8.589(1)	14.258(3)	13.614(4)
b [Å]	13.418(3)	14.944(6)	17.941(2)	10.586(2)	12.075(3)
c [Å]	18.298(5)	16.884(6)	18.195(2)	20.255(3)	30.227(6)
β [°]	108.22(2)	100.05(3)	96.47(1)	103.66(2)	90
Z	4	2	4	4	4
V [Å^3]	2824(1)	2146(2)	2785.9(5)	2970.7(9)	4969(2)
ρ_{calcd} [g cm^{-3}]	1.435	1.647	1.626	1.521	1.348
Diffractometer	Nicolet R3m/V	Nicolet R3m/V	Siemens P4	Nicolet R3m/V	Siemens P4
λ [a] [Å]	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
Crystal Size [mm^3]	0.50 × 0.40 × 0.35	0.55 × 0.18 × 0.04	0.60 × 0.55 × 0.35	0.50 × 0.40 × 0.38	0.50 × 0.40 × 0.12
T [°C]	298(2)	298(2)	295(2)	298(2)	200(2)
Absorption Correction	–	Psi-scan	Psi-scan	Psi-scan	Psi-scan
T_{min}/T_{max}	–	0.171/0.220	0.386/0.418	0.354/0.436	0.095/0.132
scan	ω	ω	ω	ω	ω
2Θ Range	$3 \le 2\Theta \le 54$	$3 \le 2\Theta \le 54$	$4 \le 2\Theta \le 50$	$4 \le 2\Theta \le 54$	$4 \le 2\Theta \le 52$
Measured Reflections	7235	5750	6718	3909	5466
Unique Reflections	6112	5231	4907	3249	4383
Observed Reflections[b]	2448	2745	2834	1473	2392
μ(Mo-K_α) [mm^{-1}]	0.814	2.849	0.914	0.854	2.044
Refined Parameters	487	514	393	227	285
Data/Parameter Ratio	12.6	10.2	12.5	14.3	15.2
$wR2$ (all data)[c]	0.0783	0.0663	0.1895	0.1168	0.1809
R 1 (obs. data)[d]	0.0406	0.0389	0.0699	0.0450	0.0724
ρ_{fin}(max/min) [e Å^{-3}]	0.406/-0.256	0.330/-0.404	0.614/-0.328	0.371/-0.244	0.570/-0.709
Weighting Scheme[e]	$k = 0.0310/l = 0$	$k = 0.0233/l = 0$	$k = 0.0763/l = 3.5962$	$k = 0.061/l = 0$	$k = 0.0707/l = 9.2413$

[a] Mo-K_α, graphite monochromator. – [b] With $F_o \ge 4\,\sigma(F)$. – [c] $wR2 = (\{\Sigma[w(F_o^2 - F_c^2)^2]\}/\{\Sigma[w(F_o^2)^2]\})^{0.5}$. – [d] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ for $F > 4\sigma(F)$. – [e] $w = 1/[\sigma^2(F_o^2) + (k\cdot P)^2] + l\cdot P$ and $P = (F_o^2 + 2\cdot F_c^2)/3$.

0.96 mmol; Na: 0.09 g, 3.84 mmol) was added dropwise over 2 h a solution of salicylaldehyde (0.12 g, 0.96 mmol) in methanol (20 mL), to give a yellow solution. Addition of $NiSO_4$·$6H_2O$ (0.27 g, 0.96 mmol) gave a red solution, from which a small amount of an orange crystalline solid precipitated upon dissolution of NH_4PF_6 (0.16 g, 0.96 mmol). Recrystallisation of this solid from methanol yielded crystals of compound **5** suitable for an X-ray structural analysis. By-products appeared ill-defined and were not characterised further. Repeated recrystallisation from methanol yielded a product for which elemental analysis data indicate the composition [(**4**)Ni]PF_6·H_2O·MeOH. – IR (KBr): $\tilde{\nu}$ = 3374m, 2933m, 1640s, 1600s, 1540m, 1471s, 1399m, 1096m, 1018s, 843 vs (PF_6), 758m, 558s cm^{-1}. MS (ESI$^+$); *m/z* (%): 412 (100) [M$^+$]. – $C_{20}H_{28}F_6N_5NiOP$·H_2O·MeOH (608.21): calcd. C 41.47, H 5.64, N 11.52; found C 41.52, H 5.47, N 11.21.

[(nacac-pyN$_4$)Ni](PF$_6$)$_2$ (7): To a solution prepared as described above for **3** (20 mL MeOH; pyN$_4$·4HBr·MeOH: 0.94 g, 1.55 mmol; Na: 0.14 g, 6.20 mmol) was added dropwise a solution of acetylacetone (0.16 g, 1.55 mmol) in methanol (20 mL), and the resulting mixture heated to reflux for 1 h. Addition of $NiCl_2$·$6H_2O$ (0.37 g, 1.55 mmol) to the colourless mixture gave a purple solution, from which a purple crystalline solid precipitated upon dissolution of NH_4PF_6 (0.25 g, 1.55 mmol). The material was isolated and recrystallised from water to give single crystals suitable for an X-ray structural analysis (0.57 g, 0.83 mmol relative to **1**, 54%). – IR (KBr): $\tilde{\nu}$ = 3380s, 2978m, 1697s (C=N), 1605s (C=O), 1471s, 1399m, 1099m, 1024s, 851s (PF_6), 559s cm^{-1}. – MS (FAB); *m/z* (%): 390 (100) [(M – H)$^+$]. – $C_{18}H_{31}F_{12}N_5NiOP_2$ (682.13): calcd. C 31.70, H 4.58, N 10.26; found C 31.69, H 4.68, N 10.02.

