FULL PAPER

Complexes of 2,6-bis[*N*-(2'-pyridylmethyl)carbamyl]pyridine: formation of mononuclear complexes, and self-assembly of double helical dinuclear and tetranuclear copper(II) and trinuclear nickel(II) complexes

Nathaniel W. Alcock,^{*a*} Guy Clarkson,^{*a*} Peter B. Glover,^{*a*} Geoffrey A. Lawrance,^{**b*} Peter Moore^{**a*} and Mery Napitupulu^{*b*}

^a Department of Chemistry, University of Warwick, Coventry, UK CV4 7AL

^b Discipline of Chemistry, School of Environmental and Life Sciences, The University of Newcastle, Callaghan N.S.W., 2308, Australia. E-mail: p.moore@warwick.ac.uk

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The potentially pentadentate ligand 2,6-bis $[N-(2'-pyridylmethyl)carbamyl]pyridine (H_2L^1)$, readily prepared from reaction of a diester of pyridine-2,6-dicarboxylic acid (H2dipic) and 2-aminomethylpyridine (ampy), shows limited tendency to form 1:1 M: L complexes with labile metal ions, although [CuL¹] and [NiL¹] were observed as minor species, the latter characterized by a crystal structure analysis. A mononuclear complex formed with inert Co(III) was characterized by a crystal structure as the neutral 1:2 complex [Co(L¹)(HL¹)] with two ligands acting as tridentate ligands, one coordinated by the central pyridine and its two flanking deprotonated amido groups, and the other by the central pyridine, one amido and one terminal pyridine group, with the remaining poorly coordinating protonated amide remaining unbound along with other terminal pyridine groups. Fe(III) is known to form a symmetrical 1:2 complex, but that complex is anionic due to binding of all four deprotonated amido groups; the unsymmetrical neutral Co(III) complex converts into a symmetrical anionic species only on heating for hours in aqueous base in the presence of activated carbon. The most remarkable tendency of H_2L^1 , however, is towards the formation of robust double helical complexes: a dinuclear Cu(II) complex $[Cu_2L_1^2]$ forms, as well as a trinuclear Ni(II) complex $[Ni_3(L^1)_2(OAc)_2(MeOH)_2]$. Moreover, in the presence of added H₂dipic, the tetranuclear complex $[Cu_4(L^1)_2(dipic)_2(OH_2)_2]$ is obtained. All helical complexes have been characterized by X-ray crystal structure analyses, and all crystals feature a racemic mixture of left- and right-handed double helices stabilized by inter-ligand π -stacking (inter-ring distances of 3.2–3.8 Å) of ligands which each span several metal ions. Using the chelating ligand pentane-2,4-dione (acac), each of the two pairs of adjacent monodentate ligands in $[Ni_3(L^1)_2(OAc)_2(OH_2)_2]$ have been shown to be available for substitution without destroying the helical structure, to form $[Ni_3(L^1)_2(acac)_2]$, also characterized by a crystal structure.

Introduction

The synthesis of ligands based on 2,6-disubstituted pyridine has attracted a great deal of attention, with a broad array of both acyclic and macrocyclic ligands reported.¹ In particular, diamides incorporating an -NH-CO-pyridine-CO-NH- core based on pyridine-2,6-dicarboxylic acid (H₂dipic) have been examined, with interest in these compounds extending to potential applications as diverse as azo dyes² and telomerase inhibitors.³ Whereas pyridine-2,6-dicarboxylic acid has been used mainly in pursuit of the synthesis of low molecular weight molecules, it has also been applied in the synthesis of poly(amide esters),⁴ with both linear and cyclic structures identified, including macrocycles with from 2 to 14 pyridine groups in the ring. Macrocycles incorporating the pyridine-2,6diamide functionality are known,⁵ but will not be discussed here, where the focus is on linear acyclic ligand systems.



