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Unsymmetrical Ni^{II}–Imidoylamidine Complexes Derived from a Novel Oxime-Mediated Single-Pot Reaction of Nitriles

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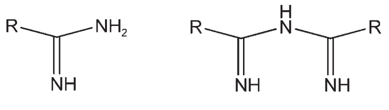
Abstract: The neutral bisimidoylamidine (or 1,3,5-triazapentadiene) Ni^{II} complexes $[Ni\{HN{=}C(R)N{=}C(C_6H_4CO)N\}_2]$ {R = Me, Et, *n*Pr, *i*Pr, $(CH_2)_3Cl$}, bearing an iminoisoindolinone moiety, have been generated by a novel 2-propanone oxime-mediated single-pot reaction of phthalonitrile and nickel(II) acetate in solution of the corresponding alkylnitrile (RCN). Single-crystal X-ray diffraction analyses indicate a square-planar geometry of the imidoylamidine core. The synthesised compounds represent rare specimens of genuine unsymmetrical imidoylamidine complexes as well as their first examples generated from nitriles in a single-pot reaction.

Keywords: imidoylamidines · N ligands · nickel · nitriles · phthalocyanines · synthetic methods

Introduction

The coordination chemistry of amidine ligands (**A**) has been intensively developed[1] for many years and widened to virtually all metals[2] due to the growing interest of both free amidines and their metal complexes in various areas, including, for example, organic synthesis, biochemistry, pharmacology, catalysis and supramolecular chemistry.[1] In contrast, much less attention has been paid to the chemistry of formally derived imidoylamidine (or 1,3,5-triazapentadiene) ligands (**B**). Although a good number of complexes (mainly with Cu and Ni) possessing an imidoylamidine core with different substituent groups (e.g., guanide, amidinothiourea and amidino-*O*-alkylurea derivatives) is known[2,3] (**C**), the "genuine" imidoylamidine compounds remain less explored, probably due to the difficulties for their syntheses.



A **B**,**C**

R=H, alkyl, etc.
(amidines or genuine imidoylamidines)
A, **B**

R=NH$_2$, NHR', NR'$_2$, OR', SR', S$^-$, etc.
(derivatives with imidoylamidine core)
C

Following the first structurally characterised bisimidoylamidine(ato) complex $[Ni\{HN{=}C(Me)N(H)_{0.75}C(Me){=}NH\}_2]Cl_{1.5}\cdot 3H_2O$ obtained by self-condensation of acetamidine with $NiCl_2\cdot 6H_2O$,[4] the information about such a type of compounds was rather scant[5] until 2001, when it was shown[6] that MeCN may undergo condensation into imidoylamidine species promoted by a dinuclear Ni–hydroxo complex bearing a pyridylamine ligand. At the same time, following our studies on the Zn^{II}– and Co^{II}–ketoxime-mediated transformations of nitriles to carboxamides, carboxylic acids and amidines,[7] and applying a similar synthetic strategy to the Ni^{II}–ketoxime system, we have achieved an easy conversion of various alkylnitriles (RCN) into imidoylamidine complexes $[Ni\{N(H){=}C(R)NHC(R){=}NH\}_2]^{2+}$.[8] The family of such compounds has been recently extended[9,10] to other metals and various substituent groups (R) by using direct synthetic procedures based on nitriles, which include the solvothermal transformation of RCN[9a,b] and arylnitrile coupling with $LiN(SiMe_3)_2$.[9c] Other recent routes to imidoylamidine species

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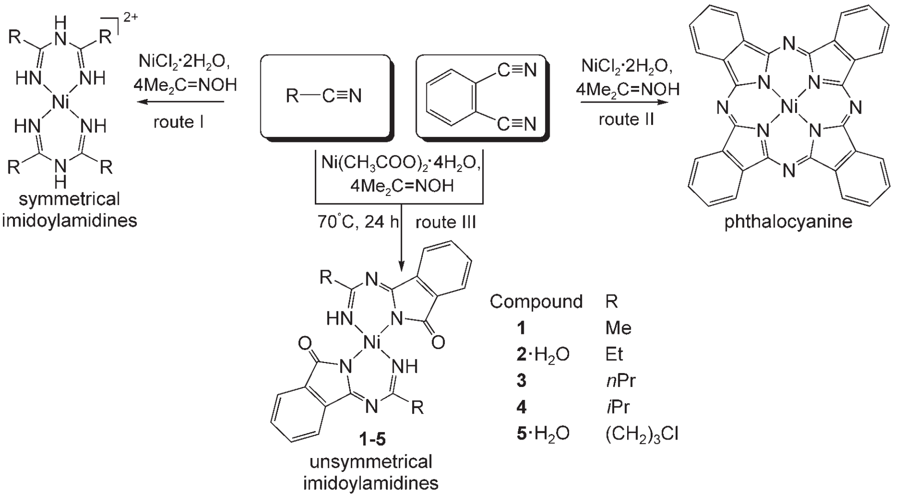
involve 1) nitrile–amidine coupling at a Pt centre,[10a] 2) metal-promoted partial decomposition of 1,3,5-triazine or its derivatives,[10b,c] 3) reaction of primary amines with the fluorinated imine species,[10d] 4) benzamidine coupling with *N*-phenylbenzimidoyl chloride[10e] or 5) 2,6-diisopropylaniline combination with an imidoyl chloride.[10f]

