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Synthesis and Electrochemical Studies of Nickel β-Diketonate Complexes Incorporating Asymmetric Diimine Ligands

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The reaction of pa^X {(4-X-phenyl)-pyridin-2-ylmethylene-amine; X = H, Me, Et, OMe, F, Cl, Br, and I} with [Ni(β -diketonate)₂(H₂O)₂] { β -diketonate = 1,3-diphenylpropanedionate (dbm), 2,2,6,6-tetramethyl-3,5-heptadionate (tmhd), or hexafluoroacetylacetonate (hfac)} yields a series of nickel complexes. X-ray crystallography reveals octahedral coordinated nickel centres with a *cis* arrangement of the β -diketonate ligands. The β -diketonate ligands adopt 'planar' or 'bent' coordination modes, whereas the aryl ring of the ppa^X ligand is twisted with respect to the pyridylimine unit. The electrochemical behaviour of the complexes reveals quasi-reversible or irreversible one-electron oxidation to Ni(III) in the case of the [Ni(tmhd)₂(ppa^X)] and [Ni(dbm)₂(ppa^X)] complexes, respectively. The peak potential for oxidation is dependent on the type of β -diketonate ligand but essentially independent of the substituent, X, on the ppa^X ligand. The [Ni(β -diketonate)₂(ppa^X)] complexes (X = F, Cl, Br, and I) also undergo ligand based reduction.

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Introduction

Metal β-diketonates represent an important class of complexes and have been extensively studied due to their ease of synthesis, ready modification, and multiple applications.^[1-3] In the case of divalent metal ions, the $[M(\beta-diketonate)_2]$ complexes are able to coordinate additional ligands forming octahedral metal complexes.^[4] The nature of the chelating ligands can have a significant effect on the properties of the complexes and therefore their subsequent application. Thus, chelating alkyl diamines are used to synthesize volatile precursors for the preparation of metal-oxide thin films^[5,6] whereas organic radicals may be used to construct single molecule magnets.^[7-10] However, in much of the reported literature on such octahedral metal-β-diketonate adducts only acac or hfac ligands (acac = acetylacetonate, hfac = hexafluoroacetyl-acetonate) are used with the larger dbm and tmhd ligands (dbm = 1,3-diphenylpropanedionate, tmhd = 2,2,6,6-tetramethylheptanedionate) remaining poorly represented.

While metal- β -diketonate adducts have found many applications, to date little research has been concerned with the redox chemistry of these systems.^[11–13] However, recent studies in our group have shown that the complexes, [Ni(β -diketonate)₂(L)] (β -diketonate = dbm, tmhd; L = bipy, phen), which incorporate the less widely used dbm and tmhd ligands and diimines are electrochemically active oxidizing to rare Ni(III) species.^[14] In an attempt to develop this area of chemistry we have undertaken a course of research into the chemistry of [M(β -diketonate)₂(L)] complexes. The bipyridine and phenanthroline ligands used in this preliminary study, while commercially available, are difficult to derivatize. In contrast, iminopyridines are easy to prepare and readily modified. Moreover, the different substituents on the aryl group might be expected to allow subtle changes in the steric and electronic properties of the ligands, which may in turn, affect the structure and redox chemistry of the complexes. A further point is that unlike bipy and phen, iminopyridines are asymmetric, which may also influence the chemistry of the system. In the following paper we report the synthesis, structural characterization, and redox chemistry of a series of novel [Ni(β -diketonate)₂(ppa^X)] complexes.

Results and Discussion

Synthesis and Characterization

The synthesis of the (4-X-phenyl)-pyridin-2-ylmethylene-amine (ppa^{X}) ligands, where X = H(1), Me (2), Et (3), OMe (4), F (5), Cl (6), Br (7), and I (8), was achieved by a simple condensation reaction between pyridine-2-carboxaldehyde and the appropriate substituted aniline in diethyl or diisopropyl ether (Scheme 1). While many of these ligands have been reported previously.^[15,16] we found that in most cases the reported procedure did not give the expected ppa^X cleanly. Instead considerable quantities of the starting materials remained. Hannon et al. recently reported the use of molecular sieves in an improved preparation of ppa^H, to remove the water produced during the course of the reaction.^[17] We therefore added molecular sieves to the reaction mixture and found that this simple addition significantly increased yields, purity, and also reduced reaction times. The molecular sieves are readily removed by filtration once the reaction is complete. The ligands have been characterized by IR, UV-vis, and ¹H NMR



Scheme 2. Synthesis of $[Ni(\beta - diketonate)_2(ppa^X)]$ complexes.

spectroscopy. IR spectroscopy of the ligands revealed a medium intensity imine stretch between 1623 and 1626 cm⁻¹ in line with those for previously reported ppa^X compounds.^[15–17] The ¹H NMR spectra were recorded in CDCl₃ showing a singlet between 8.58 and 8.68 ppm for the imino proton confirming the formation of the desired ppa^X ligands. The peaks for the pyridyl and phenylene groups are assigned on the basis of their splitting patterns, coupling constants, and intergration values and are typical of such iminopyridine ligands.

The reaction of $[Ni(dbm)_2(H_2O)_2]$, $[Ni(tmhd)_2(H_2O)_2]$, or $[Ni(hfac)_2(H_2O)_2]$ with the eight ppa^X ligands, in CH₂Cl₂, THF or acetone affords red, brown, and yellow solids of the octahedral complexes $[Ni(dbm)_2(ppa^X)]$ {X = H (9), Me (10), Et (11), OMe (12), F (13), Cl (14), Br (15), and I (16)}, $[Ni(tmhd)_2(ppa^X)]$ {X = H (17), Me (18), Et (19), OMe (20), F (21), Cl (22), Br (23), and I (24), and $[Ni(hfac)_2(ppa^X)]$ $\{X = H (25), Me (26), Et (27), OMe (28), F (29), Cl (30), Br$ (31), and I (32) { (Scheme 2). The red, brown, and yellow colours of these compounds are in marked contrast with the related $[Ni(\beta-diketonate)_2(L)]$ (L = bpy, phen) complexes, which are green^[14] and indicative of absorption by the ppa^X ligand. The expected *d-d* transitions are unfortunately obscured by these strong UV bands. IR spectroscopy of complexes 9-24 shows a C=O stretch from 1588 to 1595 cm⁻¹, similar to that reported for the [Ni(β -diketonate)₂(L)] (L = bpy, phen) complexes (1582– 1595 cm⁻¹),^[14] and indicative of a chelating coordination mode for the β -diketonate ligand.^[18] The C=O stretch for the hfac compounds, 25–32, is on average 60 cm^{-1} higher than that observed for complexes 9-24, consistent with the strong electron withdrawing effect of the CF₃ groups. The imine stretches of coordinated ppa^X ligands which are expected to be between 1580 and 1590 cm^{-1} are not observed as they masked by the strong C=O stretch of the β -diketonate ligand.

