# Precursor Catenand Complexes: Synthesis, Structure, and Electrochemistry of Bis(2,6-di-iminopyridyl) Complexes of Nickel(II). The Single-crystal *X*-Ray Structure of $[NiL^4_2][BF_4]_2$†

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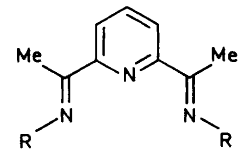
Reaction of $Ni(BF_4)_2 \cdot 6H_2O$ with 2 equivalents of the tridentate 2,6-di-iminopyridyl ligands (L) [L = $NC_5H_3(CMe{=}NR)$-2,6 (R = Et, Ph, $CH_2Ph$, or $CH_2CH_2CH_2Ph$)] in EtOH–$CH_2Cl_2$ affords the octahedral complexes $[NiL_2][BF_4]_2$. The complex $[NiL^4_2][BF_4]_2$ (R = $CH_2CH_2CH_2Ph$) crystallises in the triclinic space group $P\bar{1}$, with $a$ = 11.640(4), $b$ = 12.884 6(27), $c$ = 18.906(6) Å, $\alpha$ = 90.270(22), $\beta$ = 95.226(28), $\gamma$ = 112.098(24)°, and $Z$ = 2. The single-crystal *X*-ray structure shows a distorted octahedral geometry around nickel(II) with four imine N-donors occupying equatorial sites [Ni–N(imine) 2.135(7), 2.121(7), 2.142(7), and 2.160(7) Å] and two shorter axial bonds to pyridyl N-donors [Ni–N(py) 1.989(7) and 1.981(7) Å]. The four propylphenyl groups of L extend past the inner co-ordination sphere of the metal ion into positions which could potentially be linked together to form octahedral catenand species. Cyclic voltammetry of $[NiL_2][BF_4]_2$ (R = $CH_2Ph$ or $CH_2CH_2CH_2Ph$) in MeCN at platinum electrodes shows for each complex two reversible one-electron reductions at $^1E_{\frac{1}{2}} = -1.56$ and $-1.53$ V and at $^2E_{\frac{1}{2}} = -1.89$ and $-1.87$ V respectively, and one one-electron oxidation process at $E_{\frac{1}{2}} = +1.22$ and $+1.12$ V *vs.* ferrocene–ferrocenium respectively. The quantitative electrogeneration of the corresponding mono-reduced and -oxidised species has been accomplished and assigned by e.s.r. spectroscopy to the formation of nickel-(I) and -(III) complexes respectively.

The stabilisation of $d^9$ nickel(I) and $d^7$ nickel(III) centres by N-donor macrocyclic complexes has been the subject of much interest in recent years.[1–6] Interest in the stability and reactivity of such systems has been further aroused by the proposal of nickel-(I) and -(III) species as intermediates at the active sites of certain nickel-containing hydrogenases.[7] The design of ligands incorporating specific electronic (π-acceptor or -donor) and stereochemical features has, therefore, been an important consideration in the generation of these metal oxidation states.

The 2,6-di-iminopyridyl moiety has been successfully incorporated into several macrocyclic configurations,[8] and low-valent metal products and ligand-radical species synthesised.[9,10] We were interested in studying the complexation and redox activity of complexes of open-chain, non-macrocyclic ligands incorporating the 2,6-di-iminopyridyl moiety.[11] Our aims were to investigate the possible generation of nickel-(I) and -(III) centres within octahedral complexes, and to synthesise pendant 'long-tail' derivatives of the 2,6-di-iminopyridyl unit. Sauvage and co-workers[12] have reported the synthesis of interlocking catenand complexes *via* the cross-linking of co-ordinated 1,10-phenanthroline derivatives with polyether chains. These tetrahedral complexes show remarkable topological and redox properties.[13] We argued that a route to related octahedral complexes might be available by the cross-linking of bis(2,6-di-iminopyridyl) species incorporating pendant arm functionalities.

We report herein the synthesis, structure, and redox properties of the octahedral nickel(II) complexes $[NiL_2]^{2+}$ (L = $L^1$—$L^4$).



| | R |
|---|---|
| $L^1$ | Et |
| $L^2$ | Ph |
| $L^3$ | $CH_2Ph$ |
| $L^4$ | $CH_2CH_2CH_2Ph$ |

## Results and Discussion

The tridentate 2,6-di-iminopyridyl ligands ($L^1$—$L^4$) were prepared by condensation of 2,6-diacetylpyridine with 2 molar equivalents of the corresponding monoamine. Reaction of 2 molar equivalents of $L^1$—$L^4$ with 1 molar equivalent of $Ni(BF_4)_2 \cdot 6H_2O$ in EtOH–$CH_2Cl_2$ affords the corresponding bis (ligand) complex cations $[NiL_2]^{2+}$ which can be isolated as their $BF_4^-$ salts. Comparison of the i.r. spectra of the complexes with those of the metal-free ligands reveals that the ligands have remained intact on co-ordination to the nickel(II) centre. No absorption near 1 700 cm$^{-1}$ due to carbonyl bands, ν(C=O), or at 3 400—3 200 cm$^{-1}$ due to N–H vibrations, ν(N–H), is observed for the free ligands or for the metal complexes. The complexes show medium-intensity bands assigned to imine C=N stretching vibrations, ν(C=N), in the region 1 640—1 605 cm$^{-1}$. The complexes are hygroscopic and broad bands in the region 3 600—3 400 cm$^{-1}$ are assigned to the O–H stretching vibration, ν(O–H), of non-co-ordinated water. Bands at 1 060—1 050 and 525—530 cm$^{-1}$ are assigned to the asymmetric B–F stretching vibration, ν(B–F), and B–F bend, δ(B–F), respectively.

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† Bis[2,6-bis(3′-phenylpropyliminoethyl)pyridine-*NN′N″*]-nickel(II) tetrafluoroborate.

*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

*Non-S.I. unit employed:* G = $10^{-4}$ T.