Although some of the above-mentioned pathways for imidoylamidines are quite attractive (especially those which involve direct transformations of cheap and industrially available synthons like nitriles),[6,8,9] many of them still display significant drawbacks, such as the harsh reaction conditions,[9a,b] low yields and selectivities,[6,9a,b] require uncommon, expensive or/and moisture sensitive chemicals[9c,10d–f] or particular metal complexes with complicated ligands,[6] and/or involve amidines[4,5a,10a,e,f] and triazines,[5b,10b,c] compounds obtained by the hazardous two-stage Pinner syntheses.[11] All the more important is that most of the synthesised "genuine" imidoylamidine complexes are symmetrical (**B** with equal R groups; Scheme 1, route I) and only rare examples of unsymmetrical imidoylamidines (namely generated on Pt centers by nitrile–amidine coupling) have been obtained.[10a] Moreover, the direct synthesis of such a type of complexes has not yet been reported.



Scheme 1.

Thus, the main aims of this work were to find a facile (preferably single-pot) route for new imidoylamidine complexes and extend this growing family of compounds to a variety of unsymmetrical members. This was achieved by an oxime-mediated synthesis starting with a mixture of phthalonitrile and an alkylnitrile in the presence of a nickel(II) salt, by taking advantage of the template effect, which has been applied[12] in different cases to the preparation of a wide variety of other macrocyclic species, including, for example, metallophthalocyanines, -porphyrins and -supramolecular structures.

Results and Discussion

We show here that a combination of previously described conversions of nitriles (mediated by oximes at Ni centers) to furnish symmetrical imidoylamidines[8] (Scheme 1, route I) and phthalocyanines[13] (route II), by using a mixture of alkylnitrile with phthalonitrile (route III), provides an easy single-pot entry to a series of new unsymmetrical bisimidoylamidine complexes of general formula $[\mathrm{Ni}\{\mathrm{H}N{=}\mathrm{C(R)N}{=}\overline{\mathrm{C}\text{-}(\mathrm{C_6H_4CO})N}\}_2]$ {R = Me **1**, Et **2**, *n*Pr **3**, *i*Pr **4**, $(CH_2)_3Cl$ **5**} (Scheme 1). Thus, treatment of $Ni(CH_3COO)_2·4H_2O$ with two equivalents of phthalonitrile and four equivalents of 2-propanone oxime (less oxime leads to a rate and an yield drop) in solution in the appropriate alkylnitrile at 70 °C results in the formation of **1**–**5**. The products were isolated as neutral, air-stable, microcrystalline solids in 62–30 % yield (based on Ni salt) and characterised by IR, FAB$^+$-MS, and ^{1}H and ^{13}C{^{1}H} NMR spectroscopies, and elemental and single-crystal X-ray diffraction (for **1**, **2**, **3** and **4**) analyses.

The IR spectra of all obtained compounds exhibit characteristic ν(NH), ν(C=N) and δ(NH) bands for the imidoylamidine core with absorbance maxima in the ranges of 3185–3125, 1630–1605 and 1560–1550 cm^{-1}, respectively, as well as some additional vibrations due to ν(CH) (2970–1850 cm^{-1}) and ν(C=O) (1695–1685 cm^{-1}) of the R and C_6H_4CO moieties. The monoprotonated molecular ions $[M{+}H]^+$ are observed with the expected isotopic patterns in the FAB$^+$-MS spectra. The ^{1}H and ^{13}C{^{1}H} NMR spectra show the expected resonances at usual chemical shifts for the corresponding ligands.[8–10]