Crystallographic Studies

The molecular structures of complexes 10, 12, and 14 were determined by X-ray crystallography (Table 1). The structures of 10 and 12 are shown in Figs 1 and 2, respectively. Crystals of all complexes were grown by allowing hexane to diffuse slowly into a concentrated solution of the complex in CH_2Cl_2 at room temperature.

Table 1. Selected bond lengths $[{\rm \AA}]$ and angles $[^{\circ}]$ of 10, 12, and 14

	10	12	14
Ni–O(1)	2.013(3)	2.0349(12)	2.0091(16)
Ni-O(2)	2.005(3)	2.0135(12)	2.0205(17)
Ni–O(3)	2.027(3)	2.0479(12)	2.0165(16)
Ni-O(4)	2.010(4)	2.0163(12)	2.0128(16)
Ni–N(1)	2.090(4)	2.0812(14)	2.091(2)
Ni–N(2)	2.180(4)	2.1096(14)	2.189(2)
O(1)-Ni-O(2)	89.05(14)	88.93(5)	90.66(6)
O(3)-Ni-O(4)	90.58(14)	88.18(5)	89.29(6)
N(1)-Ni-N(2)	76.81(16)	78.60(6)	77.31(8)
β^{A}	2.98	31.94	16.57
	17.06	24.72	1.51
$\gamma^{\rm B}$	22.87	39.50	23.99
Intermolecular distances ^C			
O(1)–H(8)	2.439		
O(3)–H(8)		2.615	2.396
O(3)–H(6)		2.578	

 ${}^{A}\beta$ is the angle between the plane defined by the carbon and oxygen atoms of the β -diketonate ligand and the plane defined by the nickel and two oxygen atoms.

 $^{B}\gamma$ is the angle between the plane of the pyridylimine unit and the plane of the substituted phenyl ring.

^CNon-bonded metrics and those involving centroids were not included in the structure refinement, and thus do not have an estimated standard deviation.

Complexes **10**, **12**, and **14** assume slightly distorted octahedral coordination geometries. The β -diketonate ligands exhibit a *cis* arrangement enforced by the chelating ppa^X ligand. The Ni–O bond lengths vary between 2.005 and 2.048 Å for the three complexes and are similar to other previously reported nickel β -diketonate adducts, [Ni(dbm)₂(en)] {2.009(6), 2.060(7) Å},^[19] and [Ni(dbm)₂(phen)] {2.035(1), 2.041(1) Å}.^[14]

The nickel bond to the pyridine of the ppa^X ligand of complexes **10** and **14** is considerably shorter than the bond to the imine nitrogen, differing by ~0.1 Å. In contrast, the Ni–N bond lengths for **12** are different by only 0.03 Å. It is also interesting to note that in $[Cu(ppa^{2Me,3Me})_2]ClO_4^{[16]}$ and $[Ru(bipy)_2(ppa^H)][PF_6]_2$,^[17] the imine nitrogen metal bond is



Fig. 1. *ORTEP* diagram of [Ni(dbm)₂(ppa^{Me})] **10**. The thermal ellipsoids are drawn to 50% probability level. Hydrogen atoms are omitted for clarity.



Fig. 2. *ORTEP* diagram of [Ni(dbm)₂(ppa^{OMe})] **12**. The thermal ellipsoids are drawn to 50% probability level. Hydrogen atoms are omitted for clarity.

shorter than the pyridine nitrogen metal bond. The reason for this difference remains unclear. The phenyl ring in all the complexes is twisted with respect to the pyridylimine unit. Interestingly, the angle for **12** is 39.5°, whereas those of **10** and **14** are 22.9° and 24.0°, respectively. By comparison [Cu(ppa^{2Me,3Me})₂]ClO₄ and [Ru(bipy)₂(ppa^H)][PF₆]₂ exhibit angles of 69° and 45°, respectively.^[16,17] The phenyl ring is positioned above the



Fig. 3. Schematic diagram showing the angle β between the β -diketonate and NiO₂ planes.



Fig. 4. Mercury plot showing the CH···O and π - π interactions in [Ni(dbm)₂(ppa^{Cl})] 14. For clarity, only hydrogen atoms involved in interactions are shown.

pyridyl ring of a neighbouring ppa^X ligand but is neither co-planar with, nor perpendicular to, that pyridyl ring.

The β -diketonate ligand is essentially planar and symmetric suggesting that the negative charge is delocalized over the β -diketonate framework. As noted in other nickel β -diketonate adducts the nickel centre lies above the plane of the dbm ligand in a 'bent' coordination mode.^[14] The extent of this displacement has been determined by calculating the angle between the plane of the β -diketonate framework and the plane defined by the nickel and two oxygen atoms (Fig. 3). For complex **12** both dbm ligands exhibit a 'bent' coordination mode, whereas for **10** and **14** only one of the dbm ligands is 'bent' with the other assuming a 'planar' coordination mode. This is probably the result of the different substituents on the ppa^X ligands.