**Table 1.** Bond lengths (Å) and angles (°) with standard deviations for $[NiL^4{}_2][BF_4]_2$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ni-N(1) | 1.989(7) | N(4)-C(12) | 1.338(11) | C(7)-C(8) | 1.473(14) | C(22)-C(23) | 1.522(17) |
| Ni-N(2) | 2.135(7) | N(4)-C(16) | 1.334(11) | C(8)-C(9) | 1.492(17) | C(23)-C(24) | 1.556(15) |
| Ni-N(3) | 2.121(7) | N(5)-C(11) | 1.264(11) | C(10)-C(11) | 1.511(14) | C(31)-C(32) | 1.460(17) |
| Ni-N(4) | 1.981(7) | N(5)-C(41) | 1.476(11) | C(11)-C(12) | 1.481(12) | C(32)-C(33) | 1.551(21) |
| Ni-N(5) | 2.142(7) | N(6)-C(17) | 1.274(12) | C(12)-C(13) | 1.382(14) | C(33)-C(34) | 1.533(21) |
| Ni-N(6) | 2.160(7) | N(6)-C(51) | 1.445(15) | C(13)-C(14) | 1.378(16) | C(41)-C(42) | 1.493(13) |
| N(1)-C(3) | 1.336(12) | C(1)-C(2) | 1.508(15) | C(14)-C(15) | 1.347(16) | C(42)-C(43) | 1.527(15) |
| N(1)-C(7) | 1.330(12) | C(2)-C(3) | 1.467(14) | C(15)-C(16) | 1.395(14) | C(43)-C(44) | 1.526(14) |
| N(2)-C(2) | 1.286(12) | C(3)-C(4) | 1.389(16) | C(16)-C(17) | 1.472(13) | C(51)-C(52) | 1.295(20) |
| N(2)-C(21) | 1.449(12) | C(4)-C(5) | 1.384(20) | C(17)-C(18) | 1.515(15) | C(52)-C(53) | 1.530(22) |
| N(3)-C(8) | 1.285(12) | C(5)-C(6) | 1.388(20) | C(21)-C(22) | 1.508(14) | C(53)-C(54) | 1.514(19) |
| N(3)-C(31) | 1.489(14) | C(6)-C(7) | 1.384(16) | | | | |
| N(1)-Ni-N(2) | 77.6(3) | Ni-N(3)-C(8) | 116.1(6) | N(1)-C(7)-C(6) | 120.3(9) | N(2)-C(21)-C(22) | 112.8(8) |
| N(1)-Ni-N(3) | 76.6(3) | Ni-N(3)-C(31) | 122.2(6) | N(1)-C(7)-C(8) | 114.5(8) | C(21)-C(22)-C(23) | 113.4(9) |
| N(1)-Ni-N(4) | 178.7(3) | C(8)-N(3)-C(31) | 121.7(8) | C(6)-C(7)-C(8) | 125.2(10) | C(22)-C(23)-C(24) | 113.7(10) |
| N(1)-Ni-N(5) | 102.7(3) | Ni-N(4)-C(12) | 118.5(6) | N(3)-C(8)-C(7) | 114.0(9) | C(23)-C(24)-C(25) | 117.9(8) |
| N(1)-Ni-N(6) | 103.5(3) | Ni-N(4)-C(16) | 119.6(6) | N(3)-C(8)-C(9) | 127.0(10) | C(23)-C(24)-C(29) | 121.9(8) |
| N(2)-Ni-N(3) | 154.2(3) | C(12)-N(4)-C(16) | 121.9(7) | C(7)-C(8)-C(9) | 118.9(9) | N(3)-C(31)-C(32) | 109.8(9) |
| N(2)-Ni-N(4) | 101.2(3) | Ni-N(5)-C(11) | 114.8(5) | N(5)-C(11)-C(10) | 127.2(8) | C(31)-C(32)-C(33) | 112.2(11) |
| N(2)-Ni-N(5) | 97.4(3) | Ni-N(5)-C(41) | 123.5(5) | N(5)-C(11)-C(12) | 115.7(8) | C(32)-C(33)-C(34) | 111.5(12) |
| N(2)-Ni-N(6) | 89.7(3) | C(11)-N(5)-C(41) | 121.7(7) | C(10)-C(11)-C(12) | 117.1(8) | C(33)-C(34)-C(35) | 120.2(12) |
| N(3)-Ni-N(4) | 104.7(3) | Ni-N(6)-C(17) | 113.5(6) | N(4)-C(12)-C(11) | 113.9(7) | C(33)-C(34)-C(39) | 119.9(12) |
| N(3)-Ni-N(5) | 88.7(3) | Ni-N(6)-C(51) | 125.2(7) | N(4)-C(12)-C(13) | 119.5(8) | N(5)-C(41)-C(42) | 110.3(7) |
| N(3)-Ni-N(6) | 95.9(3) | C(17)-N(6)-C(51) | 121.2(8) | C(11)-C(12)-C(13) | 126.6(8) | C(41)-C(42)-C(43) | 112.0(8) |
| N(4)-Ni-N(5) | 77.1(3) | N(2)-C(2)-C(1) | 124.9(9) | C(12)-C(13)-C(14) | 119.5(10) | C(42)-C(43)-C(44) | 111.1(9) |
| N(4)-Ni-N(6) | 76.7(3) | N(2)-C(2)-C(3) | 116.2(8) | C(13)-C(14)-C(15) | 120.0(11) | C(43)-C(44)-C(45) | 119.0(8) |
| N(5)-Ni-N(6) | 153.7(3) | C(1)-C(2)-C(3) | 119.0(9) | C(14)-C(15)-C(16) | 119.5(10) | C(43)-C(44)-C(49) | 120.8(8) |
| Ni-N(1)-C(3) | 117.9(6) | N(1)-C(3)-C(2) | 114.4(8) | N(4)-C(16)-C(15) | 119.6(8) | N(6)-C(51)-C(52) | 118.8(12) |
| Ni-N(1)-C(7) | 118.7(6) | N(1)-C(3)-C(4) | 118.5(9) | N(4)-C(16)-C(17) | 112.9(8) | C(51)-C(52)-C(53) | 118.1(14) |
| C(3)-N(1)-C(7) | 123.3(8) | C(2)-C(3)-C(4) | 127.1(9) | C(15)-C(16)-C(17) | 127.4(8) | C(52)-C(53)-C(54) | 116.0(12) |
| Ni-N(2)-C(2) | 113.8(6) | C(3)-C(4)-C(5) | 119.6(12) | N(6)-C(17)-C(16) | 117.0(8) | C(53)-C(54)-C(55) | 121.7(10) |
| Ni-N(2)-C(21) | 125.6(6) | C(4)-C(5)-C(6) | 120.0(13) | N(6)-C(17)-C(18) | 125.0(9) | C(53)-C(54)-C(59) | 118.2(10) |
| C(2)-N(2)-C(21) | 120.5(8) | C(5)-C(6)-C(7) | 118.2(12) | C(16)-C(17)-C(18) | 118.0(8) | | |

