X-Ray Crystal Structure of the Pentagonal Bipyramidal Nickel(II) Complex $[Ni^{II}(L)(H_2O)_2](BF_4)_2$ and the Selective Stabilisation of the Nickel(I) Oxidation State by a Quinquedentate Macrocyclic Ligand

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The single crystal *X*-ray structure of the pentagonal bipyramidal nickel(II) complex $[Ni^{II}(L)(H_2O)_2](BF_4)_2$ involving the quinquedentate macrocyclic ligand L is reported; electrochemical reduction of a series of related nickel(II) complexes $[Ni^{II}(L)X_2](BF_4)_2$ yields in solution d^9 nickel(I) species.

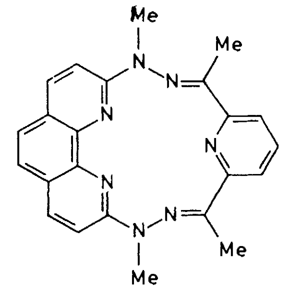
Planar quinquedentate macrocyclic ligands are potential sources for the synthesis of seven-co-ordinate, pentagonal bipyramidal transition metal complexes, the formation of such species having been readily achieved for d^5, d^6, d^7, d^9, and d^{10} metal ions.[1–3] Attempts to synthesise the corresponding d^8 nickel(II) complexes however are very often unsuccessful, the only products isolated being octahedral species.[4] The rarity of pentagonal bipyramidal nickel(II) macrocyclic complexes[3,5] has been reasonably attributed to the destabilisation of the d^8 configuration in a D_{5h} symmetry relative to the more commonly formed octahedral O_h symmetry.[1,4,6]

In this communication we report the synthesis and single crystal *X*-ray structure of the pentagonal bipyramidal nickel(II) complex $[Ni^{II}(L)(H_2O)_2](BF_4)_2$, and the electrochemical reduction of a series of related nickel(II) complexes $[Ni^{II}(L)X_2](BF_4)_2$ to yield d^9 nickel(I) species.

Condensation of 2,6-diacetylpyridine with 2,9-di(1-methylhydrazino)-1,10-phenanthroline in the presence of nickel dichloride in refluxing water yielded on addition of $NaBF_4$ the product $[Ni^{II}(L)(H_2O)_2](BF_4)_2$ as a yellow microcrystalline solid. A range of axial adducts $[Ni^{II}(L)X_2]^{2+}$ (X = pyridine, 4-aminopyridine, 4-(*N*,*N*-dimethylamino)pyridine, imidazole, 2-methylimidazole, quinoline, or diazabicyclo-octane) were synthesised by the addition of these ligands to $[Ni^{II}(L)(H_2O)_2](BF_4)_2$ in refluxing methanol. Good elemental analyses were obtained for all the above complexes; they are all high-spin d^8 and are 2:1 electrolytes in nitromethane. A single *X*-ray structural determination of $[Ni^{II}(L)(H_2O)_2](BF_4)_2$ was undertaken. Crystals were obtained as orange plates from water.

Crystal data: $[C_{23}H_{21}N_7NiO_2]^+[BF_4]^-_2$, $M = 659.80$, monoclinic, $a = 14.177(4)$, $b = 11.495(4)$, $c = 16.642(6)$ Å, $\beta = 94.63(2)°$, $U = 2703.2$ Å^3, $D_c = 1.62$ g cm^{-3}, $Z = 4$, Cu-K_α radiation, $\lambda = 1.5418$ Å, μ(Cu-K_α) = 17.67 cm^{-1}, $F(000) = 1351.95$, space group $P2_1/c$. 5161 intensities were recorded on a Syntex $P2_1$ diffractometer ($2\theta_{max} = 130.0°$) using graphite-monochromated Cu-K_α radiation and an $\omega/2\theta$ scan technique. The data were corrected for absorption and for Lorentz–polarisation effects, and averaged to give 3911 unique observed reflections [$F > 5\sigma(F)$].†

The structure was solved by Patterson and Fourier-difference techniques, and refined by blocked-full matrix least squares (Ni, O, N, C anisotropic, B isotropic, F, methyl and ring H common isotropic). The methyl and ring H atoms were constrained to ride 1.08 Å from the relevant carbon; the methyl groups were treated as rigid bodies. The two BF_4^- anions were disordered, and each was treated as a B atom surrounded by two interlocking tetrahedra of F atoms with B–F distances constrained to 1.336(1) Å; the occupancies of the F atoms in each anion were refined as k and $1-k$. The final residuals are $R = 0.121$ and $R'[=\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_0|] = 0.139$.