The complexes are packed into chiral columns with each column exhibiting the same helicity and adjacent columns of alternate helicity as shown in Figs 4 and 5. The molecules are arranged so that the ppa^X ligands are positioned above one another with the substituent alternately pointing 'in' and 'out'. The interaction principally involved here is between a C-H group from the phenyl ring of the ppa^X ligand and a coordinated oxygen atom from the dbm ligand. The structure of 12 is slightly different revealing a further interaction from the imino C-H to the same oxygen atom. As a result of the stacking of the ppa^X ligands, the dbm ligands are also stacked in columns. As might be expected, this leads to π - π interactions between two adjacent dbm phenyl rings (centroid-centroid 3.653 and 3.651 Å for 10 and 14, respectively). The absence of this interaction in the structure of 12 once again seems to stem from the extra space needed to accommodate the ppa^{OMe} ligand and the subsequent 'bent' coordination mode of both dbm ligands which preclude this interaction. Surprisingly, the π - π interaction is not replaced by any face to edge CH- π interactions.

Electrochemical Studies

The redox properties of the complexes 9-32 were studied by cyclic voltammetry (CV) in CH₂Cl₂ at 25°C (Table 2). The CVs of **13**, **21**, and **29** are shown in Fig. 6 as representative examples. Complexes 9-16 exhibit an irreversible oxidation wave, whereas



Fig. 5. Mercury plot showing the CH···O interactions in $[Ni(dbm)_2(ppa^{OMe})]$ 12. For clarity, only hydrogen atoms involved in interactions are shown.

Table	2.	Electrochemical	data	of	[Ni(β-diketonate) ₂ (ppa ^X)]	
complexes ^A						

Complex	Oxidation process $E^{o'}/E_p [V]^B$	Reduction process E_{p} [V]
9	0.67 (I)	_
10	0.66 (I)	_
11	0.66 (I)	_
12	0.66 (I)	-
13	0.68 (I)	-1.94 (I)
14	0.72 (I)	-1.84 (I)
15	0.68 (I)	-1.85 (I)
16	0.70 (I)	-1.83 (I)
17	0.33	-
18	0.32	-
19	0.31	_
20	0.32, 0.97 (I)	-
21	0.35	-2.09 (I)
22	0.35	-2.01 (I)
23	0.36	-1.98 (I)
24	0.37	-2.00 (I)
25	_	-1.76 (I)
26	_	-1.79 (I) ^C
27	_	-1.69 (I)
28	_	-1.74 (I)
29	_	-1.73 (I) ^C
30	_	-1.57 (I)
31	_	-1.61 (I)
32	0.58 (I)	-1.61 (I)

^AAll measurements were performed at 298 K, in dried and degassed CH_2Cl_2 0.1 M [NBu₄ⁿ][PF₆] solution; scan rate 100 mV s⁻¹; calibrated with [FeCp₂], and reported relative to the [FeCp₂]^{0/+} couple.

^BFor an irreversible (I) process the oxidation peak potential, $(E_p)_{ox}$, is given. ^CUncalibrated as the compound reacts with [FeCp₂].

those of **17–24** undergo quasi-reversible oxidation, albeit only at scan rates above 200 mV s⁻¹. Comparison with the related cobalt complexes [Co(β -diketonate)₂(L)] (β -diketonate = dbm, tmhd, L = bpy, phen), which oxidize between -0.15 and 0.06 V (versus [FeCp₂]^{0/+}) to give the isolable Co(III) cations, suggest that the oxidation is to Ni(III) and, as such, represent rare examples of Ni(III) species (P. Harding and D. J. Harding, unpubl. data). As expected the [Ni(β -diketonate)₂(ppa^X)] complexes are oxidized at potentials very similar to the analogous [Ni(β -diketonate)₂(L)] (β -diketonate = dbm, tmhd; L = bpy, phen) complexes.^[14] This is unsurprising given the structural similarity between the ligands. Attempts to chemically oxidize the complexes have thus far proved unsuccessful.



Fig. 6. Cyclic voltammogram of (a) $[Ni(dbm)_2(ppa^F)]$ 13, (b) $[Ni(tmhd)_2(ppa^F)]$ 21, and (c) $[Ni(hfac)_2(ppa^F)]$ 29. All potentials are versus $[FeCp_2]^{0/+}$.

The peak potentials for oxidation of **9–16** are between 0.32 and 0.37 V more positive than those of **17–24**. It is clear that the tmhd ligands are considerably more electron donating than the dbm ligands, presumably as a result of the inductive effect of the *t*-butyl groups on the tmhd ligands. The hfac ligands also have a significant effect on the peak potential for oxidation with no oxidation observed within the solvent window, with the exception of **32**. This is consistent with the findings of Villamena et al., in which the oxidation potential for [Ni(hfac)₂(2-pyBN)] (2-pyBN = N-*tert*-butyl- α -(2-pyridyl)nitrone) is observed at 1.80 V (versus Ag/AgCI).^[11]

In contrast to the considerable effect that the β -diketonate ligand has on the peak potential for oxidation, the different ppa^X ligands result in only minor changes in the peak potential for oxidation. A similar insensitivity to the substituent has been observed in a series of Cu(1) compounds, $[Cu(ppa^X)_2]ClO_4$ (X = F, Cl, Br, and I).^[16] It is possible that the substituent on the ppa^X ligand is simply too remote to significantly affect the peak potential for oxidation. Moreover, the twist between the phenyl ring and the pyridylimine unit seen in the solid state will reduce the degree of conjugation between the rings, thereby limiting the effect of the substituent on the oxidation potential. However, in the case of [Ni(tmhd)₂(ppa^{OMe})] a second irreversible oxidation is also observed, although whether this is metal-based or ligand-based remains unclear. Further spectroelectrochemical studies are currently underway to determine the nature of this second oxidation and will be reported in a later publication.



Fig. 7. Hydrogen labels of the ppa^X ligands.