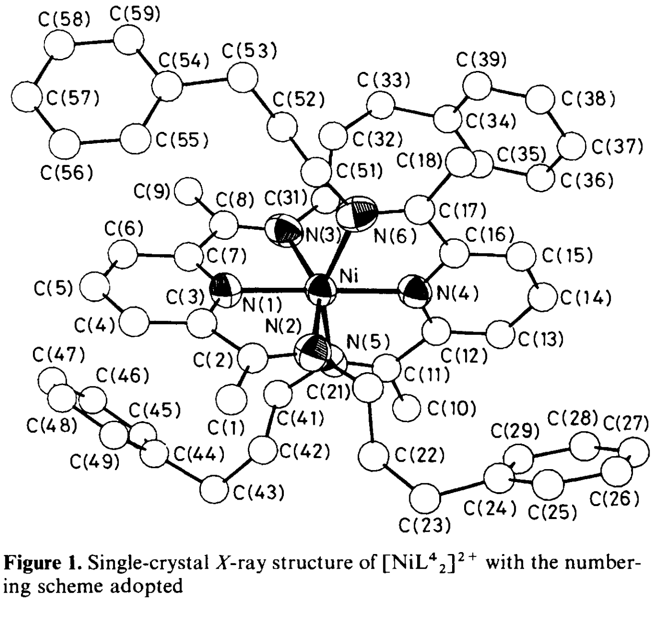


**Figure 1.** Single-crystal $X$-ray structure of $[NiL^4{}_2]^{2+}$ with the numbering scheme adopted

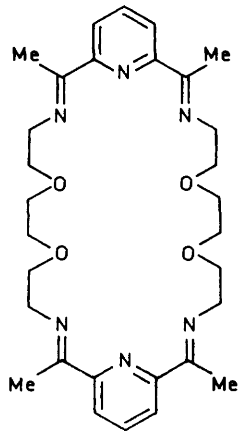
Conductivity measurements in MeCN confirm the complexes to be 2:1 electrolytes in solution, while solid-state magnetic moments (by the Gouy method), $\mu_{eff.}$ = 3.0—3.1 at 293 K are in the range expected for two unpaired electrons in octahedral $Ni^{II}$. The electronic spectra (250—1 000 nm) of the complexes were measured in solution in MeCN or $CH_2Cl_2$ and as Nujol mulls. Good correlation between the spectra in the two phases suggests that no decomposition or structural rearrangement occurs in solution. The absorbances near 800—820, 500, and 400 nm observed for all the complexes are assigned to the $^3A_{2g} \longrightarrow {}^3T_{2g}$, $^3A_{2g} \longrightarrow {}^3T_{1g}$, and $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ transitions of octahedral nickel(II) products.[14]

These data together with analytical results confirm the products to be octahedral nickel(II) complexes of the type $[NiL_2][BF_4]_2$ ($L = L^1$—$L^4$). We wished to analyse the exact stereochemical features of these complexes, and to assess the spatial orientation of the pendant phenyl moieties. Single crystals of $[NiL^4{}_2][BF_4]_2$ suitable for a crystallographic study were prepared by recrystallisation of the complex from $CH_2Cl_2$.

The single-crystal $X$-ray structure of $[NiL^4{}_2]^{2+}$ is shown in Figure 1. The complex shows two molecules of $L^4$ co-ordinated to the nickel(II) centre in a meridional manner. The stereochemistry around the $Ni^{II}$ is distorted octahedral with the four imino N-donors bound in an equatorial plane, Ni–N(2), 2.135(7), Ni–N(3) 2.121(7), Ni–N(5) 2.142(7), and Ni–N(6) 2.160(7) Å, and the two pyridyl N-donors occupying axial positions, Ni–N(1) 1.989(7) and Ni–N(4) 1.981(7) Å. The two pyridyl rings make an angle of 81.4(3)° to one another. The NNiN angles are markedly distorted from 90° with N(1)NiN(2) 77.6(3), N(1)NiN(3) 76.6(3), N(1)NiN(4) 178.7(3), N(4)NiN(5) 77.1(3), and N(4)NiN(6) 76.7(3)°. A similar stereochemistry has been observed for the cobalt(II) complex of the macrocycle $L^5$.[14] The pendant phenyl groups of the co-ordinated $L^4$ ligands are disordered and do not interact with the metal centre. In the solid-state structure the two phenyl groups of each tridentate ligand extend beyond the co-ordination sphere of the other co-ordinated $L^4$ ligand, and are situated with the 4 positions of the phenyl ring lying at distances of 7.56 and 7.91 Å from one another (Figure 2). Current work is aimed at functionalising these 4 positions of the phenyl ring in order to cross-link these