The molecular structures of complexes **1**–**4** (Figure 1) show a square-planar coordination environment around a centrosymmetric Ni centre, whereas the planarity of whole molecules depends on the R substituent. Thus, those with R = Me (**1**) and Et (**2**) are entirely planar, but in complexes **3** and **4** the propyl groups lie partially in other planes. Nevertheless, all structures **1**–**4** (albeit belong to different space groups) are rather similar and display almost equal, within 3σ, bonding parameters. The crystal structure of **2** (Figure 1, top right), as a representative of the whole synthesised family of unsymmetrical Ni imidoylamidine complexes, is discussed in detail. It is composed of a tetracoordinated Ni centre filled by two imidoylamidinate ligands, which act as bidentate *N*,*N*-chelators. Their binding through the nonequivalent Ni–N1 (1.9455(15) Å) and Ni–N2 (1.8618(13) Å) bonds involves the six-membered Ni1-N1-C8-N3-C9-N2

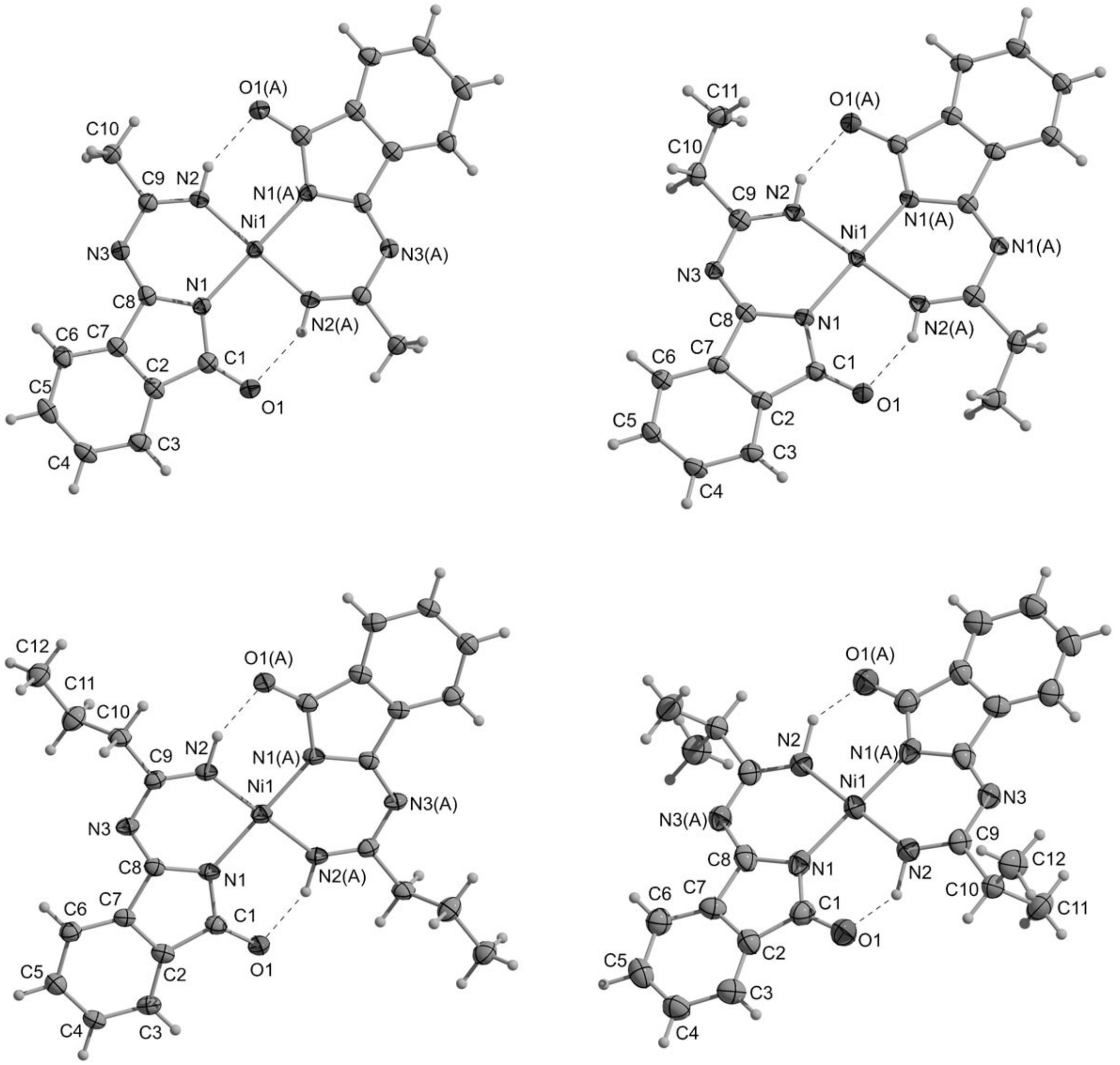


Figure 1. Thermal ellipsoid views of complexes **1** (top left), **2** (top right), **3** (bottom left) and **4** (bottom right) with atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability. In **2**, the water molecule (O99) has been omitted for clarity. Selected bond lengths (Å) and angles (°) for **2**: Ni1−N1 1.9455(15), Ni1−N2 1.8618(13), N1−C8 1.381(2), N3−C8 1.301(2), N3−C9 1.383(2), N2−C9 1.299(3), N1−C1 1.408(2), C1−O1 1.227(2), C1−C2 1.482(3), C7−C8 1.484(3), N1-Ni1-N2 88.22(6), N2-Ni1-N1(A) 91.78(6), C8-N3-C9 119.44(16). Hydrogen bonds for **2**: N2···O1(A) 2.615(2), N2−H2···O1(A) 152(2); symmetry transformations used to generate the equivalent atoms: (A): $-x$, $-y$, $-z+1$.

