Co-ordination Chemistry of Mixed Pyridine–Phenol Ligands; The Crystal Structure of $[\{NiL(HL)\}_2][PF_6]_2\cdot0.5MeCN\cdot0.5Et_2O$ [HL = 6-(2-hydroxyphenyl)-2,2′-bipyridine]

John C. Jeffery and Michael D. Ward *
School of Chemistry, Cantock's Close, Bristol BS8 1TS, UK

The crystal structure of $[\{NiL(HL)\}_2][PF_6]_2\cdot0.5MeCN\cdot0.5Et_2O$ [HL = 6-(2-hydroxyphenyl)-2,2′-bipyridine] shows that the near-octahedral NiL_2 units, with *cis*-N_4O_2 geometries, are associated into dimers *via* strong hydrogen bonding between the phenolate oxygen atoms of two NiL(HL) units; the proximity of the monomer units in the dimer results in an inter-ligand stacking interaction between parallel aromatic rings.

There is considerable current interest in developing the co-ordination chemistry of polypyridine analogues in which one or more pyridyl rings are replaced by other heterocyclic donors. Recent examples include 2-phenylpyridine,[1] an N,P bidentate pyridylphosphinine,[2] 6-(2-thienyl)-2,2′-bipyridine,[3] 6-phenyl-2,2′-bipyridine,[4] and various N_3-terdentate ligands containing pyrazole and thiazole ligands.[5] We have been studying the co-ordination behaviour of ligands containing mixed pyridine–phenol donor sets as a method of extending this new field. The first studies with 6-(2-hydroxyphenyl)-2,2′-bipyridine (HL) showed that it is a versatile ligand capable of polynucleation *via* bridging phenolates, as exemplified by the rather unusual structure of $[Cu_2L_2(\mu\text{-}MeCO_2)][PF_6]$ in which two near-planar CuL units are stacked side by side with bridging phenolates providing a $Cu_2(\mu\text{-}O)_2$ core.[6] In this communication we report the crystal structure of $[\{NiL(HL)\}_2][PF_6]_2\cdot0.5MeCN\cdot0.5Et_2O$ **1**, in which two distinct types of intermolecular interaction—π stacking and hydrogen bonding—are present in an interesting dimeric structure.

Reaction of HL (0.1 g, 0.4 mmol) with 1 equivalent (*i.e.* a two-fold excess) of $NiCl_2\cdot6H_2O$ or $Ni(MeCO_2)_2\cdot4H_2O$ in methanol (25 cm^3) at room temperature produced a brown solution from which an orange-brown solid precipitated on addition of KPF_6 and cooling. The elemental analysis was consistent with the formulation $[NiL(HL)][PF_6]$ in which one of the phenol ligands had remained protonated. The fast atom bombardment (FAB) mass spectrum confirmed this but also showed the presence of some additional unexpected peaks. The main peak (relative intensity 100%) is at *m/z* 553, which corresponds to $[NiL(HL)]^+$ (based on ^{58}Ni). There are additional peaks due to heavier fragments at *m/z* 610 ($[Ni_2L_2]^+$, 8), 857 ($[Ni_2L_3]^+$, 11) and 1250 ($\{[Ni_2L_3(HL)][PF_6]\}^+$, 1.5%). These heavier fragments suggested the presence of at least a binuclear species of more complexity than the elemental analysis suggested, and accordingly we have determined the crystal structure of **1**.[†]