In addition to the metal-based oxidation noted above, the complexes also undergo irreversible reduction. In the case of the complexes with dbm or tmhd ligands, only when X = F, Cl, Br, and I, are reduction peaks observed. Given the absence of any reduction peaks for the other complexes: i.e. where X = H. Me. Et. and OMe: it seems likely that these reductions are ligand based. Despite this, the reductions show considerable variation, with differences between the hfac and dbm complexes being on average 235 mV, whereas those between the dbm and tmhd complexes are 155 mV. The reason for this variation may be the result of the differing degrees of π -backbonding from the metal centre to the ppa^X ligand. Thus, the [Ni(tmhd)₂(ppa^X)] compounds are the most electron rich, resulting in considerable π -backbonding and are therefore, the most difficult to reduce. Conversely, the [Ni(hfac)₂(ppa^X)] complexes are the most electron poor, resulting in minimal π -backbonding, making the ppa^X ligand easier to reduce. It is also noteworthy that when X = F the complexes are more difficult to reduce by ~ 0.1 V than for [Ni(β diketonate)₂(ppa^X)] (β -diketonate = dbm, tmhd, hfac; X = Cl, Br, I). A final point of interest is that 25-28 also exhibit irreversible reduction waves. Whether this results from the reduction of the hfac or ppa^X ligands remains unclear.

Conclusions

In conclusion, we have prepared a series of [Ni(βdiketonate)₂(ppa^X)] complexes and have shown that the ppa^X ligands are convenient alternatives to substituted bipyridine or phenanthroline ligands. The crystal structures reveal octahedral coordinated nickel centres, with the β-diketonate ligands exhibiting both 'bent' and 'planar' bidentate coordination modes dependent upon the type of ppa^X ligand present. The aryl rings of the ppa^X ligands are found to be non-coplanar with the pyridylimine unit, the degree of twisting dependent on the substituent, X. The complexes are irreversibly or quasi-reversibly oxidized to Ni(III) in the case of $[Ni(dbm)_2(ppa^X)]$ and $[Ni(tmhd)_2(ppa^X)]$, respectively. With the exception of [Ni(hfac)₂(ppa^I)] the hfac complexes show no oxidation processes. The [Ni(tmhd)₂(ppa^{X})] complexes are more easily oxidized by \sim 350 mV than the [Ni(dbm)₂(ppa^X)] complexes indicating that the β -diketonate ligand has a significant effect on the redox potential. In contrast, the ppa^X ligands have only a very minor effect on the redox potential with a difference of $\sim 50 \text{ mV}$ between the various ppa^X ligands.

Experimental

General Remarks

All reactions were conducted in air using HPLC grade solvents. [Ni(tmhd)₂(H₂O)₂], [Ni(hfac)₂(H₂O)₂], and [Ni(dbm)₂(H₂O)₂] were prepared by literature methods.^[1,20] Although the ppa^X ligands are known, our synthesis differs from that previously reported and thus, their syntheses are included in the interests

of completeness. All other chemicals were purchased from Fluka Chemical Co. and used as received. Infrared spectra were recorded on a Perkin-Elmer Spectrum One infrared spectrophotometer as KBr discs, in the range $400-4000 \text{ cm}^{-1}$. Electronic spectra were recorded in CH₂Cl₂ on a Unicam UV300 UV-Visible spectrometer. Elemental analyses were carried out on a Eurovector EA3000 analyzer. ¹H NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer at 298 K in CDCl₃ with SiMe₄ added as an internal standard. Hydrogen atoms are labelled according to Fig. 7. ESI-MS were carried out on a Bruker Daltonics 7.0T Apex 4 FTICR Mass Spectrometer. Electrochemical studies were carried out using a PalmsensPC Vs 2.11 Potentiosat in conjunction with a three electrode cell. The auxiliary electrode was a platinum rod and the working electrode was a platinum disc (2.0 mm diameter). The reference electrode was a Ag-AgCl electrode (2 M LiCl). Solutions were 5×10^{-4} mol dm⁻³ in the test compound and 0.1 mol dm⁻³ in $[NBu_4^n][PF_6]$ as the supporting electrolyte. Under these conditions, $E^{0'}$ for the one-electron oxidation of [FeCp₂] added to the test solutions for internal calibration is 0.52 V.

Synthesis

Synthesis of (Phenyl)-pyridine-2-ylmethylene-amine (ppa^H) **1**

To a solution of aniline (274 μ L, 3 mmol) in diethylether (10 mL) over molecular sieves, was added pyridine-2-carboxaldehyde (266 μ L, 3 mmol). The yellow solution was stirred overnight. The solution was filtered and the molecular sieves washed with CH₂Cl₂ (5 mL). The solvent was removed under vacuum, yielding a bright yellow oil (0.273 g, 50%). ν_{max} (CH₂Cl₂)/cm⁻¹ 1630 ($\nu_{C=N}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 236 (4.07), 278 (3.82), 318 (3.50). δ_{H} = 8.70 (1H, d, ¹J_{HH} 4.8, H_a), 8.58 (1H, s, H_e), 8.19 (1H, d, ¹J_{HH} 7.8, H_d), 7.79 (1H, m, ¹J_{HH} 7.8, H_c), 7.35 (3H, m, H_f, H_b), 7.20 (3H, m, H_g, H_H).

Ligands 2–8 were synthesized using the same procedure. Analytical and spectroscopic data are given for each compound.

Synthesis of (4-Methylphenyl)-pyridine-2-ylmethylene-amine (ppa Me) **2**

Yellow crystalline solid (0.360 g, 62%). ν_{max} (KBr)/cm⁻¹ 1625 ($\nu_{C=N}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 234 (4.23), 280 (4.12), 324 (4.00 sh). $\delta_{\rm H}$ = 8.71 (1H, d, ¹J_{HH} 6.3, H_a), 8.62 (1H, s, H_e), 8.19 (1H, d, ¹J_{HH} 7.8, H_d), 7.80 (1H, m, ¹J_{HH} 7.8, H_c), 7.35 (1H, m, ¹J_{HH} 6.3, H_b), 7.24 (4H, m, H_f, H_g), 2.36 (3H, s, CH₃).

Synthesis of (4-Ethylphenyl)-pyridine-2-ylmethyleneamine (ppa^{Et}) **3**

Dull orange oil (0.375 g, 59%). ν_{max} (CH₂Cl₂)/cm⁻¹ 1630 ($\nu_{C=N}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 234 (4.10), 280 (4.03), 324 (3.93 sh). δ_{H} = 8.73 (1H, d, ¹J_{HH} 4.8, H_a), 8.68 (1H, s, H_e), 8.24 (1H, d, ¹J_{HH} 7.8, H_d), 7.85 (1H, m, ¹J_{HH} 7.5, H_c), 7.23 (5H, m, H_b, H_f, H_g), 2.69 (2H, q, ¹J_{HH} 7.2, CH₂), 1.23 (3H, t, ¹J_{HH} 7.2, CH₃).