rings with N1-Ni1-N2 bite angles of 88.22(6)°. The N2−C9 and N3−C8 distances of 1.299(3) and 1.301(2) Å, respectively, are indicative of their double bond character, being shorter than those of the N3−C9 (1.383(2) Å) and N1−C8 (1.381(2)), the last two values being in agreement with typical single NC bonds encountered in related imidoylamidine complexes.[6,8,10e] The binding of the imidoylamidine species to the Ni centre is further stabilised by rather short N2−H2···O1 (2.615(2) Å) intramolecular hydrogen bonds, forming the Ni1-N2···O1-C1-N1 rings with the N2-Ni1-N1 angles of 91.78(6)° (Figure 1, top right). Besides, in **2** the intermolecular hydrogen-bonding contacts between a water molecule of crystallisation and an unprotonated central imidoylamidine nitrogen atom N3 (that is, O99−H99···N3 = 3.036(2) Å) link the mononuclear units into 1D infinite parallel chains (Figure 2 top). The intrachain Ni···Ni separation of about 8.80 Å is shorter that the corresponding distance of about 11.65 Å between the adjacent Ni centres within the neighbouring chains. Another interesting feature of this structure is that the stairway-type chains can be alternatively arranged to form an interpenetrated network (Figure 2, bottom).

The unsymmetrical imidoylamidine ligands in complexes **1**–**5** can also be considered as isoindole derivatives, formed directly upon treatment of phthalonitrile with a Ni–ketoxime system and, although the direct transformations of phthalonitrile to a variety of species are known,[14] the observed single-pot conversion to an iminoisoindolinone moiety had not yet been reported. The complexes are intensely coloured and the reaction may provide an easy entry to industrially important isoindolinone pigments (applied either in an organic or a metal-complex form), which are

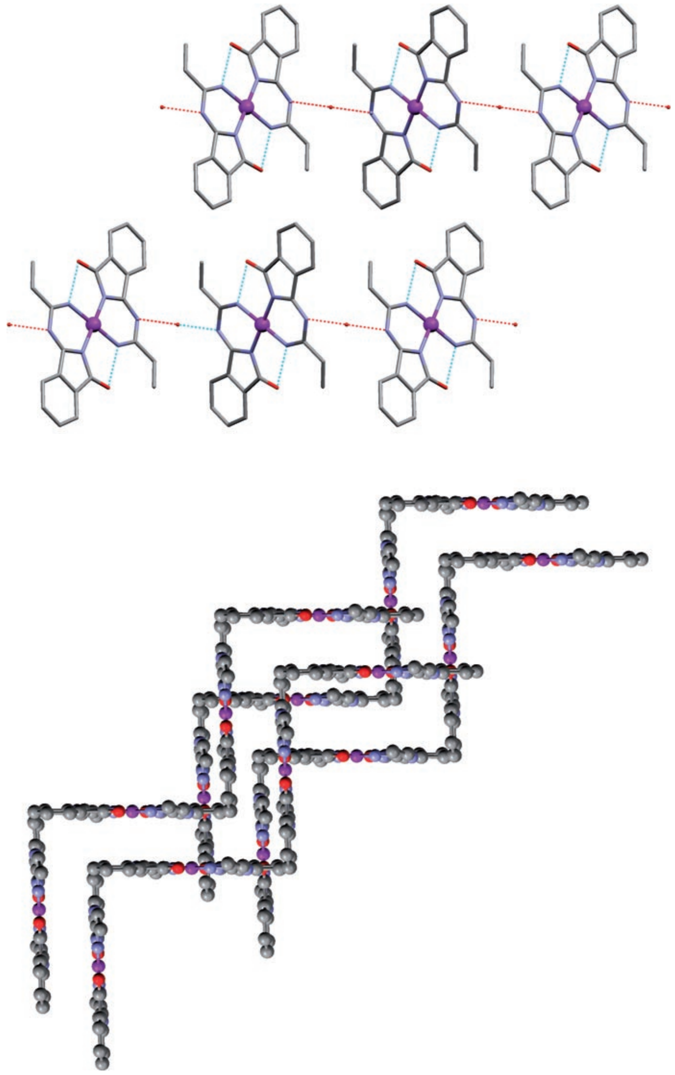
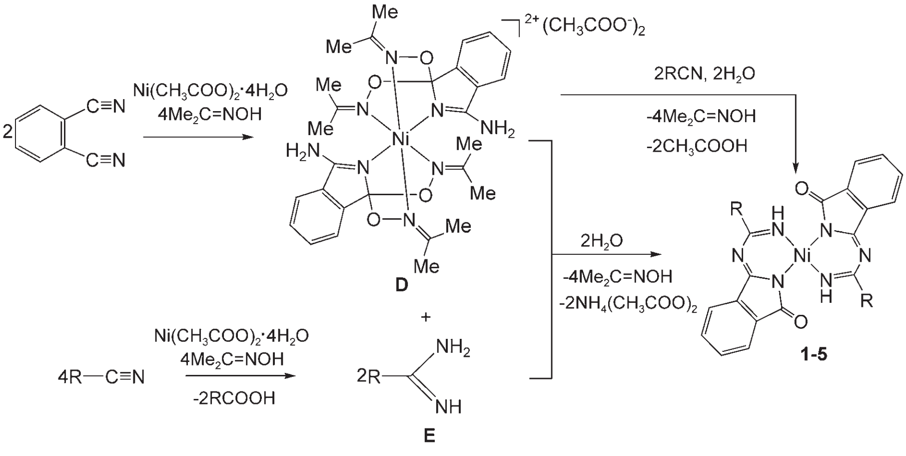


