The Co-ordination Chemistry of Mixed Pyridine–Phenol and Phenanthroline–Phenol Ligands; Effects of π-Stacking Interactions and Ligand Rigidity on Complex Structures†

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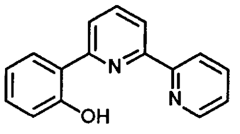
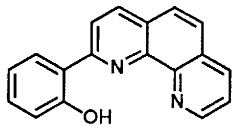
The crystal structures of $[Cu_2L^2_2(\mu\text{-}MeCO_2)][PF_6]$, $[Ni_2L^2_2(\mu\text{-}MeCO_2)(MeCN)_2][PF_6]$ and $[\{NiL^1(HL^1)\}_2][PF_6]_2\cdot0.5MeCN\cdot0.5Et_2O$ [HL^1 is the N,N,O-terdentate ligand 6-(2-hydroxyphenyl)-2,2′-bipyridine; HL^2 is the new ligand 2-(2-hydroxyphenyl)-1,10-phenanthroline, an analogue of HL^1 containing the more rigid 1,10-phenanthroline unit instead of 2,2′-bipyridyl] were determined. Both $[Cu_2L^2_2(\mu\text{-}MeCO_2)][PF_6]$ and $[Ni_2L^2_2(\mu\text{-}MeCO_2)(MeCN)_2][PF_6]$ contain two ML^2 units, in which the ligand is deprotonated and near-planar, stacked side by side such that the phenolates bridge resulting in $M_2(\mu\text{-}O)_2$ cores in each case, with an additional bridging μ-1,3-acetate. The $Ni_2(\mu\text{-}O)_2$ core is considerably contracted compared to the $Cu_2(\mu\text{-}O)_2$ core, as the apical Cu–O(bridging phenolate) bonds are rather long (2.449 Å) due to Jahn–Teller distortion. The proximity of the two ML^2 units results in π-stacking interactions between overlapping sections of the ligands. In contrast, $[\{NiL^1(HL^1)\}_2][PF_6]_2\cdot0.5MeCN\cdot0.5Et_2O$ consists of two pseudo-octahedral NiL^1_2 units held together by two strong intermolecular hydrogen bonds between phenolate residues. As a result, sections of the ligands in each monomeric unit are brought into close contact resulting in additional inter-ligand stacking interactions which are optimised by considerable distortions of the ligands from planarity. There are thus two types of non-covalent intermolecular interaction in the dimer which appear to complement each other in a co-operative manner. The differences between the structures are discussed in relation to the different stereoelectronic preferences of the metal ions, and the different steric and electronic properties of the ligands.

The polypyridine ligands 2,2′-bipyridine (bipy)[1] and 2,2′:6′,2″-terpyridine (terpy)[2] have played seminal roles in the recent development of co-ordination chemistry. Much of their popularity has resulted from the interesting photochemical and photophysical properties of their ruthenium(II) complexes;[3] other areas of interest include the use of high-oxidation-state oxo-ruthenium complexes as organic oxidants[4] and the assembly of polynuclear double-helical complexes from long, flexible, polypyridine ligands.[5,6] Recently there has been considerable interest in polypyridine-based ligands in which one (or more) pyridyl rings have been replaced by different donors such as a phenyl ring in 2-phenylpyridine[7] and 6-phenyl-2,2′-bipyridine,[8] a thiophene ring in 6-(2-thienyl)-2,2′-bipyridine,[9] five-membered N-heterocycles such as imidazoles, pyrazoles and thiazoles,[10] and phosphinines (P-donor analogues of pyridine).[11] Notably absent from this list are ligands consisting of mixed pyridine–phenol donor sets; there is just a single report of some simple complexes of 2-(2-hydroxyphenyl)pyridine from 1988.[12]

Accordingly we recently prepared the new ligand 6-(2-hydroxyphenyl)-2,2′-bipyridine (HL^1), an N,N,O-terdentate analogue of terpy, and reported the structures and properties of its complexes with Cu^{II} and Co^{III} [13] and a preliminary account of the structure of the nickel(II) complex.[14] Some features of these complexes are of interest. First, the presence of a σ-donating phenolate group results in stabilisation of metals in higher oxidation states compared to those with terpy.[15] Secondly, the presence of *bridging* phenolate ligands allows formation of binuclear species in which parallel sections of adjacent ligands appear to be stabilised by π-stacking interactions. In this paper we compare the complexes of Cu^{II} and Ni^{II} with the new ligand 2-(2-hydroxyphenyl)-1,10-phenanthroline (HL^2) with the analogous complexes of HL^1, in order to determine the effects of the increased aromaticity and lower flexibility of the ligand on the structures and properties of the complexes.



HL^1



HL^2

Experimental

The spectroscopic instrumentation and methods used have been described previously.[13] 1,10-Phenanthroline and 2-bromoanisole were obtained from Aldrich and used as received. All solvents were dried by standard methods before use.

Preparations.—2-(2-*Methoxyphenyl*)-1,10-*phenanthroline*. This compound was prepared according to the method used for HL^1.[13] To an ice-cold solution of 1,10-phenanthroline (5.0 g, 27.7 mmol) in dry toluene (100 cm^3) under N_2 was added by syringe a solution of 2-lithioanisole, prepared from 2-bromoanisole (6.75 g, 36 mmol) and freshly cut lithium (0.3 g, 43 mmol) in diethyl ether (50 cm^3). The resulting red-brown solution was allowed to warm to room temperature then stirred for 6 h. Water (50 cm^3) was added cautiously and the deep yellow organic layer was separated, dried ($MgSO_4$) and the solvent removed *in vacuo*. The crude oil was dissolved in CH_2Cl_2 (50 cm^3) and freshly precipitated MnO_2 added with vigorous stirring until thin-layer chromatography (silica, 98% CH_2Cl_2–2% MeOH) showed complete conversion of the bright yellow dihydrophenanthroline into the more polar product,[16] which was isolated by chromatography (silica, 98% CH_2Cl_2–2%

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

MeOH) in 55% yield as a yellow oil which solidified on prolonged drying *in vacuo*. Mass spectrum (electron impact, EI): $m/z = 285$ ($M^+ - H$), 268 and 255 ($M^+ - OCH_3$). ^1H NMR (270 MHz, $CDCl_3$): δ 7.02 (1 H, d, $J = 8.2$, phenyl H^6), 7.15 (1 H, td, $J = 7.5$, 1.1, phenyl H^4), 7.41 (1 H, td, $J = 7.9$, 1.8, phenyl H^5), 7.59 (1 H, dd, $J = 8.2$, 4.3, H^8), 7.76 (2 H, m, H^5 and H^6), 8.12 (1 H, dd, $J = 7.6$, 1.7, phenyl H^3), 8.14 (1 H, d, $J = 8.4$, H^3 or H^4), 8.22 (2 H, m, H^7 and H^4 or H^3) and 9.20 (1 H, dd, $J = 4.4$, 1.6 Hz, H^9).