**Table 2.** Fractional co-ordinates with standard deviations

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Ni | 0.187 09(10) | 0.234 83(9) | 0.231 35(6) |
| N(1) | 0.105 8(6) | 0.300 8(5) | 0.296 7(4) |
| N(2) | 0.118 2(6) | 0.333 6(6) | 0.162 3(4) |
| N(3) | 0.215 4(6) | 0.167 5(5) | 0.330 6(4) |
| N(4) | 0.267 8(6) | 0.171 4(5) | 0.164 6(4) |
| N(5) | 0.377 7(6) | 0.348 8(5) | 0.245 6(4) |
| N(6) | 0.036 6(6) | 0.085 2(6) | 0.187 0(4) |
| C(1) | −0.007 9(9) | 0.451 9(8) | 0.155 8(6) |
| C(2) | 0.055 1(8) | 0.381 0(7) | 0.192 7(5) |
| C(3) | 0.047 7(8) | 0.365 4(7) | 0.269 2(5) |
| C(4) | −0.014 0(10) | 0.408 2(9) | 0.313 7(8) |
| C(5) | −0.012 3(12) | 0.384 5(11) | 0.385 0(9) |
| C(6) | 0.050 2(11) | 0.317 8(10) | 0.411 6(7) |
| C(7) | 0.108 6(9) | 0.275 9(7) | 0.364 9(5) |
| C(8) | 0.175 9(9) | 0.201 8(8) | 0.383 8(5) |
| C(9) | 0.190 4(13) | 0.173 3(11) | 0.459 6(5) |
| C(10) | 0.590 0(8) | 0.382 2(9) | 0.211 7(6) |
| C(11) | 0.450 2(8) | 0.323 2(7) | 0.209 5(5) |
| C(12) | 0.390 3(8) | 0.223 4(7) | 0.160 7(4) |
| C(13) | 0.447 8(10) | 0.182 9(8) | 0.112 7(5) |
| C(14) | 0.378 0(11) | 0.089 9(9) | 0.069 6(5) |
| C(15) | 0.254 7(10) | 0.039 0(8) | 0.074 5(5) |
| C(16) | 0.198 9(8) | 0.080 7(7) | 0.123 8(4) |
| C(17) | 0.067 2(8) | 0.035 1(7) | 0.138 2(5) |
| C(18) | −0.020 8(10) | −0.068 0(9) | 0.095 0(6) |
| C(21) | 0.135 7(9) | 0.347 8(8) | 0.087 6(5) |
| C(22) | 0.242 2(10) | 0.454 7(8) | 0.074 2(5) |
| C(23) | 0.249 1(13) | 0.480 2(10) | −0.004 2(6) |
| C(24) | 0.290 6(8) | 0.399 9(5) | −0.047 6(4) |
| C(25) | 0.238 4(8) | 0.371 0(5) | −0.117 8(4) |
| C(26) | 0.279 3(8) | 0.305 8(5) | −0.160 4(4) |
| C(27) | 0.372 5(8) | 0.269 6(5) | −0.132 9(4) |
| C(28) | 0.424 8(8) | 0.298 5(5) | −0.062 7(4) |
| C(29) | 0.383 8(8) | 0.363 6(5) | −0.020 1(4) |
| C(31) | 0.279 2(11) | 0.086 9(9) | 0.338 7(6) |
| C(32) | 0.187 0(11) | −0.026 8(10) | 0.342 1(7) |
| C(33) | 0.246 7(17) | −0.116 1(12) | 0.342 1(8) |
| C(34) | 0.272 8(13) | −0.140 7(9) | 0.267 1(5) |
| C(35) | 0.391 8(13) | −0.088 6(9) | 0.245 3(5) |
| C(36) | 0.414 7(13) | −0.109 8(9) | 0.176 6(5) |
| C(37) | 0.318 5(13) | −0.183 0(9) | 0.129 7(5) |
| C(38) | 0.199 5(13) | −0.235 1(9) | 0.151 5(5) |
| C(39) | 0.176 6(13) | −0.213 9(9) | 0.220 2(5) |
| C(41) | 0.423 8(8) | 0.447 6(7) | 0.295 5(5) |
| C(42) | 0.407 7(9) | 0.545 6(7) | 0.260 5(5) |
| C(43) | 0.467 8(11) | 0.653 0(8) | 0.307 2(5) |
| C(44) | 0.414 5(9) | 0.639 1(5) | 0.378 9(4) |
| C(45) | 0.487 4(9) | 0.629 2(5) | 0.439 3(4) |
| C(46) | 0.437 2(9) | 0.607 6(5) | 0.504 4(4) |
| C(37) | 0.314 1(9) | 0.595 9(5) | 0.509 1(4) |
| C(48) | 0.241 1(9) | 0.605 8(5) | 0.448 8(4) |
| C(49) | 0.291 3(9) | 0.627 4(5) | 0.383 6(4) |
| C(51) | −0.090 1(9) | 0.046 3(11) | 0.205 7(7) |
| C(52) | −0.115 0(10) | −0.001 9(16) | 0.265 4(8) |
| C(53) | −0.251 1(12) | −0.051 3(13) | 0.281 5(8) |
| C(54) | −0.287 6(8) | 0.013 8(10) | 0.336 2(5) |
| C(55) | −0.297 9(8) | 0.116 2(10) | 0.321 5(5) |
| C(56) | −0.335 2(8) | 0.172 0(10) | 0.372 6(5) |
| C(57) | −0.362 2(8) | 0.125 5(10) | 0.438 5(5) |
| C(58) | −0.352 0(8) | 0.023 2(10) | 0.453 2(5) |
| C(59) | −0.314 7(8) | −0.032 7(10) | 0.402 1(5) |



$L^5$

sites and generate an octahedral catenand species. Preliminary experiments indicate that this may be difficult to achieve due to the reactivity of the co-ordinated imino linkages towards nucleophiles and their sensitivity to hydration.

Cyclic voltammetry of $[NiL_2][BF_4]_2$ ($L = L^3$ or $L^4$) in MeCN at platinum electrodes shows, for each complex, two reversible one-electron reductions at $^1E_{\frac{1}{2}} = -1.56$ ($\Delta E_p = 67$) and $-1.53$ V ($\Delta E_p = 68$ mV) and at $^2E_{\frac{1}{2}} = -1.89$ ($\Delta E_p = 67$) and $-1.87$ V ($\Delta E_p = 70$ mV) respectively, and one oxidation process at $E_{\frac{1}{2}} = +1.22$ ($\Delta E_p = 64$) and $+1.12$ V ($\Delta E_p = 69$ mV) *vs.* ferrocene–ferrocenium respectively (Figure 3). The complexes were quantitatively reduced and oxidised under Ar by controlled-potential electrolysis at a platinum gauze in MeCN and $CH_2Cl_2$ in the presence of 0.1 mol dm$^{-3}$ $NBu^n{}_4BF_4$ as base electrolyte, and the redox products identified by e.s.r. spectroscopy. E.s.r. spectroscopy is particularly useful since it can readily distinguish between metal- and ligand-based radical species, in this case between $d^9$ nickel(I) and $d^7$ nickel(III) or ligand-based ($L^{\bullet -}$) radical species.[1-3]