Figure 2. Partial ball-and-stick representation of the crystal packing diagram of **2**. Top: view along the *b* axis showing the formation of the 1D polynuclear chains through hydrogen bond interactions (dashed lines). Bottom: packing arrangement showing the parallel stairway-type interpenetrated chains. Hydrogen atoms and crystallisation water (in the bottom) are omitted for clarity; Ni purple, O red, N light blue, C grey.

widely used for paints, plastics, high-quality printing, and so forth.[15] In fact, some of them for example, "C.I. pigment yellow 179" $[\mathrm{Co}\{(\text{benzimidazol-2-yl})\text{-N=}\mathrm{C(C_6H_4CO)N}\}_2]$[15a,c] have a structure resembling those of **1**–**5**, with the imidoylamidine core.

Although the mechanism of the formation of complexes **1**–**5** is not yet entirely clear, it plausibly involves a combination of steps known for the Ni–ketoxime-mediated transformations, under similar reaction conditions, of alkyl nitriles to symmetrical imidoylamidines[8] and of phthalonitrile to phthalocyanines.[13] Thus, phthalonitrile undergoes a double addition of 2-propanone oxime to form an intermediate Ni complex[13] (Scheme 2, **D**), whereas alkylnitrile is converted to a corresponding amidine species[8] (Scheme 2, **E**) (examples of both type **D** and **E** species were previously characterised[8,13] by us and can also be detected in the course of the current reactions). Further hydrolytic coupling of **D** and **E**, and liberation of labile oximes would lead to the imidoylamidine complexes **1**–**5**. An alternative pathway could involve the direct reaction of **D** with alkylnitrile to afford **1**–**5**, also with regeneration of the oxime. It is worthwhile to mention that the reaction does not proceed in the absence of the oxime or a nickel(II) salt, thus showing their essential role in such a type of nitrile transformations.



Scheme 2.

Conclusion

We have found a convenient and simple route for a series of new $\mathrm{Ni^{II}}$–imidoylamidine complexes that represent the first unsymmetrical examples of genuine imidoylamidine species generated from nitriles in a single-pot template reaction. The simplicity, commercial availability and low cost of all the reagents involved and the relatively mild reaction conditions are further advantages of this synthetic approach. Besides, the properties of the obtained compounds, such as high stability, ability to sublimate, intense brown-orange colouring and structural similarity to some isoindolinone pigments and also to phthalocyanines (compounds with a diversity of uses in modern technologies, biochemistry and pharmacology),[14,15c,16] encourage the search for their applications in various areas. Further studies towards widening the family of unsymmetrical imidoylamidine complexes to other metals and functionalised derivatives generated directly by metal–ketoxime-mediated transformations of nitriles are currently under way in our laboratory.

Experimental Section

General: All synthetic work was performed in air. The solvents were obtained from commercial sources and used as received. C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Melting points were determined on a Kofler table. 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 using CsI. Infrared spectra (4000–400 $\mathrm{cm^{-1}}$) were recorded on a Jasco FT/IR-430 instrument in KBr pellets. ^{1}H and ^{13}C{^{1}H} NMR spectra were measured on a Varian UNITY 300 spectrometer at ambient temperature.