Synthesis of (4-Methoxyphenyl)-pyridine-2-ylmethyleneamine (ppa OMe) **4**

Light orange solid (0.423 g, 67%). ν_{max} (KBr)/cm⁻¹ 1626 ($\nu_{C=N}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 238 (4.11), 286 (4.01), 340 (4.08). δ_{H} = 8.70 (1H, d, ¹J_{HH} 7.2, H_a), 8.65 (1H, s, H_e), 8.20 (1H, d, ¹J_{HH} 7.8, H_d), 7.81 (1H, dd, ¹J_{HH} 8.1, 7.8,

 $\rm H_{c}),\,7.36\,(3H,\,m,\,H_{b},\,H_{g}),\,6.94\,(2H,\,m,^{1}J_{\rm HH}\,8.7,\,H_{f}),\,3.83\,(3H,\,s,\,CH_{3}).$

Synthesis of (4-Fluorophenyl)-pyridine-2-ylmethyleneamine (ppa^F) **5**

Bright yellow crystalline solid (0.491 g, 82%). ν_{max} (KBr)/ cm⁻¹ 1627 ($\nu_{C=N}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 236 (3.91), 282 (3.91), 318 (3.75 sh). δ_{H} = 8.80 (1H, d, ¹J_{HH} 4.8, H_a), 8.60 (1H, s, H_e), 8.20 (1H, d, ¹J_{HH} 7.8, H_d), 7.85 (1H, dd, ¹J_{HH} 7.5, 7.8, H_c), 7.38 (1H, dd, ¹J_{HH} 7.5, 4.8, H_b), 7.31 (2H, dd, ¹J_{HH} 8.1, 7.9, H_f), 7.09 (2H, dd, ¹J_{HH} 7.9, 8.1, H_g).

Synthesis of (4-Chlorophenyl)-pyridine-2-ylmethyleneamine (ppa^{Cl}) **6**

 $\begin{array}{l} Pale \mbox{ yellow crystalline solid } (0.452\mbox{ g},70\%). \ \nu_{max}(KBr)/cm^{-1} \\ 1624 \ (\nu_{C=N}). \ \lambda_{max}(CH_2Cl_2)/nm \ (log\ \epsilon/M^{-1}\ cm^{-1}) \ 238 \ (4.12), \\ 280 \ (4.09), \ 320 \ (3.95\ sh). \ \delta_{H} = 8.80 \ (1H,\ d,\ ^1J_{HH}\ 5.1,\ H_a), \ 8.66 \\ (1H,\ s,\ H_e), \ 8.30 \ (1H,\ d,\ ^1J_{HH}\ 8.1,\ H_d), \ 7.89 \ (1H,\ dd,\ ^1J_{HH}\ 8.1, \\ 7.8,\ H_c), \ 7.44 \ (1H,\ dd,\ ^1J_{HH}\ 5.1,\ 7.8,\ H_b), \ 7.30 \ (2H,\ d,\ ^1J_{HH}\ 8.7, \\ H_f), \ 7.01 \ (2H,\ d,\ ^1J_{HH}\ 8.7,\ H_g). \end{array}$

Synthesis of (4-Bromophenyl)-pyridine-2-ylmethyleneamine (ppa^{Br}) 7

Brown solid (0.596 g, 76%). ν_{max} (KBr)/cm⁻¹ 1623 ($\nu_{C=N}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 232 (4.12), 280 (4.12), 324 (3.97 sh). δ_{H} = 8.73 (1H, d, ¹J_{HH} 4.8, H_a), 8.62 (1H, s, H_e), 8.21 (1H, d, ¹J_{HH} 7.5, H_d), 7.86 (1H, t, ¹J_{HH} 7.5, 6.9, H_c), 7.53 (2H, d, ¹J_{HH} 7.8, H_f), 7.42 (1H, dd, ¹J_{HH} 6.9, 4.8, H_b), 7.18 (2H, d, ¹J_{HH} 7.8, H_g).

Synthesis of (4-lodophenyl)-pyridine-2-ylmethyleneamine (ppa^{l}) **8**

Pale green solid (prepared in *i*-Pr₂O) (0.605 g, 65%). $\nu_{max}(KBr)/cm^{-1}$ 1625 ($\nu_{C=N}$). $\lambda_{max}(CH_2Cl_2)/nm$ (log ε/M^{-1} cm $^{-1}$) 242 (4.21), 282 (4.07), 320 (4.00 sh). δ_{H} = 8.72 (1H, dd, $^1J_{HH}$ 1.5, 4.8, Ha), 8.58 (1H, s, He), 8.15 (1H, d, $^1J_{HH}$ 8.1, Hd), 7.96 (1H, ddd, $^1J_{HH}$ 1.5, 7.8, 8.1, Hc), 7.54 (1H, ddd, $^1J_{HH}$ 0.9, 4.8, 7.8, Hb), 7.31 (2H, d, $^1J_{HH}$ 8.4, Hf), 7.09 (2H, d, $^1J_{HH}$ 8.4, Hg).

Synthesis of $[Ni(dbm)_2(ppa^H)]$ 9

To a lime green suspension of $[Ni(dbm)_2(H_2O)_2]$ (0.135 g, 0.25 mmol) in acetone (10 mL), was added a solution of ppa^H (0.046 g, 0.25 mmol) in acetone (3 mL). The brown orange solution was stirred overnight then concentrated under vacuum. *n*-Hexane (10 mL) was added to precipitate a brown solid, which was washed with additional *n*-hexane (2 × 5 mL) and dried under vacuum, yielding a brown solid (0.106 g, 61%) (Found: C 73.4, H 4.6, N 3.9. Calc. for C₄₂H₃₂N₂NiO₄: C 73.4, H 4.7, N 4.1%). *m/z* (ESI) 463 (100%, [M-dbm⁻]⁺). ν_{max} (KBr)/cm⁻¹ 1595 ($\nu_{C=0}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 259 (4.84), 277 (4.81), 352 (4.60).