Controlled-potential electrolysis of the complexes at − 1.75 V led to the formation of intense maroon solutions ($\lambda_{max.} = 504$ nm for $L^3$) of the monoreduced species from the initial yellow-brown nickel(II) solution. The e.s.r. spectra of these reduced solutions, measured as frozen glasses at 77 K, show very strong anisotropic signals with $g_{\parallel} = 2.24$, $g_{\perp} = 2.15$ for $[NiL^3{}_2]^+$ (Figure 4) and $g_{\parallel} = 2.22$, $g_{\perp} = 2.13$ for $[NiL^4{}_2]^+$. These features with $g_{\parallel} > g_{\perp}$ are consistent with the formation of an axially symmetric $d^9$ nickel(I) species with a ground-state configuration $(d_{xy})^2(d_{xz})^2(d_{yz})^2(d_{z^2})^2(d_{x^2-y^2})^1$.[1,3] Coulometry confirms the reductions to be one-electron processes. Superhyperfine coupling to the co-ordinated N-donors is not observed; such coupling to nitrogen is usually not observed in the e.s.r. spectra of nickel(I) tetra-aza macrocyclic species.[1,9] The formation of these reduced products is not significantly dependent upon the solvent used (MeCN or $CH_2Cl_2$) suggesting that ligand dissociation and solvent co-ordination do not occur, although over extended periods (over 1 h) these highly reactive, air-sensitive species do decompose in solution. It should be noted that these compounds are rare examples of $Ni^I$ stabilised by non-macrocyclic N-donor ligands.[1] The co-ordination geometry at the metal centre in these monoreduced species is likely to be distorted octahedral with Jahn–Teller distortion due to the $d^9$ centre playing a prominent role. Sauvage and co-workers[13] have reported the increased stabilisation of $Ni^I$ in tetrahedral stereochemistries; it is possible that such a geometry can be achieved in our system by breaking

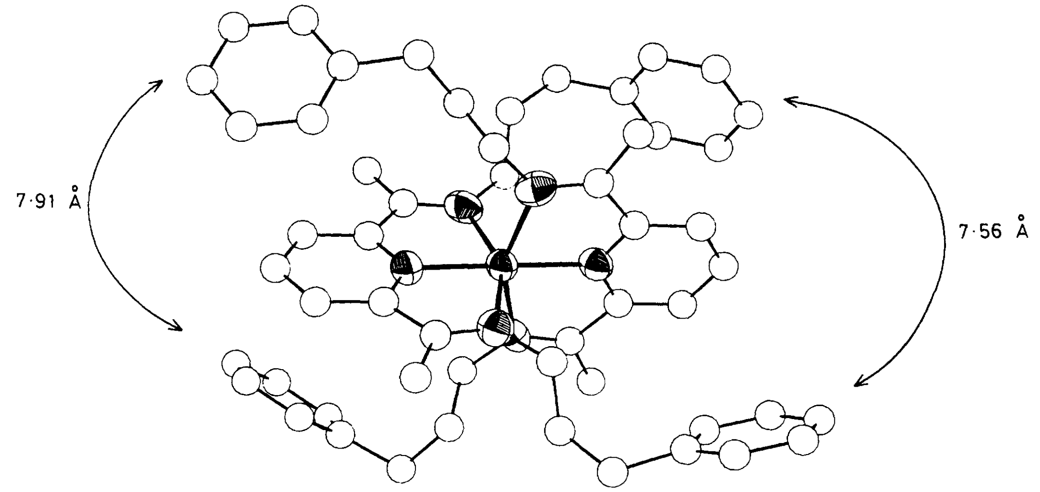


Figure 2. Structure of $[NiL^{4}{}_{2}]^{2+}$ showing intramolecular distances between pendant phenyl groups of $L^{4}$ ligands

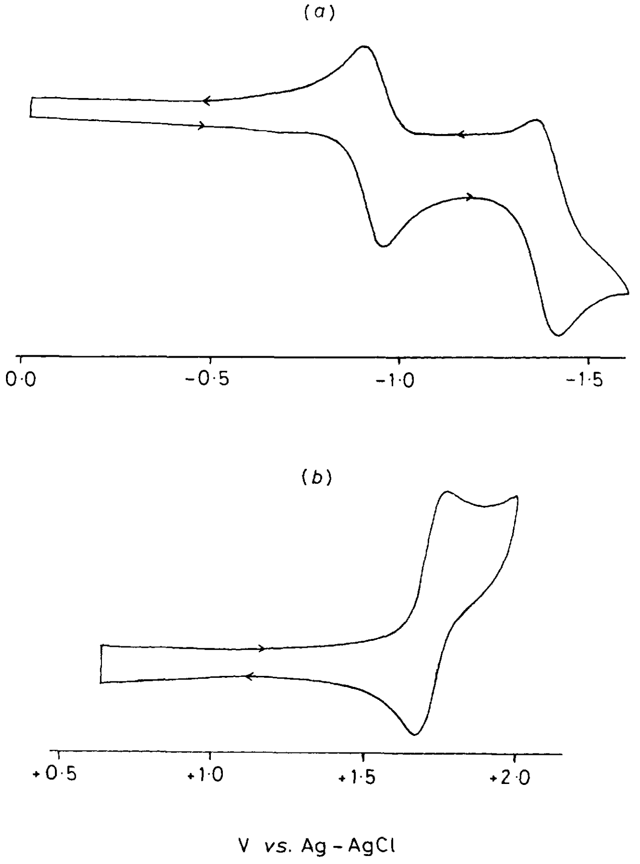


Figure 3. Cyclic voltammograms of $[NiL^{3}{}_{2}]^{2+}$ measured in MeCN (0.1 mol dm$^{-3}$ $NBu^{n}{}_{4}BF_{4}$) at platinum electrodes

two Ni–N bonds. Most nickel(I) species are usually assigned as four- or five-co-ordinate systems.[1]

Further reduction of these complexes at −2.2 V led to the solutions becoming more intensely coloured with an additional isotropic signal growing in the e.s.r. spectrum near free spin at $g = 2.007$ and 2.003 for the complexes of $L^{3}$ and $L^{4}$ respectively. The second reductive process is therefore probably ligand-based, forming a metal-stabilised ligand-radical species. It is not possible to assess the role of $Ni^{0}$ in these processes; it would appear possible for a diamagnetic, tetrahedral nickel(0) species to be generated with these ligand systems, but the presence of high concentrations of paramagnetic species in solution precludes a fuller study.