2,6-Bis[N-(2'-pyridylmethyl)carbamyl]pyridine (H₂L¹) under examination here has been described before, and displays no unusual structural features in its crystal structure when not coordinated,^{6,7} adopting the typical *syn,syn* conformation resulting from intramolecular hydrogen bonding of the amide NH-group with the central pyridine N-atom. The longer-chain analogue (H₂L²), with an additional methylene in each alkyl chain, is also well known.⁸ Notably, a bisoxazoline pyridine analogue has been observed to adopt a left-handed helical superstructure in the solid state even in the absence of metal ions,⁹ presaging helicity and chirality in complexes of this type of ligand system. Chirality has also been introduced into related ligands themselves, albeit in examples of lower denticity.¹⁰

2,6-Bis[N-(2'-pyridylmethyl)carbamyl]pyridine molecule (H_2L^1) is a potentially linear pentadentate ligand. Both mononuclear and polynuclear metal complexes formed from a family of potentially pentadentate ligands based on pyridine-2,6-dicarboxylic acid have been described. The target molecule (H₂L¹) has been reported to spontaneously form dicopper(II) complexes which display double-stranded helicate behaviour,¹¹ in contrast to the molecule with an additional methylene in each arm (H_2L^2) , which forms only monomeric copper(II) species.⁸ The Fe(III) complex of both H_2L^1 and H_2L^2 are monomeric, forming mer-[FeL₂]⁻ ions with the central pyridine and both deprotonated amides of each ligand bound and the terminal pyridines unbound.¹² A range of other related ligands featuring different 'arms' have been reported, and form monomeric or polymeric complexes.13-20

The family of linear acyclic molecules with an -NH-COpyridine–CO–NH– core have been shown to offer a range of important applications. These include uses as reagents for heavy metal selection and or removal from water,^{21–23,32} electroluminescent devices,²⁴ tryptase inhibitors,²⁵ artificial enzymes,²⁶ catalysts for aldehyde hydrophosphonylation,²⁷ and as brightening agents for synthetic fibres.²⁸ H₂L¹ is reportedly efficient as an oxygenation catalyst in concert with cobalt(II) acetate,²⁹ and as an ionophore in the polymer membrane of a copper(II)-selective electrode.³⁰ The close analogue (H₂L²), as the [Co^{III}(L²)(OOR)] complex, is effective in the catalytic oxidation of hydrocarbons,^{12,31} and H₂L² along with cobalt(II) acetate catalyses the epoxidation of olefins and the selective oxygenation of phenols to quinones.²⁹

Although most examples of the coordination chemistry of H_2L^1 and its analogue H_2L^2 reported to date have yielded monomeric complexes with 1 : 1 or 1 : 2 stoichiometry, the observation of the spontaneous formation of a 2 : 2 helical dicopper(II) complex was a spur to our deeper investigation of the chemistry of H_2L^1 . We report the ability of H_2L^1 to form not only monomer and helical dinuclear complexes, but also more elaborate double helical trinuclear and tetranuclear complexes. Synthetic, reactivity and structural details are presented herein.

Experimental

Syntheses

The ligand precursors and metal salts were commercial samples and were used in syntheses as received.

2,6-Bis(methoxycarbonyl)pyridine

To a mixture of 2,6-pyridinedicarboxylic acid (10 g, 46 mmol) in methanol (200 cm³) was added 2,2-dimethoxypropane (80 cm³) and conc. HCl (6.5 cm³). The mixture was refluxed for 4 h whilst protected from the atmosphere by a CaCl₂ guard tube, and then the heating was turned off and the mixture stirred overnight. A white solid that had formed was collected, washed with a small volume of methanol then diethyl ether, and air dried (8.0 g); it proved analytically pure as isolated. The solvent was removed from the filtrate by rotary evaporation, and the resulting brownish solid was collected, washed with diethyl ether, and the off-white solid collected (4.0 g) (overall yield 97%). Anal. C, 55.2; H, 4.6; N, 7.0. C₉H₉NO₄ requires C, 55.4; H, 4.7; N, 7.2%. NMR: δ_H (CDCl₃) 4.01 (6H, s, CH₃O), 8.01 (1H, t, pyH), 8.30 (2H, d, pyH). δ_c (CDCl₃) 53.2 (CH₃O), 128.0, 138.3 (pyCH), 148.0 (pyC_{tert}), 165.0 (C=O) ppm. EI MS: m/z 196 (M^+) , 165 $(M^+ - OMe)$, 137 $(M^+ - OCOMe)$, 105 $(M^+ - OCOMe)$ OCOMe – OMe), 77 (M⁺ – 2(OCOMe)). IR (cm⁻¹): 1740 (C=O), 1572, 1453, 1434 (in-plane C=C), 1290, 1243 (C-O), 1165, 1145, 996 (py ring breathing), 949, 852, 813, 756 (out-ofplane 2,6-disubstituted py).