2-(2-Hydroxyphenyl)-1,10-phenanthroline (HL^2). This was prepared by demethylation of the anisyl group of 2-(2-methoxyphenyl)-1,10-phenanthroline with pyridinium hydrochloride at 200 °C, also according to a published procedure.[13,17] On cooling the dark red reaction mixture, dissolving the solid mass in water and neutralising (NaOH), the product precipitated as a yellow powder which was filtered off and washed with water. The crude solid was dried by dissolving in CH_2Cl_2, washing with water and addition of $MgSO_4$ to the separated organic phase. Final purification was either by chromatography (silica, CH_2Cl_2) or recrystallisation from methanol to give yellow blocks in 83% yield. Mass spectrum (EI): $m/z = 272$ (M^+). ^1H NMR (400 MHz, $CDCl_3$): δ 6.95 (1 H, td, $J = 7.1$, 1.2, phenyl H^4), 7.19 (1 H, dd, $J = 8.3$, 1.3, phenyl H^6), 7.38 (1 H, td, $J = 7.3$, 1.6, phenyl H^5), 7.62 (1 H, dd, $J = 8.1$, 4.3, H^8), 7.73 (2 H, s, H^5 and H^6), 7.96 (1 H, dd, $J = 7.8$, 1.6, phenyl H^3), 8.17 (1 H, d, $J = 8.9$, H^3 or H^4), 8.20 (1 H, dd, $J = 8.1$, 1.6, H^7), 8.29 (1 H, d, $J = 8.6$, H^4 or H^3), 9.17 (1 H, dd, $J = 4.3$, 1.6 Hz, H^9) and 16.3 (1 H, br s, phenolic OH) (Found: C, 79.5; H, 4.3; N, 10.2. Calc. for $C_{18}H_{12}N_2O$: C, 79.4; H, 4.4; N, 10.3%).

The complex $[Cu_2L^2{}_2(\mu\text{-}MeCO_2)][PF_6]$ was prepared in *ca.* 80% yield by reaction of HL^2 with one equivalent of copper(II) acetate in methanol at room temperature to give a clear, green solution from which the complex was precipitated by addition of KPF_6. X-Ray-quality crystals were grown by diffusion of diethyl ether vapour into a concentrated acetonitrile solution of the crude material. Mass spectrum (fast atom bombardment, FAB): $m/z = 727$ $\{[Cu_2L^2{}_2(\mu\text{-}MeCO_2)]^+\}$. λ_{max} (MeCN) 627 (ε 120), 406 (15 000), 296 (44 000), 229 (75 000) and 205 nm (75 000 $dm^3\ mol^{-1}\ cm^{-1}$) (Found: C, 52.0; H, 3.1; N, 6.5. Calc. for $C_{38}H_{25}Cu_2F_6N_4O_4P$: C, 52.2; H, 2.9; N, 6.4%).

The complex $[Ni_2L^2{}_2(\mu\text{-}MeCO_2)(MeCN)_2][PF_6]$ was prepared in *ca.* 80% yield by reaction of HL^2 with 1 equivalent of nickel(II) acetate in methanol at room temperature to give a clear, yellow solution from which the complex was precipitated by addition of KPF_6. X-Ray-quality crystals were grown by diffusion of ether vapour into a concentrated acetonitrile solution of the crude material. Mass spectrum (FAB): $m/z = 717$ $\{[Ni_2L^2{}_2(\mu\text{-}MeCO_2)]^+\}$ and 658 ($[Ni_2L^2{}_2]^+$). λ_{max} (MeCN) 500 (sh) (ε 80), 381 (12 000), 295 (39 000) and 229 nm (61 000 $dm^3\ mol^{-1}\ cm^{-1}$) (Found: C, 52.2; H, 2.6; N, 6.3. Calc. for $C_{38}H_{25}F_6N_4Ni_2O_4P$: C, 52.8; H, 2.9; N, 6.5%).

The complex $[\{NiL^1(HL^1)\}_2][PF_6]_2$ was prepared and characterised as previously reported.[13,14]

Crystal Structure Determinations.—Data were collected using a Siemens R3m/V four-circle diffractometer (293 K, Mo-Kα X-radiation, graphite monochromator, $\bar{\lambda} = 0.710\ 73$ Å). They were corrected for Lorentz, polarisation and X-ray absorption effects, the latter by an empirical method based upon azimuthal scan data. The structures were solved by conventional heavy-atom or direct methods, and successive Fourier difference syntheses were used to locate all non-hydrogen atoms. All calculations were performed on a DEC micro-Vax II computer with the SHELXTL PLUS system of programs.[18] Scattering factors with corrections for anomalous dispersion were taken from ref. 19. Atom coordinates are listed in Tables 2, 4 and 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

$[Cu_2L^2{}_2(\mu\text{-}MeCO_2)][PF_6]$. Crystals were grown from MeCN–Et_2O as green plates and that used had dimensions *ca.* 0.65 × 0.30 × 0.25 mm. Of the 3235 data collected (Wyckoff ω scan, $2\theta \leqslant 50°$), 2290 unique data had $F \geqslant 5\sigma(F)$ and only these were used for structure solution and refinement.

Crystal data. $C_{38}H_{25}Cu_2F_6N_4O_4P$, $M = 873.7$, monoclinic, space group $C2/c$, $a = 18.180(5)$, $b = 13.570(3)$, $c = 15.818(4)$ Å, $\beta = 119.65(2)°$, $U = 3391(2)$ Å^3, $Z = 4$, $D_c = 1.71$ g cm^{-3}, $F(000) = 1760$, μ(Mo-Kα) = 13.9 cm^{-1}.

The $[Cu_2L^2{}_2(\mu\text{-}MeCO_2)]^+$ cation has crystallographically imposed two-fold symmetry with the two carbon atoms of the μ-$MeCO_2$ ligand lying on the two-fold axis. The corresponding $[PF_6]^-$ anion has imposed $\bar{1}$ symmetry. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters ($U_{iso} = 0.08$ Å^2). Hydrogen atoms were not included for the methyl group of the μ-$MeCO_2$ ligand since these would necessarily be disordered as a result of the imposed two-fold symmetry. Final $R = 0.037$ ($R' = 0.039$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0005F^2]$. The final electron-density difference synthesis showed no peaks > 0.66 or < -0.34 e Å^{-3}.

$[Ni_2L^2{}_2(\mu\text{-}MeCO_2)(MeCN)_2][PF_6]$. Crystals were grown from MeCN–Et_2O as brown prisms and that used had dimensions *ca.* 0.51 × 0.42 × 0.43 mm. Of the 7185 data collected (Wyckoff ω scan, $2\theta \leqslant 50°$), 4112 unique data had $F \geqslant 3\sigma(F)$ and only these were used for structure solution and refinement.

Crystal data. $C_{42}H_{31}F_6N_6Ni_2O_4P$, $M = 946.1$, triclinic, space group $P\bar{1}$, $a = 11.342(3)$, $b = 13.056(3)$, $c = 13.482(4)$ Å, $\alpha = 92.37(2)$, $\beta = 96.01(2)$, $\gamma = 93.05(2)°$, $U = 1980.5(9)$ Å^3, $Z = 2$, $D_c = 1.59$ g cm^{-3}, $F(000) = 964$, μ(Mo-Kα) = 10.7 cm^{-1}.