Complexes 10–32 were synthesized by the same general procedure using acetone, THF, or CH_2Cl_2 in the case of $[Ni(dbm)_2(H_2O)_2]$, $[Ni(tmhd)_2(H_2O)_2]$, and $[Ni(hfac)_2(H_2O)_2]$, respectively. They were crystallized from the solvents indicated.

Synthesis of [Ni(dbm)₂(ppa^{Me})] **10**

Dull green microcrystals (CH₂Cl₂/*n*-hexane) (0.207 g, 55%) (Found: C 73.5, H 4.9, N 4.1. Calc. for C₄₃H₃₄N₂NiO₄: C 73.6, H 4.9, N 4.0%). *m*/*z* (ESI) 477 (100%, [M-dbm⁻]⁺).

 $\nu_{max}(KBr)/cm^{-1}$ 1595 ($\nu_{C=O}).~\lambda_{max}(CH_2Cl_2)/nm~(log\,\varepsilon/M^{-1}\,cm^{-1})$ 248 (4.63), 358 (4.51).

Synthesis of [Ni(dbm)₂(ppa^{Et})] **11**

Brown-yellow solid (acetone/*n*-hexane) (0.115 g, 64%) (Found: C 73.5, H 5.1, N 4.0. Calc. for C₄₄H₃₆N₂NiO₄: C 73.9, H 5.1, N 3.9%). *m*/*z* (ESI) 701 (100%, [M-dbm⁻ + ppa^{Et}]⁺), 491 (28%, [M-dbm⁻]⁺). ν_{max} (KBr)/cm⁻¹ 1595 ($\nu_{C=O}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 246 (4.45), 284 (4.23 sh), 356 (4.48).

Synthesis of [Ni(dbm)₂(ppa^{OMe})] **12**

Brown-yellow solid (acetone/*n*-hexane) (0.122 g, 68%) (Found: C 72.2 H 5.0, N 3.9. Calc. for $C_{43}H_{34}N_2NiO_5$: C 72.0 H 4.8, N 3.9%). *m/z* (ESI) 493 (100%, [M-dbm⁻]⁺). $\nu_{max}(KBr)/cm^{-1}$ 1595 ($\nu_{C=O}$). $\lambda_{max}(CH_2Cl_2)/nm$ (log ε/M^{-1} cm⁻¹) 250 (4.60), 282 (4.21 sh), 358 (4.54).

Synthesis of $[Ni(dbm)_2(ppa^F)]$ **13**

Brown-yellow microcrystals (CH₂Cl₂/*n*-hexane) (0.222 g, 59%) (Found: C 71.2, H 4.6, N 4.2. Calc. for C₄₂H₃₁FN₂NiO₄: C 71.5, H 4.4, N 4.0%). *m*/*z* (ESI) 481 (100%, [M-dbm⁻]⁺). ν_{max} (KBr)/cm⁻¹ 1595 ($\nu_{C=O}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 246 (4.66), 284 (4.33 sh), 356 (4.53).

Synthesis of [Ni(dbm)₂(ppa^{Cl})] **14**

Yellow solid (acetone/*n*-hexane) (0.114 g, 63%) (Found: C 71.2, H 4.7, N 3.9. Calc. for $C_{42}H_{31}ClN_2NiO_4$: C 69.9, H 4.3, N 3.9%). *m*/*z* (ESI) 497 (100%, [M-dbm⁻]⁺). ν_{max} (KBr)/cm⁻¹ 1594 ($\nu_{C=O}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 246 (4.61), 358 (4.50).

Synthesis of $[Ni(dbm)_2(ppa^{Br})]$ **15**

Yellow solid (acetone/*n*-hexane) (0.158 g, 82%) (Found: C 65.9, H 4.0, N 3.9. Calc. for $C_{42}H_{31}BrN_2NiO_4$: C 65.8, H 4.1, N 3.6%). *m/z* (ESI) 543 (100%, [M-dbm⁻]⁺). ν_{max} (KBr)/cm⁻¹ 1593 ($\nu_{C=O}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 247 (4.66), 355 (4.47).

Synthesis of $[Ni(dbm)_2(ppa^l)]$ **16**

Brown solid (THF/*n*-hexane) (0.091 g, 44%) (Found: C 61.9, H 4.2, N 3.2. Calc. for $C_{42}H_{31}IN_2NiO_4$: C 62.0, H 3.8, N 3.4%). *m*/*z* (ESI) 897 (100%, [M-dbm⁻ + ppa¹]⁺), 589 (85%, [M-dbm⁻]⁺). ν_{max} (KBr)/cm⁻¹ 1594 ($\nu_{C=O}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 248 (4.66), 286 (4.28 sh), 354 (4.50).

Synthesis of $[Ni(tmhd)_2(ppa^H)]$ **17**

Brown solid (THF/*n*-hexane) (0.063 g, 41%) (Found: C 67.8, H 7.9, N 4.8. Calc. for $C_{34}H_{48}N_2NiO_4$: C 67.2, H 8.0, N 4.6%). *m*/*z* (ESI) 605 (37%, [M-tmhd⁻ + ppa^H]⁺), 423 (100%, [M-tmhd⁻]⁺). ν_{max} (KBr)/cm⁻¹ 1591 ($\nu_{C=O}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 240 (4.36), 294 (4.28).

Synthesis of $[Ni(tmhd)_2(ppa^{Me})]$ **18**

Brown needles (slow evaporation of CH_2Cl_2) (0.080 g, 52%) (Found: C 67.0, H 7.9, N 4.4. Calc. for $\text{C}_{35}\text{H}_{50}\text{N}_2\text{NiO}_4$: C 67.6, H 8.1, N 4.5%). *m/z* (ESI) 633 (100%, [M-tmhd⁻ + ppa^{Me}]^+), 437 (88%, [M-tmhd⁻]^+). $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1586 ($\nu_{\text{C=O}}$). $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ (log $\varepsilon/\text{M}^{-1}$ cm⁻¹) 240 (4.46), 272 (4.26 sh), 308 (4.42).