2,6-Bis[N-(2'-pyridinylmethyl)carbamyl]pyridine, H₂L¹

A solution of (2-aminomethyl)pyridine (13.9 g, 65 mmol) in toluene (40 cm³) was added rapidly to a solution of 2,6bis(methoxycarbonyl)pyridine (6.3 g, 32 mmol) in toluene (120 cm³) in a 250 cm³ round-bottomed flask. The suspension was then refluxed (oil bath) and stirred for 24 h, readily dissolving during this process to a clear solution. The heat was turned off and slow cooling allowed as the mixture was stirred overnight. During this time, a white solid crystallized; this was collected, washed with diethyl ether (*ca.* 30 cm³) and dried in a vacuum dessicator (6.9 g, 61%); it proved analytically pure. A second crop was obtained from the initial filtrate by removing the solvent by rotary evaporation, redissolving the residue in chloroform (100 cm³) and washing with water (3×50 cm³). The chloroform solution was dried over anhydrous MgSO₄, filtered, and the solvent removed by rotary evaporation. The residue was recrystallised from benzene (2.5 g). Anal. C, 64.3; H, 5.1; N, 19.7. C₁₉H₁₇N₅O₂·0.5H₂O requires C, 64.0; H, 4.9; N, 19.7%. NMR: δ_H (CDCl₃) 4.74 (4H, d, CH₂), 7.14 (2H, ddd, pyH), 7.32 (2H, dd, pyH), 7.62 (2H, ddd, pyH), 7.96 (1H, t, pyH), 8.29 (2H, d, pyH), 8.44 (2H, dd, pyH), 9.11 (2H, t, NH). $\delta_{\rm C}$ (CDCl₃) 44.5 (CH₂), 122.1, 122.3 124.9, 136.8, 138.8, 149.2 (pyCH), 148.7, 156.9 (pyC_{tert}), 163.6 (C=O) ppm. EI MS: *m/z* 347 (M⁺), 213 (M⁺ - pyCH₂NHCO), 149 (M⁺ - pyCH₂NHCOpyCH₂NH), 135 (pyCH₂NHCO⁺), 107 (pyCH₂NH⁺), 77 (py⁺). IR (cm⁻¹): 1674, 1665 (CO), 1594, 1567, 1539, 1437, 1413 (NHCO), 1310, 1258 (CH), 1001, 765, 648 (py). UV-Vis spectrum (EtOH): 204 nm (ε = 41 800 dm³ mol⁻¹ cm⁻¹), 262 (16900).

$\label{eq:linear} \begin{array}{l} (2,6-Bis[N-(2'-pyridinylmethyl)carbamido]pyridine)(2-[N-(2'-pyridinylmethyl)carbamido]-6-[N-(2'-pyridinylmethyl)carbamyl]-pyridine)cobalt(III) trihydrate, [Co(L^1)(HL^1)]\cdot3H_2O \end{array}$