All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters ($U_{iso} = 0.08$ Å^2). Final $R = 0.073$ ($R' = 0.068$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.001F^2]$. The final electron-density difference synthesis showed no peaks > 0.90 or < -0.66 e Å^{-3}.

$[\{NiL^1(HL^1)\}_2][PF_6]_2 \cdot 0.5Et_2O \cdot 0.5MeCN$. Crystals were grown from MeCN–Et_2O as irregular orange plates. That selected had dimensions *ca.* 0.22 × 0.40 × 0.67 mm and was mounted in a sealed glass capillary under N_2 saturated with MeCN–Et_2O. Of the 6721 data collected (Wyckoff ω scans, $2\theta \leqslant 40°$), 3833 unique data had $F \geqslant 5\sigma(F)$ and only these were used for structure solution and refinement. An empirical absorption correction was applied using a method based upon azimuthal scan data.

Crystal data. $C_{64}H_{46}F_{12}N_8Ni_2O_4P_2 \cdot 0.5Et_2O \cdot 0.5MeCN$, $M = 1456.0$, 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^3, $Z = 4$, $D_c = 1.45$ g cm^{-3}, $F(000) = 2976$, μ(Mo-Kα) = 7.0 cm^{-1}.

The crystal diffracted relatively poorly but there was no evidence of solvent loss or crystal decay during the course of the data collection. The asymmetric unit contains two crystallographically independent formula units of the salt $[\{NiL^1(HL^1)\}_2][PF_6]_2$, one molecule of Et_2O and a molecule of MeCN. In view of their similarity only one of the enantiomeric dications $[\{NiL^1(HL^1)\}_2]^{2+}$ is shown in Fig. 6. Because of the limited data and the large number of atoms, only the Ni atoms were refined with anisotropic thermal parameters and hydrogen atoms were not included in the refinement. Further to minimise the number of variables, aromatic rings were treated as rigid groups. Refinement converged at $R = 0.099$ ($R' = 0.099$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.001|F|^2]$. The final electron-density difference synthesis showed no peaks > 1.1 or < -0.50 e Å^{-3}. The relatively poor R factor is not unreasonable given the modest quality of the data and the large number of independent molecules in the asymmetric unit. Given the poor R factor it is not surprising that attempts to establish the absolute configuration were unsuccessful.

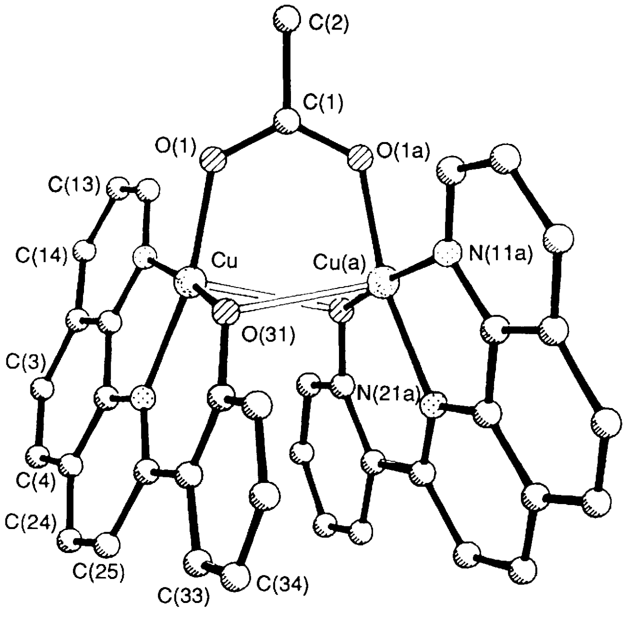

Fig. 1 Structure of the cationic part of $[Cu_2L^2_2(\mu\text{-}MeCO_2)][PF_6]$ showing the atom numbering scheme

Table 1 Selected internuclear distances (Å) and angles (°) for $[Cu_2L^2_2(\mu\text{-}MeCO_2)][PF_6]$

Cu–O(1)	1.942(2)	Cu–N(21)	1.979(3)
Cu–N(11)	2.000(3)	Cu–O(31)	1.889(3)
O(1)–C(1)	1.257(3)	C(1)–O(1A)	1.257(3)
Cu ··· O(31a)	2.449	C(1)–C(2)	1.525(7)
O(1)–Cu–N(11)	90.1(1)	Cu–N(11)–C(12)	130.0(2)
O(1)–Cu–O(31)	92.3(1)	Cu–N(21)–C(22)	111.8(2)
Cu–O(1)–C(1)	129.1(3)	Cu–O(31)–C(31)	127.0(2)
C(2)–C(1)–O(1A)	117.3(2)	N(11)–Cu–N(21)	83.4(1)
C(12)–N(11)–C(16)	118.6(3)	N(21)–Cu–O(31)	93.3(1)
C(22)–N(21)–C(26)	120.5(3)	O(1)–C(1)–O(1A)	125.5(5)
O(1)–Cu–N(21)	168.3(1)	Cu–N(11)–C(16)	111.4(2)
N(11)–Cu–O(31)	174.0(1)	Cu–N(21)–C(26)	127.6(2)
O(1)–C(1)–C(2)	117.3(2)	Cu–O(31) ··· Cu(a)	89.2
Cu(a) ··· O(31)–C(31)	108.6		

Table 2 Atomic positional parameters (fractional coordinates × 10^4) for $[Cu_2L^2_2(\mu\text{-}MeCO_2)][PF_6]$, with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Cu	4154(1)	3621(1)	1540(1)
O(1)	4343(2)	5012(2)	1864(2)
C(1)	5000	5437(4)	2500
C(2)	5000	6561(4)	2500
N(11)	3838(2)	3930(2)	164(2)
C(12)	3915(3)	4762(3)	−223(3)
C(13)	3683(3)	4828(3)	−1207(3)
C(14)	3356(3)	4035(3)	−1801(3)
C(15)	3252(2)	3140(3)	−1414(3)
C(16)	3515(2)	3127(3)	−418(3)
C(3)	2908(3)	2266(3)	−1974(3)
C(4)	2832(3)	1437(3)	−1542(3)
N(21)	3728(2)	2292(2)	1005(2)
C(22)	3444(2)	2249(3)	34(3)
C(23)	3112(2)	1400(3)	−522(3)
C(24)	3068(3)	562(3)	−21(3)
C(25)	3364(3)	612(3)	947(3)
C(26)	3712(2)	1487(3)	1492(3)
O(31)	4334(2)	3287(2)	2787(2)
C(31)	4246(2)	2403(3)	3089(3)
C(32)	4008(2)	1530(3)	2534(3)
C(33)	4030(3)	647(3)	3022(3)
C(34)	4242(3)	624(4)	3978(4)
C(35)	4416(3)	1488(4)	4500(3)
C(36)	4425(3)	2367(3)	4064(3)
P	7500	7500	5000
F(1)	7591(2)	8240(2)	5829(2)
F(2)	6717(3)	8092(3)	4253(3)
F(3)	6929(3)	6828(3)	5217(3)