General procedure for 1–5: $\mathrm{Ni(MeCO_2)_2{\cdot}4H_2O}$ (248 mg, 1.00 mmol; Merck) was stirred in the corresponding alkylnitrile (5.00 mL) for 5 min, whereupon 2-propanone oxime (292 mg, 4.00 mmol; Aldrich) and phthalonitrile (256 mg, 2.00 mmol; Lancaster) were added. The reaction mixture was stirred at room temperature for about 1 h until complete homogenisation, whereupon it was heated with stirring at 70 °C for 24 h. The colour of the reaction mixture changed with time (for ca. 1 h) from green-blue to brown and a green-brown powder was released after about 3 h. The powder was separated by filtration after 24 h, was washed with three portions of acetone (5 mL), was dried in vacuum at room temperature, and then was washed with a chloroform/methanol (50 mL, 1:1, v/v) mixture. Upon washing, one part of the powder dissolved giving a dark red solution and a blue solid of Ni–phthalocyanine[13] byproduct (5–10 % yield) remained insoluble. The solution was filtered and evaporated under vacuum at room temperature to give a brown-orange microcrystalline solid of the unsymmetrical Ni$^{\mathrm{II}}$–imidoylamidine complexes in 62–30 % yields, based on the Ni$^{\mathrm{II}}$ salt. All complexes **1–5** were slightly soluble in acetone, chloroform, methanol and DMSO (giving red-orange deeply coloured solutions) and insoluble in water.

$[\mathrm{Ni\{H}\mathit{N}{=}\mathrm{C(Me)N}{=}\overline{\mathrm{C(C_6H_4CO)}\mathit{N}}\}_2]$ (1): Yield 62 %; m.p. 270 °C (sublimation), 300 °C (decomp); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 2.33$ (s, 6H; Me), 7.54 (m, $J = 3.4$ Hz, 4H; C*H*), 7.64 (d, $J = 5.7$ Hz, 2H; C*H*), 7.80 (d, $J = 5.5$ Hz, 2H; C*H*), 10.66 ppm (brs, 2H; N*H*); ^{13}C{^{1}H} NMR (75.4 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 27.1$ (*C*$\mathrm{H_3}$), 121.5, 122.3, 131.7 and 132.9 (aryl*C*), 166.5, 168.8 (*C*=N), 191.4 ppm (*C*=O); IR (KBr): $\tilde{\nu} = 3185$, 3138 (s, ν(NH)), 2959 (m–w ν_{as}(CH)), 2910 (m–w, ν_{s}(CH)), 1687 (vs, ν(C=O)), 1626 (vs, ν(C=N), 1556 $\mathrm{cm^{-1}}$ (vs, δ(NH)); FAB$^+$-MS: *m*/*z*: 431 $[M{+}\mathrm{H}]^+$; elemental analysis calcd (%) for $\mathrm{C_{20}H_{18}N_6NiO_2}$ (433.1): C 55.47, H 4.19, N 19.40; found: C 55.16, H 4.08, N 19.20.

$[\mathrm{Ni\{H}\mathit{N}{=}\mathrm{C(Et)N}{=}\overline{\mathrm{C(C_6H_4CO)}\mathit{N}}\}_2]{\cdot}\mathrm{H_2O}$ (2·H$_2$O): Yield 50 %; m.p. 275 °C (sublimation), 310 °C (decomp); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 1.28$ (t, $J = 7.5$ Hz, 6H; Me), 2.29 (q, $J = 6.9$ Hz, 4H; C*H*$_2$), 7.54 (m, $J = 3.5$ Hz, 4H; C*H*), 7.67 (d, $J = 5.5$ Hz, 2H; C*H*), 7.82 (d, $J = 5.5$ Hz, 2H; CH), 10.45 ppm (brs, 2H; N*H*); ^{13}C{^{1}H} NMR (75.4 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 10.74$ (*C*$\mathrm{H_3}$), 33.77 (*C*$\mathrm{H_2}$), 121.5, 122.3, 131.6, 132.8 (aryl*C*), 161.2, 162.6 (*C*=N), 195.8 ppm (*C*=O); IR (KBr): $\tilde{\nu} = 3414$ (m–w, br, ν(OH)), 3165, 3126 (m–w, ν(NH)), 2967 (m–w, ν_{as}(CH)), 2922 (m–w, ν_{s}(CH)), 1694 (vs, ν(C=O)), 1624 (vs, ν(C=N)), 1558 $\mathrm{cm^{-1}}$ (vs, δ(NH)); FAB$^+$-MS: *m*/*z*: 459 $[M{+}\mathrm{H}]^+$; elemental analysis calcd (%) for $\mathrm{C_{22}H_{24}N_6NiO_3}$ (479.2): C 55.15, H 5.05, N 17.54; found: C 55.38, H 4.92, N 17.33.