To a solution of H_2L^1 (0.35 g, 0.001 mol) in MeOH (30 cm³) was added with stirring a solution of Co(OAc)₂·4H₂O (0.25 g, 0.001 mol) in MeOH (20 cm³). The colour changed immediately to a red-brown. After stirring at room temperature for 1 h, the solution was evaporated to dryness with a rotary evaporator, redissolved in EtOH (30 cm³), evaporated to dryness, and redissolved in water (20 cm³). On slow evaporation, a small amount of brown crystals formed, which were separated and air dried (40 mg). Alternatively, chromatography of the reaction mixture on SP-Sephadex C25 or Dowex 50W \times 2 cation exchange resins can be used to separate the major neutral freerunning band from those of minor ionic byproducts prior to isolation in high yield as a brown powder by rotary evaporation of the eluent to dryness. Anal. C, 57.6; H, 3.9; N, 17.9. C₃₈H₃₂N₁₀CoO₄·3H₂O requires C, 57.9; H, 4.1; N, 17.8%. NMR: $\delta_{\rm H}({\rm D_2O})$ 3.79 (2H, q, CH₂), 4.00 (4H, br s, CH₂ pendant), 5.47 (2H, d, CH₂ pendant), 6.39 (2H, br. s, pyH), 6.87 (4H, m, pyH), 7.07 (2H, br s, pyH), 7.25 (6H, m, pyH), 7.53 (1H, t, pyH), 7.73 (1H, t, pyH), 7.80 (1H, t, pyH), 7.86 (1H, br. s, pyH), 8.36 (1H, d, pyH), 8.41 (2H, d, pyH), 8.79 (1H, d, pyH). $\delta_{\rm C}$ (D₂O) 43.4, 43.9, 52.8, 62.7 (CH₂), 121.2, 121.4, 121.6, 121.8, 122.7, 124.4, 124.9, 125.4, 125.5, 127.6, 128.1, 137.8, 137.9, 139.2, 139.4, 139.6 (pyCH), 145.2, 146.4, 147.7, 147.9, 154.7, 155.9 (pyC_{terl}), 165.9, 168.7, 204.0, 219.3 (C=O) ppm. IR (cm⁻¹): 3546 (H₂O), 3289 (NH), 3053, 2925 (CH), 1683, 1656 (C=O), 1594, 1569, 1437 (NH), 1474, 1418, 1365 (amide), 1310, 1240 (CH), 1177, 1161, 996, 773, 742, 650 (py). UV-Vis spectrum (water): ~350sh nm (ε $\sim 920 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), 476 (158).

Bis(2,6-bis[*N*-(2'-pyridinylmethyl)carbamido]pyridine)dicopper(II), [Cu₂L¹₂]

To a solution of H_2L^1 (0.2 g, 0.58 mmol) in ethanol (8 cm³) in a 50 cm3 round-bottomed flask was added with swirling a solution of copper(II) acetate monohydrate (0.115 g, 0.58 mmol) in ethanol (6 cm³) and water (2 cm³). The resulting blue solution was brought briefly to boiling, then allowed to cool and evaporated to dryness with a rotary evaporator. The blue-green solid was redissolved in a small volume of ethanol (*ca.* 5 cm^3) and crystals grown in a diethyl ether atmosphere. Large dark green crystals formed overnight, and were collected, washed with a small amount of diethyl ether and air dried (0.15 g, 56%). Further standing for several days yielded more green solid and a small amount of a blue crystalline material. Anal. C, 55.2; H, 4.2; N, 14.9. C₃₈H₃₀N₁₀Cu₂O₄·2EtOH·0.5H₂O requires C, 54.9; H, 4.7; N, 15.2%. FAB MS: m/z 881 (Cu₃L¹₂), 819 (Cu₂L¹₂), 471 (Cu₂L¹), 410 (CuL¹), 348 (L¹). IR (cm⁻¹): 3495 (OH₂), 1590, 1560 (C=O), 1481, 1424, 1383 (amide), 1278 (CH), 1148, 1088, 960, 760 (py) cm⁻¹. UV-Vis spectrum (EtOH): 206 nm ($\varepsilon =$ 60000 dm³ mol⁻¹ cm⁻¹), 264 (28,600), 644 (160), 735sh (150). The minor blue product appears to be the 1 : 1 complex; FAB MS: *m*/*z* 410 (CuL¹), 348 (L¹).

$\label{eq:linear} Diacetatodimethanolbis(2,6-bis[$N-(2'-pyridinylmethyl)-carbamido]pyridine)trinickel(11), [Ni_3(L^1)_2(OOCCH_3)_2-(HOCH_3)_2]$