Results and Discussion

Ligand Synthesis.—Synthesis of the new ligand HL^2 was readily accomplished by reaction of 2-lithioanisole with 1,10-phenanthroline in toluene at room temperature, followed by rearomatisation of the intermediate dihydrophenanthroline with MnO_2, to give 2-(2-methoxyphenyl)-1,10-phenanthroline; subsequent demethylation of the anisole group to give HL^2 was performed with molten pyridinium chloride. The addition of lithium reagents to phenanthroline and polypyridines in this manner is a well established reaction,[16,17,20,21] which has recently been used to prepare sterically hindering phenanthrolines which enforce tetrahedral geometries on first-row transition metals. Under the mild conditions we employed (slight excess of lithium reagent, room temperature) only monosubstitution of the phenanthroline occurs; disubstitution typically requires large (*e.g.* eight-fold) excesses of the lithium reagent, elevated temperatures and prolonged reaction times. The identities of 2-(2-methoxyphenyl)-1,10-phenanthroline and HL^2 were confirmed by mass and ^1H NMR spectroscopy. The NMR assignments were made on the basis of two-dimensional ^1H–^1H correlation spectroscopy (COSY); the only ambiguity is that in each case the two doublets due to the phenanthroline H^3 and H^4 protons cannot be uniquely assigned. As with HL^1, the high chemical shift of the phenolic proton of HL^2 (δ 16.3) suggests a cisoid arrangement of the phenanthroline and phenol groups, such that the phenolic proton hydrogen bonds to the adjacent N atom. In 2,9-bis(4-hydroxyphenyl)-1,10-phenanthroline, where such an interaction is clearly impossible, the phenolic protons resonate at δ 10.14.[17]

Preparation and Structure of $[Cu_2L^2_2(\mu\text{-}MeCO_2)][PF_6]$.—Reaction of HL^2 with 1 equivalent of copper(II) acetate in methanol produced a clear, dark green solution from which a green solid precipitated on addition of KPF_6. Elemental analysis and FAB mass spectrometry indicated that this material was $[Cu_2L^2_2(\mu\text{-}MeCO_2)][PF_6]$, *i.e.* a phenolate-bridged binuclear complex similar to $[Cu_2L^1_2(\mu\text{-}MeCO_2)][PF_6]$.[13] The crystal structure of the complex cation is shown in Fig. 1; relevant bond lengths and angles are in Table 1, and atomic coordinates in Table 2. As expected from the formulation, the structure of $[Cu_2L^2_2(\mu\text{-}MeCO_2)]^+$ is basically similar to that of $[Cu_2L^1_2(\mu\text{-}MeCO_2)]^+$. The binuclear core contains two CuL^2 units, in which the ligand is tridentate and deprotonated, stacked adjacent to one another such that the phenolates bridge the copper centres giving a $Cu_2(\mu\text{-}O)_2$ unit, with an additional μ-1,3-acetate ligand. The two CuL^2 units are equivalent due to the presence of a C_2 axis through the acetate carbon atoms. The ligands are near planar, with a torsion angle of *ca.* 7° between the terminal phenolate and central phenanthroline rings, which may be contrasted with torsion angles of over 20° between the aromatic rings of L^1 in $[Cu_2L^1_2(\mu\text{-}MeCO_2)]^+$. The bite angle between the terminal N and O-donor atoms of L^2 is 174.0(1)°, confirming (as with L^1) that the presence of a six-membered chelate ring involving the phenol allows the ligand to confer near-ideal tetragonal geometries on metal ions; by comparison the bite angle of terpy in $[Cu(terpy)_2]^+$ is 153.8°.[22] Apart from the N,N,O donor set of L^2, the square-pyramidal co-ordination sphere of each copper(II) ion is completed by an acetate oxygen in the basal plane and an apical interaction with a bridging phenolate, which is rather long (2.449 Å) in keeping with the Jahn–Teller

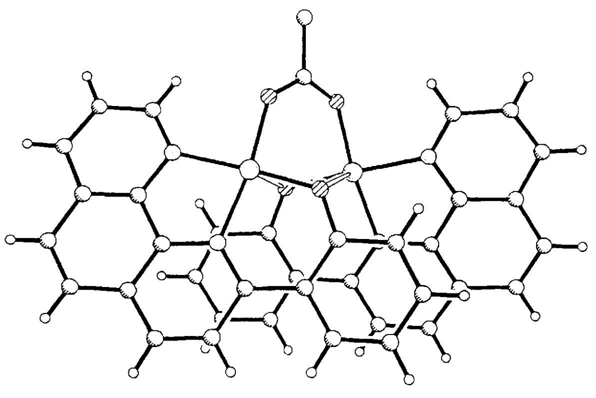

Fig. 2 A view of the overlap of the two ligands of $[Cu_2L^2{}_2(\mu\text{-}MeCO_2)][PF_6]$

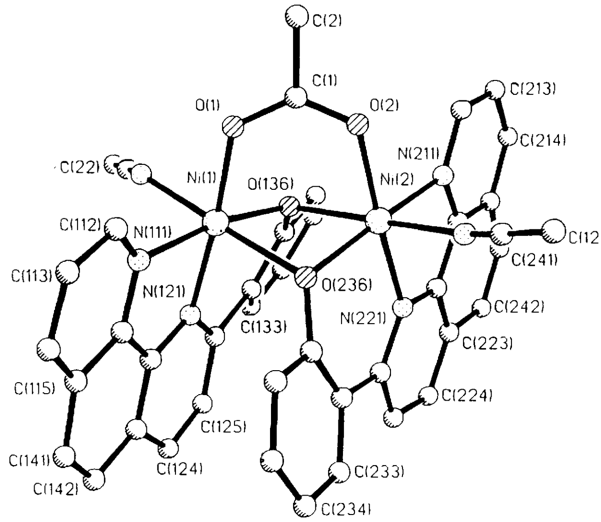

Fig. 3 Structure of the cationic part of $[Ni_2L^2{}_2(\mu\text{-}MeCO_2)(MeCN)_2][PF_6]$ showing the atom numbering scheme

Table 3 Selected internuclear distances (Å) and angles (°) for $[Ni_2L^2{}_2(\mu\text{-}MeCO_2)(MeCN)_2][PF_6]$