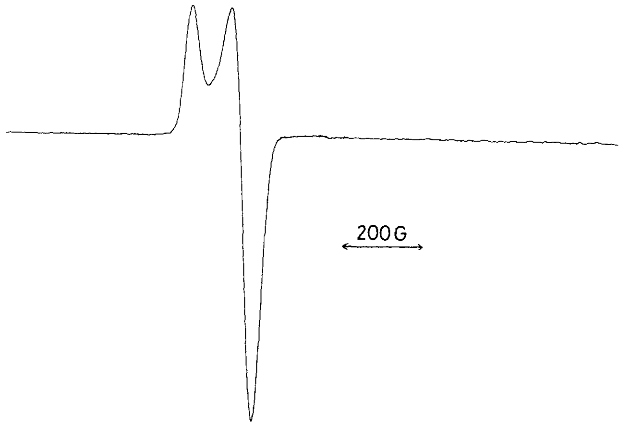


Figure 4. X-Band e.s.r. spectrum of $[NiL^{3}{}_{2}]^{+}$ measured at 77 K as a MeCN glass

The complexes $[NiL_{2}]^{2+}$ show reversible oxidation processes in MeCN at $E_{\frac{1}{2}} = +1.22$ V ($\Delta E_{p} = 64$ mV) (for L = $L^{3}$) and at $E_{\frac{1}{2}} = +1.12$ V ($\Delta E_{p} = 69$ mV) (for L = $L^{4}$) *vs.* ferrocene–ferrocenium. Controlled-potential electrolysis of these complexes at +1.45 and +1.40 V respectively affords brown oxidised solutions, the e.s.r. spectra of which measured at 77 K as frozen MeCN glasses show broad anisotropic signals with $g_{\parallel} = 2.03$, $g_{\perp} = 2.13$ for $[NiL^{3}{}_{2}]^{3+}$ (Figure 5) and $g_{\parallel} = 2.05$, $g_{\perp} = 2.12$ for $[NiL^{4}{}_{2}]^{3+}$. These spectral features with $g_{\parallel} \approx 2.00$ and $g_{\perp} > 2.00$ and the observation of superhyperfine coupling to nitrogen donors ($A_{\parallel} = 24$ G) are consistent with the formation of $d^{7}$ nickel(III) species with a $(d_{xy})^{2}(d_{xz})^{2}(d_{yz})^{2}(d_{z^{2}})^{1}$ ground-state configuration.[1,3,4] Coulometry confirms these oxidations to be one-electron processes. The stereochemistries of these nickel(III) intermediates are likely to be octahedral with a shortening of the Ni–N bond lengths relative to those in the nickel(II) precursors.

The complex $[NiL^{2}{}_{2}]^{2+}$ shows two reversible one-electron reductions in MeCN at ${}^{1}E_{\frac{1}{2}} = -1.30$ V ($\Delta E_{p} = 65$ mV) and

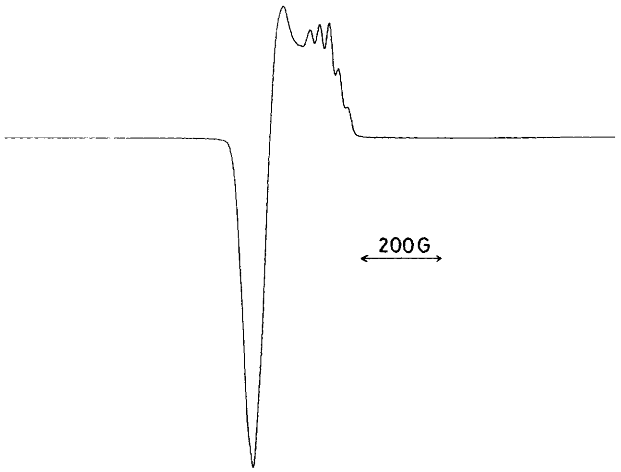


**Figure 5.** *X*-Band e.s.r. spectrum of $[NiL^3_2]^{3+}$ measured at 77 K as a MeCN glass

$^2E_{\frac{1}{2}} = -1.69$ V ($\Delta E_p = 70$ mV) and a one-electron oxidation at $+1.30$ V ($\Delta E_p = 64$ mV) *vs.* ferrocene–ferrocenium. This reflects an increased stabilisation of the low-valent species in the presence of $L^2$ compared to $L^3$ and $L^4$, presumably due to the increased delocalisation within the ligand $L^2$.

The results described herein show that 2,6-substituted di-imino pyridyl ligands can be utilised in non-macrocyclic configurations to stabilise both low-and high-valent nickel complexes. Work is underway to compare these products with related redox-active tetra-aza and mixed-donor macrocyclic nickel(II) complexes.

## Experimental

Infrared spectra were measured as Nujol mulls, KBr and CsI discs using a Perkin-Elmer 598 spectrometer over the range 200—4 000 cm$^{-1}$. Ultraviolet–visible spectra were measured in quartz cells using a Pye Unicam SP8-400 and Perkin-Elmer Lambda 9 spectrophotometers. Microanalyses were performed by the Edinburgh University Chemistry Department micro-analytical service. E.s.r. spectra were recorded as solids or as frozen glasses down to 77 K using a Bruker ER200D *X*-band spectrometer. Electrochemical measurements were performed on a Bruker E310 Universal Modular Polarograph. All readings were taken using a three-electrode potentiostatic system in MeCN containing 0.1 mol dm$^{-3}$ $NBu^n_4BF_4$ as supporting electrolyte. Cyclic voltammetric measurements were carried out using a double platinum electrode and a silver–silver chloride reference electrode. All potentials are quoted *versus* ferrocene–ferrocenium. Mass spectra were run by electron impact on a Kratos MS 902 and by fast-atom bombardment (f.a.b.) on a Kratos MS 50TC spectrometer.