The asymmetric unit is large, containing two crystallographically independent formula units of the salt $[\{NiL(HL)\}_2][PF_6]_2$, one molecule of Et_2O and one molecule of MeCN. The two enantiomeric dications are structurally very similar, and only one such unit is shown in Fig. 1. It consists of two near-octahedral $[NiL_2]$ units in which each ligand co-ordinates in the expected meridional fashion giving a *cis*-N_4O_2 donor set to each nickel. The bite of each ligand is such that the bite angles at the metal between the terminal N and O donor atoms of each ligand lie between 163.3 and 165.5°, considerably less than the near-180° bite angles achieved in $[Cu_2L_2(\mu\text{-}MeCO_2)]^+$ and $[CoL_2]^+$.[6] Two such monomeric units are held adjacent to each other by two intermolecular hydrogen bonds which link O(161) to O(231) and O(131) to O(261). The short O ··· O distances (2.37 and 2.39 Å)—only slightly more than double a typical O–H distance—are at the lower limit for a pair of hydrogen-bonded oxygen atoms, indicative of strong hydrogen bonds ($\Delta H > 30$ kJ mol^{-1}) in which the hydrogen atom is symmetrically placed between the two oxygen atoms: weak, asymmetric (O–H ··· O) hydrogen bonds more typically have O ··· O distances of 2.7 Å and upwards.[9] The hydrogen atoms could not be located in the crystal structure, but their presence is required to balance the two hexafluorophosphate anions present per dimer unit, and the +2 oxidation state of the nickel was confirmed by the room-temperature magnetic moment μ_B of 2.7 per nickel. It is in any case inconceivable that four negatively charged oxygen atoms would lie so close to each other for any other reason. A strong hydrogen bond of this sort will result in a very low O–H stretching frequency, probably below 1000 cm^{-1} given the O ··· O distance.[9] Unfortunately the broad, shallow nature to be expected of the peak in the infrared spectrum together with the numerous other peaks in the fingerprint

---

[†] Crystal data for **1**: $C_{64}H_{46}F_{12}N_8Ni_2O_4P_2\cdot0.5MeCN\cdot0.5Et_2O$, $M = 1456.0$, monoclinic, space group $P2_1$, $a = 16.530(6)$, $b = 21.890(7)$, $c = 18.869(7)$ Å, $\beta = 102.09(3)°$, $U = 6676(4)$ Å, $Z = 4$, $D_c = 1.45$ g cm^{-3}, $F(000) = 2976$, $\mu(\text{Mo-K}\alpha) = 7.0$ cm^{-1}, $R = 0.099$ ($R' = 0.099$), with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.001\,|F|^2]$, for 3833 unique data [293 K, Wyckoff ω scans, $2\theta < 40°$, $F > 5\sigma(F)$]. Data were collected using a Siemens R3m/V diffractometer (Mo-Kα X-radiation, graphite monochromator, $\bar{\lambda} = 0.710\,69$ Å). The data were corrected for Lorentz, polarisation and X-ray absorption effects. The structure was solved by conventional heavy-atom methods and successive Fourier difference syntheses were used to locate all non-hydrogen atoms. The asymmetric unit contains two crystallographically independent formula units of the salt $[\{NiL(HL)\}_2][PF_6]_2$, one molecule of Et_2O and a molecule of MeCN. Final refinements by full-matrix least-squares procedures were performed on a Micro Vax computer with the SHELXTL system of programs.[7] The modest *R* factor reflects the large number of molecules in the asymmetric unit and the fact that the crystal diffracted poorly. Scattering factors with corrections for anomalous dispersion were taken from ref. 8. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, 1992, Issue 1, pp. xx–xxv.