Ni(1)–O(1)	2.018(6)	Ni(1)–N(121)	2.035(7)
Ni(1)–O(236)	2.141(5)	Ni(2)–O(2)	2.009(6)
Ni(2)–N(211)	2.055(7)	Ni(2)–O(236)	1.984(5)
Ni(1)–N(111)	2.056(7)	Ni(1)–O(136)	1.989(5)
Ni(1)–N(2)	2.191(8)	Ni(2)–O(136)	2.130(5)
Ni(2)–N(221)	2.039(7)	Ni(2)–N(1)	2.129(8)
C(1)–O(1)	1.268(11)	N(1)–C(11)	1.112(13)
N(2)–C(21)	1.133(14)	C(1)–O(2)	1.245(11)
C(1)–C(2)	1.514(12)	C(21)–C(22)	1.459(15)
C(11)–C(12)	1.448(15)		
O(1)–Ni(1)–N(111)	92.6(3)	O(2)–Ni(2)–N(211)	91.9(3)
O(1)–Ni(1)–O(136)	94.8(2)	O(136)–Ni(2)–N(221)	89.8(2)
O(1)–Ni(1)–O(236)	93.0(2)	O(136)–Ni(2)–O(236)	81.9(2)
O(136)–Ni(1)–O(236)	81.5(2)	O(2)–Ni(2)–N(1)	85.3(3)
N(121)–Ni(1)–N(2)	87.1(3)	N(221)–Ni(2)–N(1)	95.8(3)
O(2)–Ni(2)–O(136)	89.8(2)	Ni(2)–O(236)–Ni(1)	93.7(2)
O(2)–Ni(2)–N(221)	174.0(2)	N(111)–Ni(1)–N(121)	82.1(3)
O(2)–Ni(2)–O(236)	94.8(2)	N(121)–Ni(1)–O(136)	90.7(2)
N(221)–Ni(2)–O(236)	91.1(2)	N(121)–Ni(1)–O(236)	89.1(2)
N(211)–Ni(2)–N(1)	94.8(3)	N(111)–Ni(1)–N(2)	98.3(3)
Ni(2)–O(136)–Ni(1)	93.9(2)	O(236)–Ni(1)–N(2)	169.3(3)
O(1)–Ni(1)–N(121)	174.3(3)	O(136)–Ni(2)–N(211)	92.4(2)
N(111)–Ni(1)–O(136)	169.8(3)	N(211)–Ni(2)–N(221)	82.1(3)
N(111)–Ni(1)–O(236)	91.1(2)	N(211)–Ni(2)–O(236)	171.2(3)
O(1)–Ni(1)–N(2)	91.7(3)	O(136)–Ni(2)–N(1)	171.4(3)
O(136)–Ni(1)–N(2)	88.5(3)	O(236)–Ni(2)–N(1)	91.4(2)

effect. Unlike $[Cu_2L^1{}_2(\mu\text{-}MeCO_2)]^+$ there is no additional interaction between binuclear units.

It is clear from Fig. 1 that there is a π-stacking interaction between the superimposed sections of the ligands within the binuclear core. The distances of atoms in one ligand from the mean plane of the other ligand vary between 3.1 and 4.3 Å, which may be compared with 3.35 Å between the layers of graphite[23] and 3.4 Å between stacked nucleotide residues in DNA.[24] The wide range of distances reflects the fact that the ligands are not parallel but diverge (see below). Interligand π-stacking interactions are becoming increasingly common in co-ordination complexes involving aromatic ligands,[5,25] and have been deliberately used to control binding of aromatic substrates in host–guest systems.[26] Theoretical estimations of the magnitudes of these interactions are still sparse, but it has recently been shown that face-to-face (rather than edge-to-face) stacking becomes more favourable with increasing size of the aromatic systems, and that the most favourable relative orientation of the stacked systems is not eclipsed but offset, with hydrogen atoms roughly over ring centres.[27] The offset nature of the ligand overlap in $[Cu_2L^2{}_2(\mu\text{-}MeCO_2)]^+$ is illustrated in Fig. 2; whether this interaction controls the gross structure of the complex or is merely a fortunate side effect arising from optimisation of the metal–ligand interactions is as yet unclear.

The two ligands are not parallel, but diverge. The angle of intersection of the mean ligand planes is *ca.* 30°; they thus form a 'tent-like' structure. This raises the interesting possibility of large, hydrophobic substituents attached to the phenanthroline and phenol rings *para* to the donor atoms encompassing a cavity which, as the substituents diverge, may be large enough to act as a host for small hydrophobic species. The formation of hydrophobic cavities of this type in complexes of tris(pyrazolyl)borate ligands with bulky substituents at the 3 positions of the pyrazole rings has recently been demonstrated.[28]

The room-temperature magnetic moment is 2.0 μ_B per copper(II), which is typical for magnetically dilute ions; however it is likely that, as with $[Cu_2L^1{}_2(\mu\text{-}MeCO_2)][PF_6]$, the presence of bridging phenolates will result in a magnetic interaction which is apparent at lower temperatures, and the results of a variable-temperature EPR and magnetic study will be reported in a future paper.[29] Cyclic voltammetry in acetonitrile revealed only an irreversible, ligand-based oxidation at +0.90 V *vs.* the ferrocene–ferrocenium couple and an irreversible reduction at −2.15 V.

Preparation and Structure of $[Ni_2L^2{}_2(\mu\text{-}MeCO_2)(MeCN)_2][PF_6]$.—Reaction of HL^2 with 1 equivalent of nickel(II) acetate in methanol resulted in a clear yellow solution, from which a yellow precipitate was obtained on addition of KPF_6. The FAB mass spectrum and elemental analysis of this material indicated the formulation $[Ni_2L^2{}_2(\mu\text{-}MeCO_2)][PF_6]$, *i.e.* a phenolate-bridged binuclear complex similar to both of the copper(II) complexes. The crystal structure of the complex cation is shown in Fig. 3; relevant bond lengths and angles are in Table 3, and atomic coordinates in Table 4. As expected from the molecular formula, the structure is grossly similar to those of $[Cu_2L^1{}_2(\mu\text{-}MeCO_2)][PF_6]$ and $[Cu_2L^2{}_2(\mu\text{-}MeCO_2)][PF_6]$. There are minor differences in the ligand conformation between $[Ni_2L^2{}_2(\mu\text{-}MeCO_2)(MeCN)_2][PF_6]$ and $[Cu_2L^2{}_2(\mu\text{-}MeCO_2)][PF_6]$: the torsion angles of *ca.* 16 and 22° between the central phenanthroline and terminal phenol rings are rather larger, and the ligand bite angles of 171.2(3) and 169.8(3)° in the nickel(II) complex are slightly smaller than those in the copper(II) complex.

The two major structural differences between $[Ni_2L^2{}_2(\mu\text{-}MeCO_2)(MeCN)_2][PF_6]$ and $[Cu_2L^2{}_2(\mu\text{-}MeCO_2)][PF_6]$ are both consequences of the fact that nickel(II) adopts a regular octahedral geometry, as opposed to the elongated-tetragonal geometries favoured by copper(II). First, each nickel(II) ion has an additional MeCN ligand (from the recrystallisation solvent). It is attached at an angle rather than in the expected linear geometry; the Ni–N≡C angles are 163.5 and 145.2°. The two