To a solution of H_2L^1 (0.3 g, 0.86 mmol) in methanol (15 cm³) in a 50 cm³ round-bottomed flask was added with swirling a solution of nickel(II) acetate tetrahydrate (0.215 g, 0.86 mmol) in methanol (15 cm³). The immediately formed orange solution was rotary evaporated to dryness, washed with diethyl ether (2 \times 20 cm³), then was redissolved in a small volume of methanol (ca. 8 cm³) and crystals grown in a diethyl ether/ethanol atmosphere. Copious amounts of dark brown crystals formed after two days, and were collected, washed with a small amount of diethyl ether and air dried (0.22 g, 63%). Further standing for several days yielded more dark brown solid and a small amount of a red crystalline material. Anal. C, 48.1; H, 4.5; N, 12.1. C₄₄H₄₄N₁₀Ni₃O₁₀·3H₂O requires C, 47.9; H, 4.5; N, 12.6%. FAB MS: m/z 925 (Ni₄L¹₂), 867 (Ni₃L¹₂), 520 (Ni₃L¹), 404 (NiL¹). IR (cm⁻¹): 3370 (OH₂), 1606, 1573 (C=O), 1560 (COO⁻), 1487, 1446, 1415, 1341 (amide), 1273 (CH), 1183, 1030, 850, 760 (py). UV-Vis spectrum (EtOH): 204 nm ($\epsilon = 60700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), 264 (23 500), 343 (7960), 908 (36), 1015 (120).

(2,6-Bis[*N*-(2'-pyridinylmethyl)carbamido]pyridine)nickel(II), [NiL¹]

The second crop of crystals in the above synthesis included red crystals of this monomeric material as a minor species (< 5%), which were separated and air dried. Anal. C, 55.6; H, 3.6; N, 16.9. $C_{19}H_{15}N_5NiO_2 \cdot 0.5H_2O$ requires C, 55.7; H, 3.9; N, 17.1%. NMR: $\delta_{\rm H}$ (CDCl₃) 4.55 (4H, s, CH₂), 7.14 (2H, ddd, pyH), 7.60 (2H, d, pyH), 7.61 (2H, d, pyH), 7.66 2H, ddd, pyH), 7.94 (1H, t, pyH), 8.29 (2H, d, pyH). FAB MS: m/z 462 (Ni₂L¹), 404 (NiL¹), 348 (L¹). IR (cm⁻¹): 1643, 1614, 1601, 1564 (amide C=O), 1483, 1473, 1420, 1387 (amide), 1180, 1015, 855, 760 (py). UV-Vis spectrum (EtOH): 264 nm (ε = 8390 dm³ mol⁻¹ cm⁻¹), 351 (3860), 908 (40), 1014 (90).

$Bis(2,6-bis[N-(2'-pyridinylmethyl)carbamido]pyridine)bis-(pentane-2,4-dionate)trinickel(II), [Ni_3(L^1)_2(acac)_2]$

To a solution of H_2L^1 (0.1 g, 0.29 mmol) in methanol (10 cm³) in a 50 cm3 round-bottomed flask was added with swirling a solution of nickel(II) acetate tetrahydrate (0.108 g, 0.43 mmol) in methanol (10 cm³). The resultant orange solution was rotary evaporated to dryness, washed with diethyl ether $(2 \times 20 \text{ cm}^3)$, and redissolved in a small volume of methanol (ca. 10 cm³). Pentane-2,4-dione (29 mg, 0.29 mmol) was added, resulting in a green-orange solution. After 10 min, the solvent was removed by rotary evaporation and the solid redissolved in a minimum volume of methanol and crystals grown in a diethyl etherethanol atmosphere. Brown crystals formed after two days, and were collected and air dried (0.10 g, 70%). A small amount of red crystals of the monomer were also collected. Anal. C, 53.2; H, 4.5; N, 12.2. C₄₈H₄₄N₁₀Ni₃O₈·2MeOH requires C, 53.2; H, 4.6; N, 12.4%. FAB MS: *m*/*z* 925 (Ni₄L¹₂), 867 (Ni₃L¹₂), 520 (Ni₃L¹), 404 (NiL¹). IR (cm⁻¹): 2965, 2937 (acac Me), 1594, 1571 (C=O), 1513 (acac C=O), 1486, 1458, 1400, 1340 (amide), 1286, 1183 (CH), 1155, 1110, 1076, 765 (py). UV-Vis spectrum (EtOH): 204 nm (ε = 44200 dm³ mol⁻¹ cm⁻¹), 264 (22400), 304 (17900), 930 (45).