[((nac)$_2$-pyN$_4$)Ni](PF$_6$)$_2$ (9): To a solution prepared as described above for **3** (20 mL MeOH; pyN$_4$·4HBr·MeOH: 0.39 g, 0.63 mmol; Na: 0.06 g, 2.52 mmol) was added dropwise over 1 h a solution of acetone (0.39 g, 2.52 mmol) in methanol (20 mL), followed by addition of solid Ni(ac)$_2$·$4H_2O$ (0.18 g, 0.63 mmol) to give a purple solution. Dissolution of NH_4PF_6 (0.21 g, 1.26 mmol) led to the precipitation of a purple microcrystalline solid which was isolated by filtration and recrystallised from water to yield, after isolation and drying in air, single crystals suitable for X-ray structure analysis (0.34 g, 0.50 mmol, 79% relative to **1**). – IR (KBr): $\tilde{\nu}$ = 3378m, 1663s (C=N), 1603m, 1470m, 1376m, 1268m, 1108m, 1016m, 848s (PF_6), 558s cm^{-1}. – UV/Vis (water): λ_{max} (ε) = 509 nm (26 dm^3·mol^{-1}·cm^{-1}). – MS (ESI$^+$); *m/z* (%): 389 (65) [M$^+$], 447 (100) [M$^+$ + 58 (acetone)]. – $C_{19}H_{33}F_{12}N_5NiP_2$ (680.15): calcd. C 33.55, H 4.89, N 10.30; found C 33.43, H 5.13, N 10.07.

[{(cin)$_4$-pyN$_4$}Ni(X)]Y (X = H$_2$O, Y = Br$_2$ 11): To a stirred suspension of pyN$_4$·4HBr·MeOH (1.90 g, 3.13 mmol) in methanol (20 mL) was added LiOMe (1M stock solution in MeOH, 12.52 mL, 12.52 mmol), resulting in a clear solution after ca. 2 min. To this was added *trans*-cinnamaldehyde (1.65 g, 12.52 mmol) in one portion. The mixture was heated to reflux for 4 h, during which time the solution became yellow. Removal of the solvent in vacuo and triturating the residue by stirring with diethyl ether (30 mL) gave a yellow solid which was separated by filtration, washed with ether and dried in vacuo. Elemental analytical results of the products of repeated preparations in a variety of solvents, although unsatisfactory, agree best with a formulation of the solid as the fourfold condensation product. In the IR spectrum, a strong band is observed at 1635 cm^{-1}, which is assigned to the C=N stretching vibration. ^{1}H NMR spectra show broad and badly resolved signals in each case. The material was therefore used in the subsequent preparations without further characterisation. No effort was made to exclude air or moisture. The yellow condensation product (presumed as py(Ncinald)$_4$; 0.26 g, ≤ 0.38 mmol) was dissolved in methanol (20 mL), and solid Ni(ac)$_2$·$4H_2O$ (0.09 g, 0.38 mmol) added to give an orange solution. Reduction of the volume to ca. 10 mL led to the formation of an orange-brown microcrystalline precipitate which was filtered off and washed with methanol. IR and MS data indicate the solid to contain the acetato complex cation (X = ac). − IR (KBr): $\tilde{\nu}$ = 3447w, 3053w, 1627s (C=N), 1592s, 1449m, 1425m, 1262m, 1175m, 749s, 733s, 705s, 688s, 612m cm^{-1}. − MS (ESI$^+$); *m/z* (%): 825 (100) [(**10**)Ni(ac)]$^+$. − Repeated recrystallisation from methanol gave crystals of the aqua complex (X = H_2O; Y = Br_2) which were used in the X-ray structure analysis (0.29 g, 0.29 mmol, ≤ 75%, calculated for formula **11**). Apparently, acetate is exchanged for an aqua ligand, and lithium bromide is not removed in the course of the recrystallisations, which explains the presence of bromide counterions in the structurally characterised sample. The perchlorato perchlorate salt (X = Y = ClO_4) was obtained by recrystallisation in the presence of $NaClO_4$, but did not give satisfactory single crystals. Data for this salt are as follows: MS (FAB); *m/z* (%): 765 (75) [(**10**)Ni]$^+$; 864 (100) [(**10**)Ni(ClO_4)]$^+$. − $C_{49}H_{51}Cl_2N_5NiO_9$ {983.57, [(**10**)Ni(ClO_4)]$ClO_4\cdot H_2O$}: calcd. C 59.83, H 5.22, N 7.12; found C 59.83, H 5.45, N 6.75.

Acknowledgments

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