$[\mathrm{Ni\{H}\mathit{N}{=}\mathrm{C(}\mathit{n}\mathrm{Pr)N}{=}\overline{\mathrm{C(C_6H_4CO)}\mathit{N}}\}_2]$ (3): Yield 44 %; m.p. 240 °C (sublimation), 265 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 1.00$ (t, $J = 7.5$ Hz, 6H; Me), 1.75 (q, $J = 7.5$ Hz, 4H; C*H*$_2$), 2.52 (t, $J = 7.2$ Hz, 4H; C*H*$_2$), 7.54 (m, $J = 3.5$ Hz, 4H; C*H*), 7.66 (d, $J = 5.5$ Hz, 2H; C*H*), 7.81 (d, $J = 5.5$ Hz, 2H; C*H*), 10.50 ppm (brs, 2H; N*H*); ^{13}C{^{1}H} NMR (75.4 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 13.6$ (*C*$\mathrm{H_3}$), 19.8 (Me*C*$\mathrm{H_2}$), 42.6 (Et*C*$\mathrm{H_2}$), 121.5, 122.3, 131.6, 132.8 (aryl*C*), 171.9, 175.7 (*C*=N), 195.8 ppm (*C*=O); IR (KBr): $\tilde{\nu} = 3181$, 3128 (m–w, ν_{s}(NH)), 2956, 2930 (m–w, ν_{as}(CH)), 2871 (ν_{s}(CH)), 1692 (s, ν(C=O)), 1624 (vs, ν(C=N)), 1553 $\mathrm{cm^{-1}}$ (vs δ(NH)); FAB$^+$-MS: *m*/*z*: 487 $[M{+}\mathrm{H}]^+$; elemental analysis calcd (%) for $\mathrm{C_{24}H_{26}N_6NiO_2}$ (489.2): C 58.92, H 5.36, N 17.18; found: C 58.68, H 5.43, N 16.96.

$[\mathrm{Ni\{H}\mathit{N}{=}\mathrm{C(}\mathit{i}\mathrm{Pr)N}{=}\overline{\mathrm{C(C_6H_4CO)}\mathit{N}}\}_2]$ (4): Yield 56 %; m.p. 240 °C (sublimation), 295 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 1.25$ (d, $J = 6.6$ Hz, 12H; Me), 2.76 (q, $J = 7.5$ Hz, 2H; C*H*(Me)$_2$), 7.53 (m, $J = 3.5$ Hz, 4H; C*H*), 7.66 (d, $J = 5.5$ Hz, 2H; C*H*), 7.82 (d, $J = 5.5$ Hz, 2H; C*H*), 10.34 ppm (brs, 2H; N*H*); ^{13}C{^{1}H} NMR (75.4 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 20.1$ (*C*$\mathrm{H_3}$), 39.1 (*C*H(Me)$_2$), 121.5, 122.2, 131.5, 132.7 (aryl*C*), 165.9, 167.6 (*C*=N), 197.3 ppm (*C*=O); IR (KBr): $\tilde{\nu} = 3184$, 3130 (m–w, ν(NH)), 2965, 2925 (m–w, ν_{as}(CH)), 2871 (ν_{s}(CH)), 1691 (s, ν(C=O)), 1626, 1607 (s, ν(C=N)), 1552 $\mathrm{cm^{-1}}$ (vs, δ(NH)); FAB$^+$-MS: *m*/*z*: 487 $[M{+}\mathrm{H}]^+$; elemental analysis calcd (%) for $\mathrm{C_{24}H_{26}N_6NiO_2}$ (489.2): C 58.92, H 5.36, N 17.18; found: C 58.60, H 5.12, N 16.98.