$\label{eq:linear} Diaquabis(2,6-bis[N-(2'-pyridinylmethyl)carbamido]pyridine)-bis(pyridine-2,6-dicarboxylato)tetracopper(11) tetrahydrate, [Cu_4(L^1)_2(dipic)_2(H_2O)]\cdot 4H_2O$

To a solution of H_2L^1 (0.05 g, 0.145 mmol) in ethanol (10 cm³) and water (1 cm³) in a 50 cm³ round-bottomed flask was added dropwise with stirring a solution of copper(II) acetate monohydrate (0.057 g, 0.29 mmol) in ethanol (10 cm³). The resultant blue solution was stirred for 1 h then the solvent was removed with a rotary evaporator. The blue solid was washed with diethyl

ether $(2 \times 20 \text{ cm}^3)$, redissolved in ethanol (10 cm^3) and water (1 cm³) and a solution of pyridine-2,6-dicarboxylic acid (24 mg, 0.145 mmol) in ethanol (10 cm³) added dropwise. The solution was boiled briefly, allowed to stand overnight, then evaporated to dryness, yielding a dark blue solid. The solid was washed with acetone and dissolved in a minimum volume of water. Dark blue crystals were grown in an acetone atmosphere (yield 40 mg, 85%). Anal. C, 45.5; H, 3.3; N, 12.1. C₅₂H₄₈Cu₄N₁₂O₁₈ requires C, 45.2; H, 3.50; N, 12.2%. EI MS: *m*/*z* 1278 (Cu₄L¹₂dipic₂), 1216 (Cu₃L¹₂dipic₂), 1111 (Cu₄L¹₂dipic), 1050 (Cu₃L¹₂dipic), 943 (Cu₄L¹₂), 930 (Cu₄L¹dipic₂), 881 (Cu₃L¹₂), 869 (Cu₃L¹dipic₂), 819 (Cu₂L¹₂), 806 (Cu₂L¹dipic₂), 764 (Cu₄L¹dipic), 757 (CuL¹₂), 702 (Cu₃L¹dipic), 639 (Cu₂L¹dipic), 576 (CuL¹dipic), 472 (Cu_2L^1) , 410 (CuL^1) , 348 (L^1_2) . IR (cm^{-1}) : 3435 (H_2O) , 1629 (COO⁻), 1608, 1566 (amide C=O), 1492, 1431, 1371, 1354 (amide), 1180, 1010, 865, 765 (py). UV-Vis spectrum (EtOH): 206 nm ($\varepsilon = 110000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), 262 (39800), 646 (255), 714sh (270).

Spectroscopy

NMR spectra were recorded on solutions of complexes in $CDCl_3$ or D_2O using a Bruker DPX300 spectrometer, UV-visible spectra were measured with a Hitachi 220A spectrophotometer, and FT-IR spectra were recorded on Nicolet Avatar 370 spectrometer fitted with a germanium golden gate accessory. FAB mass spectra were recorded on a Kratos MS80 spectrometer.

X-Ray crystallographic data collection and processing

Data were collected with a Siemens SMART three-circle system with CCD area detector.³³ The crystal was held at 180(2) K with an Oxford Cryosystem Cryostream Cooler. Absorption correction was carried out by a semi-empirical method from equivalents.³⁴ No crystal decay was observed in any structure.

Structure analysis and refinement. For $[Co(L^1)(HL^1)] \cdot xH_2O$, there were no systematic absences; space group $P\overline{I}$ was chosen on the basis of intensity statistics. For $[NiL^1]$, the merging *R*-values indicated clearly that it is monoclinic; systematic absences indicated space group $P2_1/c$. For $[Cu_2(L^1)_2] \cdot 2EtOH \cdot 0.5H_2O$, there were no systematic absences, and space group $P\overline{I}$ was chosen. For $[Ni_3(L^1)_2(OAC)_2(MeOH)_2]$ and $[Ni_3(L^1)_2(acac)_2] \cdot 1.75MeOH \cdot 2H_2O$, systematic absences indicated space groups *Pbcn* and *P2_1cn*, respectively; the crystals of the latter are relatively weakly diffracting and include a region of disordered solvent modeled as 4 methanol molecules (one with 0.5 occupancy) and 11 water molecules (with 0.5 and 0.25 occupancy). For $[Cu_4(L^1)_2(dipic)_2(OH_2)_2] \cdot 4H_2O$, space group *C2/c* was chosen on the basis of intensity statistics.