Table 4 Atomic positional parameters (fractional coordinates × 10^4) for $[Ni_2L^2_2(\mu\text{-}MeCO_2)(MeCN)_2][PF_6]$, with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni(1)	−1036(1)	2457(1)	3524(1)	C(215)	4327(8)	3604(7)	2497(8)
Ni(2)	1343(1)	1754(1)	3067(1)	C(216)	3301(7)	2938(6)	2480(7)
C(1)	531(8)	1520(6)	5067(6)	N(221)	1514(6)	2155(5)	1642(5)
C(2)	767(8)	1160(8)	6118(7)	C(222)	2492(7)	2801(6)	1601(6)
O(1)	−473(5)	1884(4)	4847(4)	C(223)	2735(8)	3297(7)	746(7)
O(2)	1338(5)	1444(4)	4514(4)	C(224)	1927(9)	3133(7)	−86(7)
N(111)	−2658(6)	1658(6)	3449(6)	C(225)	927(9)	2503(7)	−34(7)
C(112)	−3050(9)	977(8)	4025(8)	C(226)	709(7)	1999(6)	833(6)
C(113)	−4081(10)	348(9)	3774(10)	C(231)	−759(7)	907(6)	1761(6)
C(114)	−4704(9)	436(9)	2887(10)	C(232)	−332(7)	1288(6)	864(6)
C(115)	−4328(8)	1153(7)	2212(8)	C(233)	−936(8)	900(7)	−48(7)
C(116)	−3277(7)	1759(7)	2537(7)	C(234)	−1901(8)	193(7)	−104(7)
N(121)	−1771(6)	3001(5)	2221(5)	C(235)	−2273(8)	−182(7)	751(7)
C(122)	−2795(7)	2453(6)	1880(7)	C(236)	−1701(8)	162(6)	1674(7)
C(123)	−3393(8)	2530(8)	913(7)	O(236)	−330(4)	1249(4)	2686(4)
C(124)	−2836(9)	3232(8)	310(7)	C(241)	4542(9)	4123(8)	1626(9)
C(125)	−1853(9)	3766(7)	668(7)	C(242)	3797(9)	3980(7)	784(8)
C(126)	−1284(8)	3668(6)	1634(7)	N(1)	1944(6)	247(6)	2887(6)
C(131)	642(7)	3999(6)	2841(6)	C(11)	2073(8)	−587(8)	2951(8)
C(132)	−182(8)	4281(6)	2028(6)	C(12)	2214(12)	−1675(8)	3053(11)
C(133)	100(10)	5205(7)	1572(7)	N(2)	−1518(7)	3880(6)	4259(6)
C(134)	1085(11)	5837(8)	1878(8)	C(21)	−1456(8)	4749(9)	4257(7)
C(135)	1862(10)	5560(7)	2632(8)	C(22)	−1328(11)	5866(7)	4241(8)
C(136)	1653(8)	4666(6)	3120(7)	P	4372(3)	2817(3)	7479(3)
O(136)	524(5)	3154(4)	3342(4)	F(1)	4012(16)	3485(9)	8267(12)
C(141)	−4893(8)	1257(9)	1224(9)	F(2)	3211(11)	2505(12)	6980(16)
C(142)	−4440(9)	1918(9)	599(9)	F(3)	4753(16)	2136(9)	6628(8)
N(211)	3019(6)	2457(5)	3319(5)	F(4)	5573(9)	3155(11)	7872(11)
C(212)	3729(8)	2577(7)	4153(7)	F(5)	4482(15)	3738(7)	6842(8)
C(213)	4790(9)	3225(9)	4243(8)	F(6)	4347(17)	1912(7)	8075(8)
C(214)	5051(8)	3701(8)	3423(9)				

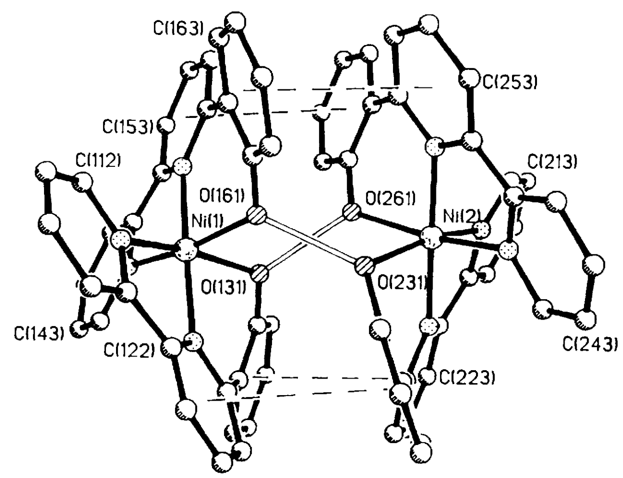

Fig. 4 Structure of the cationic part of $[\{NiL^1(HL^1)\}_2][PF_6]_2\cdot 0.5MeCN\cdot 0.5Et_2O$ showing the atom numbering scheme

Table 5 Selected internuclear distances (Å) and angles (°) for one of the formula units of the salt $[\{NiL^1(HL^1)\}_2][PF_6]_2$

Ni(1)–N(111)	2.033(22)	Ni(1)–O(131)	2.068(21)
Ni(1)–N(151)	1.984(20)	Ni(2)–N(211)	2.076(17)
Ni(2)–O(231)	2.048(19)	Ni(2)–N(251)	2.033(22)
Ni(1)–N(121)	2.063(18)	Ni(1)–N(141)	2.023(23)
Ni(1)–O(161)	2.034(24)	Ni(2)–N(221)	2.047(19)
Ni(2)–N(241)	2.047(21)	Ni(2)–O(261)	2.071(23)
O(131) ··· O(261)	2.37	O(161) ··· O(231)	2.39
N(111)–Ni(1)–N(121)	80.9(8)	N(211)–Ni(2)–O(231)	164.2(9)
N(111)–Ni(1)–N(141)	103.7(9)	N(221)–Ni(2)–N(241)	98.3(9)
N(111)–Ni(1)–N(151)	101.7(9)	N(221)–Ni(2)–N(251)	179.0(9)
N(141)–Ni(1)–N(151)	81.0(9)	N(211)–Ni(2)–O(261)	88.5(8)
O(131)–Ni(1)–O(161)	84.8(9)	N(241)–Ni(2)–O(261)	164.5(9)
N(211)–Ni(2)–N(221)	79.1(8)	N(121)–Ni(1)–O(131)	85.6(8)
N(211)–Ni(2)–N(241)	103.1(8)	O(131)–Ni(1)–N(141)	87.8(8)
N(211)–Ni(2)–N(251)	101.8(9)	O(131)–Ni(1)–N(151)	91.9(8)
N(241)–Ni(2)–N(251)	81.0(9)	N(121)–Ni(1)–O(161)	93.5(8)
O(231)–Ni(2)–O(261)	83.5(8)	N(151)–Ni(1)–O(161)	86.8(9)
N(111)–Ni(1)–O(131)	163.3(8)	N(221)–Ni(2)–O(231)	87.9(8)
N(121)–Ni(1)–N(141)	98.4(8)	O(231)–Ni(2)–N(241)	87.5(8)
N(121)–Ni(1)–N(151)	177.5(8)	O(231)–Ni(2)–N(251)	91.3(9)
N(111)–Ni(1)–O(161)	86.4(9)	N(221)–Ni(2)–O(261)	93.9(9)
N(141)–Ni(1)–O(161)	165.5(8)	N(251)–Ni(2)–O(261)	86.6(9)