$[\mathrm{Ni\{H}\mathit{N}{=}\mathrm{C(CH_2CH_2CH_2Cl)N}{=}\overline{\mathrm{C(C_6H_4CO)}\mathit{N}}\}_2]{\cdot}\mathrm{H_2O}$ (5·H$_2$O): Yield 30 %; m.p. 175 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 2.23$ (t, $J = 7.4$ Hz, 4H; C*H*$_2$C=N), 2.70 (q, $J = 7.3$ Hz, 4H; C*H*$_2$CH$_2$Cl), 3.64 (t, $J = 7.1$ Hz, 4H; C*H*$_2$Cl), 7.54 (m, $J = 3.5$ Hz, 4H; C*H*), 7.65 (d, $J = 5.0$ Hz, 2H; C*H*), 7.78 (d, $J = 5.3$ Hz, 2H; C*H*), 10.67 ppm (brs, 2H; N*H*); ^{13}C{^{1}H} NMR (75.4 MHz, $\mathrm{CDCl_3}$, TMS): $\delta = 20.7$, 30.8 (*C*$\mathrm{H_2}$), 47.7 (*C*H$_2$Cl), 122.5, 123.6, 134.3 (aryl*C*), 166.4, 167.8 (*C*=N), 187.5 ppm (*C*=O); IR (KBr): $\tilde{\nu} = 3398$ (m–w, br, ν(OH)), 3180, 3127 (s, ν(NH)), 2959, 2922 (w, ν_{as}(CH)), 2851 (w, ν_{s}(CH)), 1690 (vs, ν(C=O)), 1606 (vs, ν(C=N)), 1551 $\mathrm{cm^{-1}}$ (vs, δ(NH)); FAB$^+$-MS: *m*/*z*: 555 $[M{+}\mathrm{H}]^+$; elemental analysis calcd (%) for $\mathrm{C_{24}H_{26}Cl_2N_6NiO_3}$ (576.1): C 50.04, H 4.55, N 14.59; found: C 49.82, H 4.29, N 14.61.

X-ray crystal structure determinations: The X-ray quality single crystals of **1–4** were grown by slow evaporation at room temperature of solutions of the compounds in $\mathrm{CHCl_3}$/MeOH. They 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. The Denzo-Scalepack[17] program package was used for cell refinement and data reduction. Structures were solved by direct methods by using the SHELXS-97, SIR-97, or SIR-2002 programs.[18–20] A multiscan absorption correction based on equivalent reflections (XPREP in SHELXTL or SADABS)[21,22] was applied to all data (min/max transmission values

Table 1. Crystal data and structure refinement details for compounds **1–4**.

	1	**2**·H$_2$O	**3**	**4**
formula	$\mathrm{C_{20}H_{16}N_6NiO_2}$	$\mathrm{C_{22}H_{22}N_6NiO_3}$	$\mathrm{C_{24}H_{24}N_6NiO_2}$	$\mathrm{C_{24}H_{24}N_6NiO_2}$
M_{r}	431.10	477.17	487.20	487.20
T [K]	120(2)	120(2)	120(2)	120(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$P\bar{1}$	$P2_1/c$
a [Å]	4.8941(2)	27.7597(5)	5.0270(9)	5.1658(5)
b [Å]	18.9695(10)	4.9310(1)	9.8017(12)	15.639(3)
c [Å]	9.8447(6)	17.6084(4)	11.7414(18)	13.708(2)
α [°]	90	90	72.271(9)	90
β [°]	103.543(3)	125.082(2)	80.381(7)	98.494(9)
γ [°]	90	90	84.613(9)	90
V [Å^3]	888.55(8)	1972.42(8)	542.74(14)	1095.3(3)
Z	2	4	1	2
ρ_{calcd} [$\mathrm{Mg\,m^{-3}}$]	1.611	1.607	1.491	1.477
$\mu(\mathrm{Mo_{K\alpha}})$ [$\mathrm{mm^{-1}}$]	1.124	1.024	0.929	0.921
collected reflns	7632	11 575	5911	1914
unique reflns	2037	2273	2113	1914
$R1$[a] [$I > 2\sigma(I)$]	0.0355	0.0321	0.0508	0.0714
$wR2$[b] [$I > 2\sigma(I)$]	0.0775	0.0755	0.0997	0.1724

[a] $R1 = \Sigma||F_{\mathrm{o}}| - |F_{\mathrm{c}}||/\Sigma|F_{\mathrm{o}}|$. [b] $wR2 = [\Sigma[w(F_{\mathrm{o}}^2 - F_{\mathrm{c}}^2)^2]/\Sigma[w(F_{\mathrm{o}}^2)^2]]^{1/2}$.

were 0.7657/0.9346, 0.7176/0.9506, 0.8281/0.9404, 0.7263/0.9597 for **1–4**, respectively). All structures were refined with SHELXL-97[23] and the WinGX graphical user interface.[24] In all structures NH and H_2O hydrogen atoms were located from the difference Fourier map and refined isotropically or with a fixed N−H distance of 0.85 Å (**2**). The structure of **4** was refined as twinned with the twin law (0.984 0 −0.031 0 −1 0 −0.992 0 −0.984) and BASF refined to 0.12408. The crystallographic details for **1–4** are summarised in Table 1. CCDC–607991–607994 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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