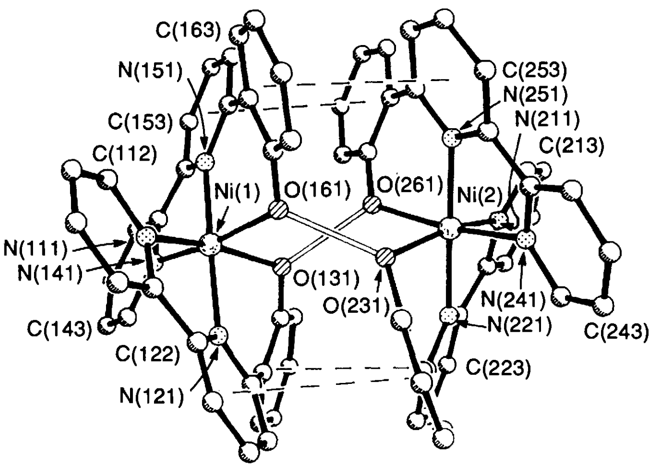

Fig. 1 Molecular structure of the dication $[\{NiL(HL)\}_2]^{2+}$ of **1**. Dimensions: Ni(1)–N(111) 2.03(2), Ni(1)–N(121) 2.06(2), Ni(1)–O(131) 2.07(2), Ni(1)–N(141) 2.02(2), Ni(1)–N(151) 1.98(2), Ni(1)–O(161) 2.03(2), Ni(2)–N(211) 2.08(2), Ni(2)–N(221) 2.05(2), Ni(2)–O(231) 2.05(2), Ni(2)–N(241) 2.05(2), Ni(2)–N(251) 2.03(2), Ni(2)–O(261) 2.07(2), O(131)···O(261) 2.39, O(161)···O(231) 2.37 Å; N(111)–Ni(1)–N(121) 80.9(8), N(121)–Ni(1)–O(131) 85.6(8), N(111)–Ni(1)–O(131) 163.3(8), N(141)–Ni(1)–N(151) 81.0(9), N(151)–Ni(1)–O(161) 86.8(9), N(141)–Ni(1)–O(161) 165.5(8), N(211)–Ni(2)–N(221) 79.1(8), N(221)–Ni(2)–O(231) 87.9(8), N(211)–Ni(2)–O(231) 164.2(9), N(241)–Ni(2)–N(251) 81.0(9), N(251)–Ni(2)–O(261) 86.6(9), N(241)–Ni(2)–O(261) 164.5(9)°

region of the spectrum meant that we were unable to identify the O–H stretch. The four phenol oxygen atoms are thus brought together to generate a four-co-ordinate cavity, whose geometry is mid-way between square-planar and tetrahedral; we are currently attempting to replace the two protons by small, oxophilic metal ions such as Li^+ and Mg^{2+} which might lie within the cavity formed by the four oxygen atoms.

As a result of the proximity of monomer units due to the hydrogen bonding, sections of the aromatic ligands are also brought into close contact. The resulting stacking interactions between near-parallel aromatic rings are indicated by the dashed lines in Fig. 1; the distances between the centroids of the aromatic rings concerned vary between 3.69 and 3.88 Å, which may be compared with 3.35 Å between graphite layers[10] and 3.4 Å between stacked nucleotide residues in nucleic acids.[11] Recently several crystal structures of polynuclear double-helical complexes with oligopyridine ligands have been reported in which inter-ligand stacking distances of between 3.2 and 3.7 Å have been observed,[12] and similar stacking interactions are a common feature of other complexes containing aromatic ligands.[13] In **1** this interaction manifests itself most noticeably in large dihedral angles (*ca.* 40°) between the central pyridyl and terminal phenolate rings of each ligand; this twisting appears to allow the ligand conformations to adjust such that the inter-ligand interactions are maximised, and is much larger than observed in the crystal structures of $[Cu_2L_2(\mu\text{-}MeCO_2)][PF_6]$ and $[CoL_2][PF_6]$.[6] The twist between two aromatic rings of a ligand in one monomer unit is mirrored by the corresponding pair of aromatic rings in the adjacent monomer unit, such that the stacked pairs of aromatic rings remain near-parallel in all four cases.