(L)

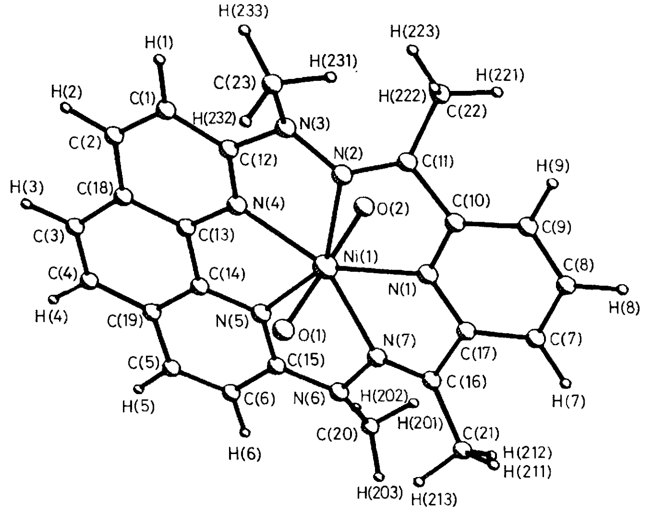


Figure 1. The molecular structure of the $[Ni(L)(H_2O)_2]^{2+}$ cation. Bond lengths are Ni(1)–O(1), 2.101(5); Ni(1)–O(2), 2.076(5); Ni(1)–N(1), 2.117(6); Ni(1)–N(2), 2.313(6); Ni(1)–N(4), 2.095(5); Ni(1)–N(5), 2.081(5); Ni(1)–N(7), 2.276(5); N(2)–N(3), 1.391(9); N(6)–N(7), 1.388(9) Å.

The structure of the cation is shown in Figure 1 together with some important bond parameters; some H atoms have been omitted for clarity. The *X*-ray analysis confirms the presence of seven-co-ordinate, pentagonal bipyramidal nickel(II), the rigid macrocyclic ligand occupying five equatorial positions with two water molecules in the axial sites. The equatorial plane is only very slightly distorted [deviations Ni(1): −6(3), N(1): +5(3), N(2): +3(3), N(4): −6(3), N(5): +11(3), N(7): −7(3) Å × 10^3] and shows no tendency to octahedral co-ordination as observed for more flexible quinquedentate macrocyclic ligands.[4] The five Ni–N bonds may be divided into three groups. The Ni–N(pyridine) distance is the shortest, the two Ni–N(phenanthroline) are intermediate in length, and the two Ni–N(hydrazino) bond lengths are the longest. The cation is isostructural with the Fe^{II} and Co^{II} analogues.[7]

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Cyclic voltammetry of the nickel(II) complexes in acetonitrile at a platinum microsphere all show a reversible or quasi-reversible reduction wave in the range -1.15 to -1.30 V relative to a $Ag/AgNO_3$ reference electrode. Addition of excess of $P(OMe)_3$ or CO to $[Ni^{II}(L)(H_2O)_2](BF_4)_2$ in acetonitrile shifts the reduction wave from -1.15 to -0.88 and -0.95 V, respectively. Coulometric measurements confirm all the above reductions to be one-electron processes. Controlled potential electrolysis in acetonitrile of $[Ni^{II}(L)X_2]^{2+}$, and $[Ni^{II}(L)(H_2O)_2]^{2+}$ in the presence of $P(OMe)_3$ or CO at their respective reduction potentials as determined by cyclic voltammetry led to the reduction of the nickel(II) species with concomitant change of colour from orange to dark green. The e.s.r. spectra of the reduced solutions as acetonitrile glasses at 77 K all showed characteristic features of d^9 nickel(I) species; for example $g_{\parallel} = 2.3023$, $g_{\perp} = 2.0575$ for X = $P(OMe)_3$; $g_{\parallel} = 2.2783$, $g_{\perp} = 2.0935, 2.1823$ for X = pyridine; $g_{\parallel} = 2.2831$, $g_{\perp} = 2.1079, 2.1923$ for X = imidazole. We therefore propose the formation of six-co-ordinate pentagonal pyramidal or seven-co-ordinate pentagonal bipyramidal nickel(I) complexes.