Synthesis of [Ni(tmhd)₂(ppa^{Et})] **19**

Brown oil (0.066 g, 40%) (Found: C 67.8, H 8.0, N 4.1. Calc. for $C_{36}H_{52}N_2NiO_4$: C 68.0, H 8.2, N 4.4%). *m/z* (ESI) 451 (100%, [M-tmhd⁻]⁺). ν_{max} (KBr)/cm⁻¹ 1591 ($\nu_{C=O}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 240 (4.40), 308 (4.35).

Synthesis of $[Ni(tmhd)_2(ppa^{OMe})]$ **20**

Red-brown solid (THF/*n*-hexane) (0.079 g, 37%) (Found: C 65.7, H 7.4, N 4.5. Calc. for $C_{35}H_{50}N_2NiO_5$: C 65.9, H 7.9, N 4.4%). *m*/*z* (ESI) 665 (100%, [M-tmhd⁻ + ppa^{OMe}]⁺), 453 (73%, [M-tmhd⁻]⁺). $\nu_{max}(KBr)/cm^{-1}$ 1592 ($\nu_{C=O}$). $\lambda_{max}(CH_2Cl_2)/nm (log \varepsilon/M^{-1} cm^{-1})$ 242 (4.51), 316 (4.42) 354 (4.31 sh).

Synthesis of $[Ni(tmhd)_2(ppa^F)]$ **21**

Brown needles (slow evaporation of CH₂Cl₂) (0.048 g, 32%) (Found: C 65.3, H 7.5, N 4.8. Calc. for C₃₄H₄₇FN₂NiO₄: C 65.3, H 7.6, N 4.5%). *m/z* (ESI) 641 (13%, [M-tmhd⁻ + ppa^F]⁺), 441 (100%, [M-tmhd⁻]⁺). ν_{max} (KBr)/cm⁻¹ 1591 ($\nu_{C=O}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 238 (4.46), 272 (4.27), 308 (4.45).

Synthesis of [Ni(tmhd)₂(ppa^{Cl})] 22

Red-brown solid (THF/*n*-hexane) (0.068 g, 42%) (Found: C 63.3, H 7.3, N 4.7. Calc. for $C_{34}H_{47}ClN_2NiO_4$: C 63.6, H 7.4, N 4.4%). *m*/*z* (ESI) 675 (13%, [M-tmhd⁻ + ppa^{Cl}]⁺), 457 (100%, [M-tmhd⁻]⁺). $\nu_{max}(KBr)/cm^{-1}$ 1588 ($\nu_{C=O}$). $\lambda_{max}(CH_2Cl_2)/nm (\log \varepsilon/M^{-1} cm^{-1})$ 240 (4.27), 303 (4.24).

Synthesis of [Ni(tmhd)₂(ppa^{Br})] 23

Brown solid (THF/*n*-hexane) (0.051 g, 29%) (Found: C 59.2, H 6.6, N 4.3. Calc. for $C_{34}H_{47}BrN_2NiO_4$: C 59.5, H 6.9, N 4.1%). *m*/*z* (ESI) 763 (100%, [M-tmhd⁻ + ppa^{Br}]⁺), 503 (88%, [M-tmhd⁻]⁺). ν_{max} (KBr)/cm⁻¹ 1592 ($\nu_{C=O}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 244 (4.39).

Synthesis of [Ni(tmhd)₂(ppa¹)] **24**

Brown solid (THF/*n*-hexane) (0.091 g, 49%) (Found: C 55.2, H 6.5, N 3.7. Calc. for C₃₄H₄₇IN₂NiO₄: C 55.7, H 6.5, N 3.8%). *m*/*z* (ESI) 857 (100%, [M-tmhd⁻ + ppa¹]⁺), 549 (90%, [M-tmhd⁻]⁺). ν_{max} (KBr)/cm⁻¹ 1592 ($\nu_{C=O}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 252 (4.50), 276 (4.38).

Synthesis of [Ni(hfac)₂(ppa^H)]·0.5THF **25**

Yellow solid (THF/*n*-hexane) (0.076 g, 46%) (Found: C 41.3, H 2.2, N 4.3. Calc. for C₂₄H₁₆F₁₂N₂NiO_{4.5}: C 41.7, H 2.3, N 4.0%). *m*/*z* (ESI) 447 (100%, [M-hfac⁻]⁺). ν_{max} (KBr)/cm⁻¹ 1652 ($\nu_{C=O}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 243.5 (4.26), 285 (4.36), 315 (4.35).

Synthesis of [Ni(hfac)₂(ppa^{Me})]·0.5CH₂Cl₂ 26

Green-brown solid (CH₂Cl₂/*n*-hexane) (0.181 g, 98%) (Found: C 40.3, H 2.6, N 3.6. Calc. for C_{23.5}H₁₅ClF₁₂N₂NiO₄: C 40.0, H 2.1, N 3.9%). *m*/*z* (ESI) 657 (100%, [M-hfac⁻ + ppa^{Me}]⁺), 461 (26%, [M-hfac⁻]⁺). ν_{max} (KBr)/cm⁻¹ 1653 ($\nu_{C=O}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 242 (4.20), 318 (4.40).

Synthesis of [Ni(hfac)₂(ppa^{Et})] 27

Brown solid (THF/*n*-hexane) (0.055 g, 31%) (Found: C 42.5, H 2.5, N 4.2. Calc. for $C_{24}H_{16}F_{12}N_2NiO_4$: C 42.2, H 2.4, N 4.1%). *m*/*z* (ESI) 685 (100%, [M-hfac⁻ + ppa^{Et}]⁺), 475 (84%,

$$\label{eq:masses} \begin{split} & [M\text{-hfac}^-]^+). \ \nu_{max}(KBr)/cm^{-1} \ 1654 \ (\nu_{C=O}). \ \lambda_{max}(CH_2Cl_2)/nm \\ & (\log \varepsilon/M^{-1} \ cm^{-1}) \ 247 \ (4.23), \ 320 \ (4.31). \end{split}$$

Synthesis of [Ni(hfac)₂(ppa^{OMe})] 28

Deep yellow solid (THF/*n*-hexane) (0.098 g, 54%) (Found: C 40.3, H 2.4, N 4.3. Calc. for $C_{23}H_{14}F_{12}N_2NiO_5$: C 40.3, H 2.1, N 4.1%). *m/z* (ESI) 477 (100%, [M-hfac⁻]⁺). ν_{max} (KBr)/cm⁻¹ 1647 ($\nu_{C=O}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 255 (4.27), 325 (4.26).