*Synthesis of Metal-free Ligands.*—The free ligands were prepared by condensation of 2 molar equivalents of monoamine ($2.0 \times 10^{-2}$ mol) with 1 molar equivalent of 2,6-diacetylpyridine ($1 \times 10^{-2}$ mol). The monoamines and 2,6-diacetylpyridine were purchased from Aldrich or Fisons Chemical Co. and used without further purification. Best results were obtained by carrying out the condensations in benzene (100 cm$^3$) over molecular sieves in the dark over a period of 5—10 d. The solutions gradually changed from colourless to intense yellow as the reactions proceeded. The reactions were monitored using i.r. spectroscopy by observing the disappearance of the carbonyl C=O stretching vibration at 1 700 cm$^{-1}$ and the N–H stretching vibration at 3 200—3 400 cm$^{-1}$, and the appearance of the imino C=N stretching vibration near 1 610 cm$^{-1}$. The reaction was complete when the first two bands had disappeared. Refluxing the benzene solutions and removal of water azeotropically appeared to lower the yields of di-imino products. The free ligands were isolated by removal of the solvent and any excess of amine by rotary evaporation. The resulting yellow oils were purified by column chromatography (silica, $CH_2Cl_2$) and recrystallised from dry $CH_2Cl_2$ to yield low-melting-point yellow solids (crystalline plates for $L^2$ and $L^4$).

$L^1$. Yield 90%. Mass spectrum: found $M^+$, 217; calc. 217. Infrared spectrum: 2 970, 2 940, 1 640, 1 570, 1 450, 1 250, 1 110, 820, and 630 cm$^{-1}$. $^1H$ N.m.r. spectrum ($CDCl_3$, 60 MHz, 298 K); δ 7.91 (m, py, 3 H), 3.41 (q, $CH_2$, 4 H), 2.26 (s, $CH_3$, 6 H), and 1.21 (t, $CH_3$, 6 H).

$L^2$. Yield >90%. Mass spectrum: found $M^+$, 313; calc. 313. Infrared spectrum: 3 060, 2 940, 1 630, 1 590, 1 450, 1 260, 750, 710, and 530 cm$^{-1}$. $^1H$ n.m.r. spectrum ($CDCl_3$, 60 MHz, 298 K); δ 8.32 (m, py, 3 H), 7.1 (m, Ph, 10 H), and 2.41 (s, $CH_3$, 6 H) (Found: C, 76.8; H, 6.0; N, 12.7. Calc. for $L^2{\cdot}H_2O$: C, 76.1; H, 6.4; N, 12.7%).

$L^3$. Yield >90%. Mass spectrum: found $M^+$, 341; calc. 341. Infrared spectrum: 3 020, 2 860, 1 630, 1 600, 1 570, 1 450, 730, 690, and 460 cm$^{-1}$. $^1H$ N.m.r. spectrum ($CDCl_3$, 60 MHz, 298 K); δ 8.24 (m, py, 3 H), 7.50 (m, Ph, 10 H), 4.82 (s, $CH_2$, 4 H), and 2.55 (s, $CH_3$, 6 H) (Found: C, 75.7; H, 6.5; N, 10.9. Calc. for $L^3{\cdot}H_2O$: C, 76.8; H, 7.0; N, 11.6%).

$L^4$. Yield >90%. Mass spectrum: found $M^+$, 397; calc. 397. Infrared spectrum: 3 030, 2 960, 2 860, 1 640, 1 605, 1 570, 1 500, 1 455, 820, 750, and 705 cm$^{-1}$. $^1H$ N.m.r. spectrum ($CDCl_3$, 60 MHz, 298 K); δ 7.95 (m, py, 3 H), 7.30 (m, Ph, 10 H), 3.45 (t, $CH_2$, 4 H), 2.66 (m, $CH_2$, 4 H), 2.25 (s, $CH_3$, 6 H), and 2.05 (m, $CH_2$, 4 H) (Found: C, 80.7; H, 8.2; N, 10.9. Calc. for $L^4$: C, 81.6; H, 7.9; N, 10.6%).

*Synthesis of Metal Complexes* $[NiL_2]^{2+}$.—$[NiL^1_2][BF_4]_2$. The salt $Ni(BF_4)_2{\cdot}6H_2O$ (0.17 g, $5 \times 10^{-4}$ mol) was added to a solution of $L^1$ (0.22 g, $1 \times 10^{-3}$ mol) in EtOH–$CH_2Cl_2$ (50 cm$^3$; 4:1 v:v) and the solution refluxed for 1 h. The solution was allowed to cool and the light brown precipitate was collected, recrystallised from EtOH–MeCN, and the resultant micro-crystalline product dried *in vacuo*. Yield 70%. Crystals of the complex were obtained from $CH_2Cl_2$ (Found: C, 43.9; H, 5.1; N, 10.5. Calc. for $[NiL^1_2][BF_4]_2{\cdot}CH_2Cl_2$: C, 43.2; H, 5.4; N, 11.1%). Infrared spectrum: 2 980, 1 640, 1 620, 1 590, 1 375, 1 250, 1 055, 815, and 525 cm$^{-1}$. Electronic spectrum: $\lambda_{max.} = 860$ ($\varepsilon = 40$ dm$^3$ mol$^{-1}$ cm$^{-1}$), 810 (sh), 540, and 420 nm (MeCN); 850, 800, 540, and 420 nm (solid). Conductivity (in MeCN): $\Lambda_m = 420$ ohm$^{-1}$ cm$^2$ mol$^{-1}$.

$[NiL^2_2][BF_4]_2$. The complex was prepared *via* a similar procedure to the above using $L^2$ (0.31 g, $1 \times 10^{-3}$ mol) and $Ni(BF_4)_2{\cdot}6H_2O$ (0.17 g, $5 \times 10^{-4}$ mol). The product was recrystallised from EtOH–$CH_2Cl_2$ to yield dark brown platelets which were dried *in vacuo*. Yield 75% (Found: C, 56.5; H, 4.4; N, 9.2. Calc. for $[NiL^2_2][BF_4]_2{\cdot}2H_2O$: C, 56.4; H, 4.7; N, 9.4%). Infrared spectrum: 3 400, 3 020, 2 930, 1 630, 1 590, 1 450, 1 375, 1 265, 1 050, 750, 705, and 525 cm$^{-1}$. Electronic spectrum: $\lambda_{max.} = 855$ ($\varepsilon = 55$ dm$^3$ mol$^{-1}$ cm$^{-1}$), 810 (sh), 520 (sh), and 320 nm (sh) (MeCN); 850, 805, 520, and 320 nm (solid). Conductivity (in MeCN): $\Lambda_m = 390$ ohm$^{-1}$ cm$^2$ mol$^{-1}$. F.a.b. mass spectrum: found $M^+$, 771, 684, and 371; calc. for $[NiL^2_2(BF_4)]^+$ 771 ($M^+$); calc. for $[NiL^2_2]^+$ 684 ($M^+$); calc. for $[NiL^2]^+$ 371 ($M^+$).