The stabilisation of the nickel(I) oxidation state in the above complexes is of particular significance since the potentials at which their reductions to the univalent state occur are at markedly lower negative values when compared with other macrocyclic systems.[8]

The stabilisation of nickel(I) in the presence of net π-donor axial ligands such as 4-dimethylaminopyridine or imidazole, ligands that would be expected to destabilise the lower oxidation states, is unprecedented, and indicates that the bulk reductive properties of the system are dominated by the macrocyclic ligand. Thus L may be regarded to exert a selective stabilisation of the nickel(I) oxidation state. We attribute the relative stability of these reduced species to the inherent destabilisation of pentagonal bipyramidal nickel(II), no such destabilisation being present for the reduced d^9 pentagonal pyramidal or pentagonal bipyramidal systems.

It is of interest to note here that up to now we have only been able to isolate d^8 cobalt(I) complexes of L in the presence of strong π-acceptor ligands such as $P(OMe)_3$. In the absence of such ligands no metal reduced species could be isolated, thus again suggesting a net destabilisation for d^8 metal centres in these systems.

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References

1 S. M. Nelson, *Pure Appl. Chem.*, 1980, **52**, 2461.

2 M. G. B. Drew, J. Grimshaw, P. D. A. McIlroy, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1976, 1388; M. G. B. Drew, A. H. Othman, and S. M. Nelson, *ibid.*, p. 1394; M. G. B. Drew, A. H. Othman, P. D. A. McIlroy, and S. M. Nelson, *ibid.*, 1975, 2507; S. M. Nelson, F. S. Esho, M. G. B. Drew, and P. Bird, *J. Chem. Soc., Chem. Commun.*, 1979, 1035.

3 M. G. B. Drew, J. Nelson, and S. M. Nelson *J. Chem. Soc., Dalton Trans.*, 1981, 1685.

4 'Coordination Chemistry of Macrocyclic Compounds,' ed. G. A. Nelson, Plenum Press, New York, 1980; M. C. Rakowski, M. Rycheck, and D. H. Busch, *Inorg. Chem.*, 1975, **14**, 1194; C. Cairns, S. G. McFall, S. M. Nelson, and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1979, 446; M. G. B. Drew, J. Nelson, and S. M. Nelson, *ibid.*, 1981, 1691.

5 D. Webster and G. J. Palenik, *J. Am. Chem. Soc.*, 1974, **96**, 7565; T. J. Giordano, G. J. Palenik, R. C. Palenik, and D. A. Sullivan, *Inorg. Chem.*, 1979, **18**, 2445.

6 F. Basolo and R. G. Pearson, 'Mechanisms in Inorganic Reactions,' Wiley, New York, 1968, p. 146.

7 M. M. Bishop, J. Lewis, T. D. O'Donoghue, P. R. Raithby, and J. N. Ramsden, *J. Chem. Soc., Chem. Commun.*, 1978, 828; C. W. G. Ansell, J. Lewis, P. R. Raithby, M. C. Liptrot, and M. Schröder, *J. Chem. Soc., Dalton Trans.*, in the press; M. M. Bishop, J. Lewis, T. D. O'Donoghue, P. R. Raithby, and J. N. Ramsden, *ibid.*, 1980, 1390; L. R. Hanton and P. R. Raithby, *Acta Crystallogr., Sect. B*, 1980, **36**, 1489.

8 K. Nag and A. Chakravorty, *Coord. Chem. Rev.*, 1980, **33**, 87.