The structures were solved by direct methods using SHELXS³⁵ with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined with isotropic displacement parameters using a riding model; solvent H-atoms were not usually located, but the H-atoms of the bound water molecules were observed on difference syntheses and were included with their positional parameters refined. Anisotropic displacement parameters were used for all non-H atoms. Refinement used SHELXTL.³⁶

Crystal data. Crystal data are collected in Table 1. Selected bond lengths and angles are listed in Tables 2–4. The atomic numbering scheme is included in Figs. 1–6.

CCDC reference numbers 246446 (2), 246447 (6), 246448 (1), 246449 (5), 246450 (3) and 246451 (4).

See http://www.rsc.org/suppdata/dt/b4/b414251a/ for crystallographic data in CIF or other electronic format.

	1	2	3	4	5	9
Empirical formula M	C ₃₈ H ₅₁ CoN ₁₀ O ₁₄ 930.82	$C_{42}H_{43}Cu_2N_{10}O_{6.5}$ 917.94	C ₁₉ H ₁₅ NiN ₅ O ₂ 404.07	$C_{46}H_{52}N_{13}N_{10}O_{12}$ 1113.11	${ m C_{49,75}H_{46}Ni_3N_{10}O_{11.75}}$ 1148.10	C ₅₆ H ₅₅ Cu ₄ N ₁₂ O ₂₀ 1470.28
T/K	180(2)	180(2)	180(2)	180(2)	180(2)	180(2)
Crystal system	Triclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P\overline{1}$	$P\overline{1}$	$P2_1/c$	Pbcn	$P2_1 cn$	C2/c
aíÅ	14.4465(9)	12.2100(2)	7.71769(4)	23.5075(7)	21.9970(9)	20.9193(6)
$b/\text{\AA}$	15.0309(9)	17.9411(2)	21.8946(13)	9.0184(3)	22.7871(9)	22.0981(7)
c/Å	21.0726(13)	19.74770(10)	10.2138(6)	22.3163(6)	21.3414(9)	13.0496(4)
a/ ⁰	91.2969(10)	72.5980(10)	90.0	90.0	90.0	0.06
$\beta/^{\circ}$	97.0280(10)	81.2180(10)	90.0290(10)	90.0	92.4170(10)	99.4380(10)
y /0	106.3940(10)	88.8730(10)	90.0	90.0	90.0	90.0
$U/Å^3$	4348.9(5)	4078.01(8)	1604.95(16)	4731.1(2)	10687.8(8)	5950.9(3)
$Z, D_{\rm c}/{ m g~cm^{-3}}$	4, 1.422	4, 1.495	4, 1.672	4, 1.563	8, 1.427	4, 1.641
μ/mm^{-1}	0.472	1.106	1.236	1.256	1.114	1.498
θ Range for data collection/ ^o	1.48 - 25.50	1.87 - 29.13	1.86 - 29.14	1.73 - 29.09	1.91 - 24.00	1.84-25.00
Crystal dimensions/mm	$0.46 \times 0.1 \times 0.1$	0.4 imes 0.4 imes 0.4	0.4 imes 0.15 imes 0.15	$0.56 \times 0.16 \times 0.14$	$0.36 \times 0.2 \times 0.06$	0.4 imes 0.3 imes 0.04
Reflections collected/restraints/parameters	23401/49/1240	26331/0/1137	10218/0/244	28704/0/329	48984/0/1379	15270/0/432
Independent reflections (R_{int})	15862 (0.0574)	18908 (0.0212)	3941 (0.0500)	5990 (0.0788)	16688(0.1169)	5227 (0.0690)
Max., min. transmission	0.93, 0.62	0.93, 0.70	0.93, 0.69	0.93, 0.69	0.93, 0.63	0.89, 0.78
Goodness of fit on F^2	0.916	0.979	1.003	1.030	1.009	1.103
$R1, wR2 [I > 2\sigma(I)]$	0.0653, 01192	0.0482, 0.1147	0.0465, 0.0811	0.0536, 0.1049	0.0751, 0.1647	0.0537, 0.1140
R1, wR2 (all data) ^b	0.1646, 0.1506	0.0792, 0.1018	0.0909, 0.0942	0.1093, 0.1225	0.1720, 0.2097	0.1031, 0.1328
Largest peak, hole/e Å $^{-3}$	0.803, -0.555	0.545, -0.681	0.374, -0.451	1.260, -0.545	0.850, -0.504	1.042, -0.599
" 1 = [Co(L ¹)(HL ¹)].xH ₂ O; 2 = [Cu ₂ (L ¹) ₂].2EtOH.0.5H ₂ $F_c F_c F_0 $ for $F_o > 2\sigma(F_o)$ and $wR2 = (\sum w(F_o^2 - F_c^2)^2$ 0.0371, $B = 0.3256;$ (4), $A = 0.0470$, $B = 5.6000;$ (5), $A =$	O; $3 = [\text{NiL}]; 4 = [\text{Ni}_3],$ $\sum (wF_c^2)^2 / t^2$, with $w = 0.0940, B = 2.6700; (6).$	$\begin{aligned} (L^{1})_{2}(OAc)_{2}(MeOH)_{2}]; & 5\\ 1/[\sigma^{2}(F_{o}^{2}) + (AP)^{2} + BH\\ A &= 0.0530, B = 10.0000 \end{aligned}$	$i = [Ni_3(L^1)_2(acac)_2] \cdot 1.7^2$] where $P = (F_o^2 + 2F_o^2)_0$	$(CH_3OH.2H_2O; 6 = [Cu, 0)/3 and A and B are as for$	$_{\rm (L^1)_2(dipic)_2(OH_2)_2].4H_2O.^b$ llows: (1), $A = 0.0511, B = 0$	Residuals are $R1 = \sum F_0 - (2), A = 0780, B = 0; (3), A =$