Synthesis of $[Ni(hfac)_2(ppa^F)] \cdot 0.5C_6H_{14}$ **29**

Brown solid (CH₂Cl₂/*n*-hexane) (0.131 g, 78%) (Found: C 41.6, H 2.3, N 3.7. Calc. for C₂₅H₁₈F₁₃N₂NiO₄: C 41.9, H 2.5, N 3.9%). *m/z* (ESI) 665 (100%, [M-hfac⁻ + ppa^F]⁺), 465 (27%, [M-hfac⁻]⁺). ν_{max} (KBr)/cm⁻¹ 1651 ($\nu_{C=O}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 238 (4.26), 318 (4.45).

Synthesis of [Ni(hfac)₂(ppa^{Cl})] **30**

Golden brown solid (CH₂Cl₂/*n*-hexane) (0.101 g, 58%) (Found: C 38.5, H 1.7, N 4.2. Calc. for C₂₂H₁₁ClF₁₂N₂NiO₄: C 38.3, H 1.6, N 4.1%). *m/z* (ESI) 481 (100%, [M-hfac⁻]⁺). ν_{max} (KBr)/cm⁻¹ 1651 ($\nu_{C=0}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 240 (4.25), 319 (4.38).

Synthesis of [Ni(hfac)₂(ppa^{Br})] **31**

Deep yellow solid (CH₂Cl₂/*n*-hexane) (0.096 g, 52%) (Found: C 36.2, H 1.7, N 3.9. Calc. for C₂₂H₁₁BrF₁₂N₂NiO₄: C 36.0, H 1.5, N 3.8%). *m*/*z* (ESI) 527 (100%, [M-hfac⁻]⁺). ν_{max} (KBr)/cm⁻¹ 1651 ($\nu_{C=O}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 319 (4.46), 342 (4.34).

Synthesis of [Ni(hfac)₂(ppa^l)] **32**

Yellow solid (THF/*n*-hexane) (0.107 g, 54%) (Found: C 33.6, H 1.9, N 3.6. Calc. for $C_{22}H_{11}F_{12}IN_2NiO_4$: C 33.8, H 1.4, N 3.6%). *m/z* (ESI) 881 (100%, [M-hfac⁻ + ppa¹]⁺), 573 (82%, [M-hfac⁻]⁺). ν_{max} (KBr)/cm⁻¹ 1654 ($\nu_{C=O}$). λ_{max} (CH₂Cl₂)/nm (log ε /M⁻¹ cm⁻¹) 244 (4.40), 320 (4.41).

Crystal Structure Determinations

Crystal data for the structures of 10, 12, and 14 are given in Table 1. X-ray quality crystals of 10, 12, and 14 were grown by allowing hexane to diffuse into a concentrated solution of the complex in CH₂Cl₂. Crystals were mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 K for 10 and 12 and 100 K for 14 in a stream of cold nitrogen. All diffraction data were collected on a Bruker Smart CCD area detector with graphite monochromated *Mo* K α ($\lambda = 0.71073$ Å). After data collection, in each case an empirical absorption correction (SADABS) was applied,^[21] and the structures were then solved by direct methods and refined on all F^2 data using the SHELX suite of programs.^[22] In all cases non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters, which were $\sim 1.2 \times (\text{aromatic CH})$ or $1.5 \times (Me)$ the equivalent isotropic thermal parameters of their parent carbon atoms.

10: $C_{43}H_{34}N_2NiO_4$, *M* 701.43, yellow needle, triclinic, space group *P-1*, *a* 9.6344(15), *b* 11.9506(18), *c* 16.267(3) Å, *α* 85.726(12), *β* 87.747(11), *γ* 66.802(10)°, *U* 1716.6(5) Å³, *Z* 2, *D* 1.357 Mg m⁻³, $\mu(Mo_{K\alpha})$ 0.612 mm⁻¹, *F*(000) 732, *T* 150 K, 20118 reflections, 6429 unique (R_{int} 0.0806), R_1 0.0655 (6429 reflections, $I > 2.0\sigma(I)$), wR_2 0.1449, R_1 0.1316 (all data), wR_2 0.1796 (all data), *S* 1.008. **12**: C₄₃H₃₄N₂NiO₅, *M* 717.43, yellow plate, triclinic, space group *P-1*, *a* 9.9252(3), *b* 11.2859(3), *c* 17.4359(4) Å, *α* 73.2240(10), *β* 86.0220(10), *γ* 68.8910(10)°, *U* 1743.17(8) Å³, *Z* 2, *D* 1.367 Mg m⁻³, μ (Mo_{Kα}) 0.607 mm⁻¹, *F*(000) 748, *T* 150 K, 23492 reflections, 7901 unique (R_{int} 0.0318), R_1 0.0372 (7901 reflections, $I > 2.0\sigma(I)$), wR_2 0.0922, R_1 0.0480 (all data), wR_2 0.0987 (all data), *S* 1.037.

14: C₄₂H₃₁ClN₂NiO₄, *M* 721.85, red needle, triclinic, space group *P*-*I*, *a* 9.6098(4), *b* 12.0443(5), *c* 16.1292(7) Å, *α* 85.154(2), *β* 86.882(2), *γ* 66.725(2)°, *U* 1708.34(12) Å³, *Z* 2, *D* 1.403 Mg m⁻³, μ (Mo_{Kα}) 0.693 mm⁻¹, *F*(000) 748, *T* 100 K, 31160 reflections, 7710 unique (*R*_{int} 0.0334), *R*₁ 0.0466 (7710 reflections, *I* >2.0 σ (*I*)), *wR*₂ 0.1209, *R*₁ 0.0626 (all data), *wR*₂ 0.1278 (all data), *S* 1.094.

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