more strongly bent acetonitrile ligands of adjacent complexes are close to each other (related by an inversion centre) in the unit cell, apparently resulting in a weak hydrogen-bonding interaction between the methyl protons of one MeCN ligand and the N atom of the other (N ··· H 2.7 Å). Secondly, the apical interactions to the bridging phenolates (2.130 and 2.141 Å) are much shorter than those in $[Cu_2L^2_2(\mu\text{-}MeCO_2)][PF_6]$ (2.449 Å). This causes a contraction of the $M_2(\mu\text{-}O)_2$ core relative to the copper(II) complex, bringing the two ligands closer together and resulting in very short π-stacking distances. The distances of atoms in one ligand from the mean plane of the other ligand vary from 2.86 [C(231) to mean plane of adjacent ligand] to 3.90 Å [C(234) to mean plane of adjacent ligand]. Again, the considerable variation in these values reflects the fact that the phenols are twisted out of the planes of the phenanthroline fragments, and that the ligands are not parallel but are diverging slightly with an angle of intersection of their mean planes of *ca.* 12°, but it is clear that the contraction of the $Ni_2(\mu\text{-}O)_2$ core compared to the $Cu_2(\mu\text{-}O)_2$ core is responsible for some very short inter-ligand contacts. The mutually offset nature of the ligand overlap is very similar to that shown in Fig. 2 for the copper complex. The room-temperature magnetic moment is 2.9 μ_B per nickel(II), a typical value for magnetically dilute ions; the results of a variable-temperature susceptibility study will be reported in due course. Cyclic voltammetry in acetonitrile revealed only irreversible redox processes at extreme potentials (above +0.7 and below −1.7 V *vs* ferrocene–ferrocenium).

Preparation and Structure of [{NiL^1(HL^1)}$_2$][PF$_6$]$_2$.—This was prepared and characterised as previously described[13] (a preliminary account of its crystal structure has recently been published).[14] The structure is shown in Fig. 4, and is unusual in displaying two distinct types of intermolecular interaction, π stacking and hydrogen bonding. Relevant bond lengths and angles are in Table 5, and atomic coordinates in Table 6. The asymmetric unit is large, and contains two crystallographically

Table 6 Atomic positional parameters (fractional coordinates × 10^4) for [{NiL^1(HL^1)}$_2$][PF$_6$], with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Ni(1)	5 059(3)	4 444(3)	6 204(2)
N(111)	5 237(15)	3 871(11)	7 072(10)
C(112)	4 756	3 355	7 116
C(113)	4 771	3 082	7 787
C(114)	5 267	3 326	8 413
C(115)	5 748	3 842	8 368
C(116)	5 734	4 115	7 697
N(121)	6 072(12)	4 864(9)	6 843(10)
C(122)	6 156	4 693	7 568
C(123)	6 679	5 024	8 110
C(124)	7 117	5 524	7 928
C(125)	7 033	5 694	7 204
C(126)	6 510	5 364	6 662
O(131)	4 986(12)	5 212(9)	5 556(10)
C(131)	5 669(11)	5 442(10)	5 368(11)
C(132)	6 407	5 472	5 884
C(133)	7 129	5 674	5 686
C(134)	7 113	5 846	4 972
C(135)	6 374	5 816	4 455
C(136)	5 652	5 614	4 653
N(141)	5 645(14)	4 020(10)	5 502(10)
C(142)	6 499	4 017	5 548
C(143)	6 817	3 858	4 945
C(144)	6 283	3 702	4 295
C(145)	5 429	3 705	4 249
C(146)	5 111	3 864	4 852
N(151)	4 086(13)	4 068(10)	5 556(10)
C(152)	4 282	3 908	4 896
C(153)	3 656	3 735	4 313
C(154)	2 835	3 721	4 390
C(155)	2 640	3 881	5 050
C(156)	3 265	4 054	5 633
O(161)	4 238(13)	4 892(11)	6 684(11)
C(161)	3 585(14)	4 611(11)	6 832(15)
C(162)	3 111	4 206	6 344
C(163)	2 472	3 877	6 546
C(164)	2 308	3 953	7 237
C(165)	2 783	4 358	7 725
C(166)	3 421	4 687	7 522
Ni(2)	3 586(3)	6 503(3)	5 931(2)
N(211)	3 186(14)	7 013(9)	4 996(9)
C(212)	2 373	7 103	4 622
C(213)	2 216	7 370	3 936
C(214)	2 873	7 547	3 623
C(215)	3 686	7 458	3 997
C(216)	3 843	7 191	4 683
N(221)	4 673(10)	6 897(9)	5 811(10)
C(222)	4 640	7 093	5 102
C(223)	5 365	7 260	4 884
C(224)	6 124	7 230	5 375
C(225)	6 156	7 033	6 083
C(226)	5 431	6 866	6 302
O(231)	4 264(13)	5 973(9)	6 735(10)
C(231)	4 844(13)	6 293(10)	7 277(11)
C(232)	5 394	6 711	7 080
C(233)	5 945	7 030	7 613
C(234)	5 946	6 931	8 344
C(235)	5 395	6 513	8 541
C(236)	4 844	6 194	8 008
N(241)	3 340(14)	7 063(10)	6 729(9)
C(242)	3 826	7 554	7 039
C(243)	3 733	7 790	7 703
C(244)	3 153	7 536	8 058
C(245)	2 666	7 045	7 748
C(246)	2 759	6 809	7 084
N(251)	2 515(12)	6 113(11)	6 070(13)
C(252)	2 310	6 301	6 717
C(253)	1 695	5 995	6 982
C(254)	1 286	5 500	6 602
C(255)	1 490	5 311	5 956
C(256)	2 105	5 617	5 690
O(261)	3 709(13)	5 760(10)	5 283(12)
C(261)	3 050(14)	5 538(12)	4 802(12)
C(262)	2 249	5 504	4 928
C(263)	1 605	5 285	4 388
C(264)	1 762	5 100	3 722
C(265)	2 563	5 134	3 596
C(266)	3 207	5 353	4 136
Ni(3)	898(3)	0	9 419(2)
N(311)	1 220(13)	−445(11)	10 404(9)
C(312)	1 624	−1 007	10 527
C(313)	1 840	−1 241	11 229
C(314)	1 651	−913	11 808
C(315)	1 247	−352	11 684
C(316)	1 032	−118	10 982
N(321)	369(13)	564(9)	10 074(10)
C(322)	661	450	10 810
C(323)	484	858	11 325
C(324)	14	1 379	11 104
C(325)	−278	1 494	10 367
C(326)	−101	1 086	9 852
O(331)	587(12)	650(10)	8 593(11)
C(331)	−115(12)	942(11)	8 480(14)
C(332)	−475	1 114	9 056
C(333)	−1 266	1 370	8 919
C(334)	−1 697	1 453	8 206
C(335)	−1 337	1 280	7 631
C(336)	−546	1 025	7 768
N(341)	−146(12)	−479(10)	8 947(11)
C(342)	−926	−396	9 105
C(343)	−1 626	−629	8 639
C(344)	−1 546	−945	8 015
C(345)	−765	−1 029	7 858
C(346)	−65	−796	8 324
N(351)	1 370(13)	−586(9)	8 789(9)
C(352)	747	−860	8 273
C(353)	951	−1 192	7 704
C(354)	1 776	−1 250	7 650
C(355)	2 399	−976	8 166
C(356)	2 195	−644	8 735
O(361)	2 038(12)	468(9)	9 598(10)
C(361)	2 785(11)	152(10)	9 675(12)
C(362)	2 876	−399	9 327
C(363)	3 637	−699	9 466
C(364)	4 308	−448	9 953
C(365)	4 217	102	10 300
C(366)	3 455	402	10 161
Ni(4)	2 250(3)	1 828(3)	8 381(2)
N(411)	2 212(14)	2 132(10)	7 331(8)
C(412)	2 793	2 035	6 902
C(413)	2 582	2 147	6 158
C(414)	1 791	2 356	5 844
C(415)	1 211	2 453	6 273
C(416)	1 421	2 341	7 017
N(421)	1 162(10)	2 328(9)	8 263(11)
C(422)	833	2 455	7 536
C(423)	19	2 661	7 324
C(424)	−465	2 739	7 840
C(425)	−136	2 612	8 568
C(426)	678	2 407	8 779
O(431)	2 020(12)	1 536(10)	9 348(10)
C(431)	1 710(13)	1 919(10)	9 779(11)
C(432)	1 111	2 357	9 509
C(433)	814	2 743	9 985
C(434)	1 115	2 691	10 730
C(435)	1 713	2 253	11 000