$[NiL^3_2][BF_4]_2$. The complex was prepared *via* a similar procedure using $L^3$ (0.34 g, $1 \times 10^{-3}$ mol) and $Ni(BF_4)_2{\cdot}6H_2O$ (0.17 g, $5 \times 10^{-4}$ mol). The product was recrystallised from EtOH–$CH_2Cl_2$ (1:1, v/v) to yield a dark brown crystalline product which was dried *in vacuo*. Yield 80% (Found: C, 58.2; H, 4.9; N, 8.7. Calc. for $[NiL^3_2][BF_4]_2{\cdot}2H_2O$: C, 58.1; H, 5.3; N, 8.8%). Infrared spectrum: 3 030, 2 940, 1 630, 1 590, 1 455, 1 380, 1 270, 1 060, 755, 710, and 530 cm$^{-1}$. Electronic spectrum: $\lambda_{max.}$ = 800 ($\varepsilon$ = 30 dm$^3$ mol$^{-1}$ cm$^{-1}$), 520 (sh), and 390 (sh) nm (MeCN); 795, 520 (sh), and 400 (sh) nm ($CH_2Cl_2$); 805, 510, and 400 nm (solid). Conductivity (in MeCN): $\Lambda_m$ = 500 ohm$^{-1}$ cm$^2$ mol$^{-1}$; $\mu_{eff.}$ = 3.05 (Gouy method). F.a.b. mass spectrum: found $M^+$, 827, 741, and 399; calc. for $[NiL^3{}_2(BF_4)]^+$ 828 ($M^+$); calc. for $[NiL^3{}_2]^+$ 740 ($M^+$); calc. for $[NiL^3]^+$ 399 ($M^+$).

$[NiL^4{}_2][BF_4]_2$. The complex was prepared *via* a similar procedure using L$^4$ (0.4 g, 1 × 10$^{-3}$ mol) and $Ni(BF_4)_2 \cdot 6H_2O$ (0.17 g, 5 × 10$^{-4}$ mol). The product was recrystallised from EtOH–$CH_2Cl_2$ to yield light brown needles which were dried *in vacuo*. Yield 75% (Found: C, 60.0; H, 6.1; N, 7.6. Calc. for $[NiL^4{}_2][BF_4]_2 \cdot 2H_2O$: C, 61.0; H, 6.3; N, 7.9%). Infrared spectrum: 3 030, 2 940, 1 630, 1 605, 1 590, 1 455, 1 380, 1 060, 760, 710, and 525 cm$^{-1}$. Electronic spectrum: $\lambda_{max.}$ = 800 ($\varepsilon$ = 35 dm$^3$ mol$^{-1}$ cm$^{-1}$), 520 (sh), 400 (sh), and 285 nm (MeCN); 805, 515 (sh), and 415 nm (sh) ($CH_2Cl_2$); 810, 520, and 390 nm (solid). Conductivity (in MeCN): $\Lambda_m$ = 430 ohm$^{-1}$ cm$^2$ mol$^{-1}$; $\mu_{eff.}$ = 3.11 (Gouy method).

*Single-crystal X-Ray Structure of* $[NiL^4{}_2][BF_4]_2$.—Recrystallisation from $CH_2Cl_2$ and EtOH afforded pale brown crystals suitable for a crystallographic study.

*Crystal data.* $C_{54}H_{62}B_2F_8N_6Ni$, $M$ = 1 027.5, triclinic, space group $P\bar{1}$ (from intensity statistics and successful refinement), $a$ = 11.640(4), $b$ = 12.884 6(27), $c$ = 18.906(6) Å, $\alpha$ = 90.270(22), $\beta$ = 95.226(28), $\gamma$ = 112.098(24)°, $U$ = 2 614 Å$^3$ (by least-squares refinement on diffractometer angles for 2$\varphi$ automatically centred reflections with $\theta$ = 14.5—15.0°, $\lambda$ = 0.710 69 Å), $Z$ = 2, $D_c$ = 1.305 g cm$^{-3}$, $F(000)$ = 1 076, $\mu$(Mo-$K_\alpha$) = 4.09 cm$^{-1}$.

*Data collection and processing.* CAD4 diffractometer, $\omega$—2$\theta$ mode with $\omega$ scan width (0.85 + 0.35tan$\theta$)°, graphite-monochromated Mo-$K_\alpha$ radiation; 6 459 reflections measured ($1 \leqslant \theta \leqslant 22°$, $\pm h$, $\pm k$, $-l$), 6 384 unique, 4 080 with $F \geqslant 2\sigma(F)$. Absorption correction from $\psi$ scans on (572). Random variations of $< \pm 2\%$ in intensity standards, no action taken.

*Structure analysis and refinement.* Patterson synthesis (Ni) followed by tangent expansion methods. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions with fixed $U_{iso}$ values; phenyl rings were refined as ideal hexagons and $BF_4^-$ groups as rigid tetrahedra.[15] The weighting scheme $w^{-1} = \sigma^2(F) + 0.001\,07F^2$ gave satisfactory agreement analyses. At convergence, $R$, $R'$ = 0.093, 0.102 respectively, $S$ = 1.807 for 574 parameters, and the final difference Fourier synthesis showed no feature above 0.64 or below −0.47 e Å$^{-3}$. Illustrations were prepared using ORTEP,[16] molecular geometry calculations utilised CALC,[17] and scattering factor data were inlaid[15] or taken from ref. 18. Bond lengths, angles, and fractional co-ordinates are given in Tables 1 and 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

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