References

1 E. C. Constable, T. A. Leese and D. A. Tocher, *Polyhedron*, 1990, **9**, 1613; E. C. Constable and C. E. Housecroft, *Polyhedron*, 1990, **9**, 1939; E. C. Constable, A. M. W. Cargill Thompson, T. A. Leese, D. G. F. Reese and D. A. Tocher, *Inorg. Chim. Acta*, 1991, **182**, 93; J. H. van Diemen, J. G. Haasnoot, R. Hage, J. Reedijk, J. G. Vos and R. Wang, *Inorg. Chem.*, 1991, **30**, 4038; J. H. van Diemen, J. G. Haasnoot, R. Hage, E. Müller and J. Reedijk, *Inorg. Chim. Acta*, 1991, **181**, 245; K. Dedeian, P. I. Djurovich, F. O. Garces, G. Carlson and R. J. Watts, *Inorg. Chem.*, 1991, **30**, 1685; H. Drevs, *Z. Anorg. Allg. Chem.*, 1991, **605**, 145.

2 B. Schmid, L. M. Venanzi, A. Albinati and F. Mathey, *Inorg. Chem.*, 1991, **30**, 4693; P. LeFloch, D. Carmichael, L. Ricard and F. Mathey, *J. Am. Chem. Soc.*, 1991, **113**, 667.

3 E. C. Constable, R. P. G. Henney and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1991, 2335; E. C. Constable, R. P. G. Henney, P. R. Raithby and L. R. Sousa, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1363.

4 J.-P. Collin, M. Beley, J.-P. Sauvage and F. Barigelletti, *Inorg. Chim. Acta*, 1991, **186**, 91; T. Karlen, A. Ludi, H. U. Güdel and H. Riesen, *Inorg. Chem.*, 1991, **30**, 2249; E. C. Constable, R. P. G. Henney, T. A. Leese and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1990, 443; E. C. Constable, R. P. G. Henney and T. A. Leese, *J. Organomet. Chem.*, 1989, **361**, 277.

5 A. J. Downard, G. E. Honey and P. J. Steel, *Inorg. Chem.*, 1991, **30**, 3733; C. A. Bessel, R. F. See, D. L. Jameson, M. R. Churchill and K. J. Takeuchi, *J. Chem. Soc., Dalton Trans.*, 1991, 2801; A. T. Baker, P. Singh and V. Vignevich, *Aust. J. Chem.*, 1991, **44**, 1041; A. T. Baker, D. C. Craig and P. Singh, *Aust. J. Chem.*, 1991, **44**, 1659.

6 J. C. Jeffery, E. Schatz and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1992, 1921.

7 G. M. Sheldrick, SHELXTL programs for use with a Siemens X-Ray System, Cambridge, 1976, updated Göttingen, 1981.

8 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

9 A. Novak, *Struct. Bonding (Berlin)*, 1974, **18**, 177.

10 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1984.

11 P. O. P. Ts'O (Editor), *Basic Principles in Nucleic Acid Chemistry*, Academic Press, New York, 1974, vol. 1.

12 E. C. Constable, M. D. Ward and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1991, 1675; E. C. Constable, S. M. Elder, P. R. Raithby and M. D. Ward, *Polyhedron*, 1991, **10**, 1395; E. C. Constable, S. M. Elder, J. Healy, M. D. Ward and D. A. Tocher, *J. Am. Chem. Soc.*, 1990, **112**, 4590; C. J. Cathey, E. C. Constable, M. J. Hannon, D. A. Tocher and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1990, 621; E. C. Constable, M. D. Ward, M. G. B. Drew and G. A. Forsyth, *Polyhedron*, 1989, **8**, 2551; M. Barley, E. C. Constable, S. A. Corr, R. C. S. McQueen, J. C. Nutkins, M. D. Ward and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1988, 2655.

13 A. Yuchi, M. Shiro, H. Wada and G. Nakagawa, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 760; A. Furuhashi, I. Ono, A. Ouchi and A. Yamasaki, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 149; E. C. Constable, J. M. Holmes and P. R. Raithby, *Polyhedron*, 1991, **10**, 127; L. A. Castonguay, A. K. Rappé and C. J. Casewit, *J. Am. Chem. Soc.*, 1991, **113**, 7177.

Received 24*th March* 1992; *Communication* 2/01563C