Table 6 (*continued*)

Atom	x	y	z	Atom	x	y	z
C(436)	2 011	1 867	10 524	F(21)	6 047(21)	−321(16)	8 374(18)
N(441)	3 052(13)	2 461(11)	8 945(10)	F(22)	5 122(19)	−1 026(14)	8 409(16)
C(442)	2 838	3 038	9 158	F(23)	5 394(17)	−1 471(13)	7 453(15)
C(443)	3 381	3 358	9 696	F(24)	6 422(17)	−785(13)	7 467(14)
C(444)	4 140	3 099	10 022	F(25)	5 064(19)	−510(15)	7 384(16)
C(445)	4 354	2 521	9 809	F(26)	6 375(17)	−1 288(14)	8 460(15)
C(446)	3 811	2 202	9 271	P(3)	833(11)	9 297(9)	3 748(9)
N(451)	3 344(10)	1 376(10)	8 497(11)	F(31)	763(31)	9 933(30)	3 501(27)
C(452)	3 993	1 635	8 999	F(32)	391(21)	9 098(17)	2 931(19)
C(453)	4 749	1 332	9 188	F(33)	97(25)	9 290(21)	4 155(20)
C(454)	4 857	768	8 874	F(34)	1 662(24)	9 356(20)	3 479(20)
C(455)	4 208	509	8 372	F(35)	1 261(25)	9 459(22)	4 547(23)
C(456)	3 451	813	8 183	F(36)	954(32)	8 653(29)	4 077(27)
O(461)	1 637(13)	1 029(10)	8 006(11)	P(4)	7 148(12)	2 350(10)	−89(10)
C(461)	1 972(15)	661(10)	7 551(12)	F(41)	6 926(25)	1 841(22)	−564(22)
C(462)	2 817	560	7 612	F(42)	6 393(22)	2 206(17)	243(19)
C(463)	3 094	196	7 104	F(43)	7 963(27)	2 495(21)	−332(22)
C(464)	2 525	−67	6 535	F(44)	7 456(29)	2 955(23)	468(26)
C(465)	1 680	33	6 473	F(45)	7 674(20)	1 992(16)	540(18)
C(466)	1 403	397	6 981	F(46)	6 686(48)	2 886(39)	−416(41)
P(1)	8 810(10)	7 301(7)	6 769(8)	O	7 936(21)	−187(16)	734(17)
F(11)	8 122(24)	7 621(19)	7 047(20)	C(4)	9 122(29)	−866(24)	1 271(25)
F(12)	8 955(24)	7 971(20)	6 506(21)	C(2)	7 566(44)	405(33)	658(35)
F(13)	9 541(27)	7 129(21)	6 473(22)	C(3)	8 786(32)	−225(24)	1 142(26)
F(14)	8 529(25)	6 697(22)	7 091(21)	C(1)	6 691(49)	328(34)	427(37)
F(15)	9 317(18)	7 465(14)	7 552(16)	C(5)	3 924(33)	6 042(25)	2 428(27)
F(16)	8 246(20)	7 163(15)	6 007(18)	C(6)	4 646(32)	6 413(23)	2 692(24)
P(2)	5 751(8)	−912(6)	7 935(7)	N	5 229(27)	6 680(20)	3 000(21)

independent formula units of the salt $[\{NiL^1(HL^1)\}_2][PF_6]_2$, one molecule of Et_2O and one molecule of MeCN; the two enantiomeric dications are very similar and only one such unit is shown in Fig. 4. It consists of two near-octahedral NiL^1_2 units, each with a *cis*-N_4O_2 donor set. The bite angles between the terminal N- and O-donor atoms of L^1 lie between 163.3 and 165.5°, considerably less than the near-180° bite angles achieved in $[Cu_2L^1_2(\mu\text{-}MeCO_2)][PF_6]$ and $[CoL^1_2][PF_6]$[13] but more than the 156° in $[Ni(terpy)_2]^{2+}$.[30] 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, are only slightly more than double a typical O–H distance (*ca.* 1.0 Å), and as such are at the lower limit for a pair of hydrogen-bonded oxygen atoms, indicative of strong hydrogen bonds ($\Delta H > 30$ kJ mol^{-1} per hydrogen bond) 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 2.7–3.0 Å or more,[31] and the well known strong hydrogen bonds which occur in square-planar nickel(II) dioxime complexes vary between 2.4 and 2.5 Å.[31] 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 of 2.7 μ_B per nickel. 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.[32] Unfortunately the broad, shallow nature to be expected of the peak in the infrared spectrum together with the numerous other peaks in the fingerprint region 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 midway between square-planar and tetrahedral.

As a result of the proximity of monomer units due to the hydrogen bonding, sections of the aromatic ligands are brought into close contact. The resulting stacking interactions are indicated by the broken lines in Fig. 4; the distances between the centroids of the aromatic rings concerned vary between 3.69 and 3.88 Å. 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 interligand interactions are maximised. There are also smaller torsion angles between the two pyridine rings of between 1 and 7°. 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. There appears to be an element of co-operativity between the two different intermolecular interactions in this complex which reinforce each other neatly.

Comparison of the Structures.—It is clear that a necessary prerequisite for the structure of $[\{NiL^1(HL^1)\}_2][PF_6]_2$ to form is a high degree of flexibility in the ligand. Confirmation of this is provided by comparison with the structure of $[Ni_2L^2_2(\mu\text{-}MeCO_2)(MeCN)_2][PF_6]$, in which the extra rigidity provided by the phenanthroline groups results in a completely different structure. Also, the additional aromatic ring of phenanthroline compared to bipy would be expected to favour face-to-face stacking interactions between the ligands in complexes of L^2 compared to L^1,[27] and we have already seen that $[Ni_2L^2_2(\mu\text{-}MeCO_2)(MeCN)_2][PF_6]$ does contain some very short stacking interactions in which the phenanthroline fragments are involved.

It is less clear why the copper(II) and nickel(II) complexes of HL^1 should have such different structures. The two different structural types may be energetically similar, so that the electronic preference of copper(II) for an elongated geometry is sufficient to tip the balance.

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