Table 1 Crystallographic data and details of refinement for structures $1-6^{a}$

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					-		
	[Co(L ¹)(HL ¹)] (1)					
	<i>Co1</i> N111 N18 N28 N21 N117	distance 1.862(4) 1.946(4) 1.878(4) 1.945(4) 1.962(4)	N211 100.43(17) 93.52(16) 82.87(17) 165.24(17) 88.61(16)	N117 81.79(17) 162.99(17) 97.51(17) 91.44(16)	N21 94.19(17) 90.74(16) 82.49(18)	N28 176.59(18) 99.50(18)	N18 81.23(18)
	N211	1.983(4)	00101(10)				
	[NiL ¹] (3	3)					
	<i>Ni1</i> N12 N8 N1	distance 1.834(2) 1.835(2) 1.930(2)	N19 82.59(10) 164.80(10) 110.69(10)	N1 166.52(10) 84.51(10)	N8 82.22(10)		
	N19	1.933(2)					
able 3 Distance	s (Å) and a	ingles (°) subten	ded around the m	etal in trinuclear	nickel complexes	s 4 and 5	
	$[Ni_3(L^1)_2$	(OAc) ₂ (MeOH)	2] (4)				
	Ni1 N1 N22# O011 O021 N19#	distance 2.034(3) 2.048(3) 2.056(2) 2.147(3) 2.191(3) 2.197(2)	N8 80.40(11) 99.65(11) 171.20(10) 94.45(10) 90.92(10)	N19# 100.83(11) 80.18(11) 86.81(10) 167.56(11)	O021 91.13(11) 87.86(11) 89.48(10)	O011 91.67(11) 88.35(11)	N22# 178.99(11)
	N8 Ni2 N12 N12# N8 N8# N19# N19	2.197(3) distance 1.9779(3) 1.977(3) 2.172(3) 2.172(3) 2.166(3) 2.166(3)	N19 78.38(11) 104.62(11) 157.03(11) 92.27(10) 92.93(15)	N19# 104.62(11) 78.38(11) 92.27(10) 157.03(11)	N8# 98.35(11) 78.65(11) 91.62(15)	N8 78.65(11) 98.35(11)	N12# 175.76(17)
	$[Ni_3(L^1)_2$	(acac) ₂] (5)					
	Ni11 O136 O133 N11 N21 N18 N28	distance 1.989(6) 2.018(6) 2.053(8) 2.078(7) 2.187(7) 2.224(7)	N28 88.1(3) 172.3(3) 98.0(3) 79.6(3) 91.2(2)	N18 171.4(3) 88.6(3) 80.3(3) 100.4(3)	N21 87.9(3) 92.9(3) 177.5(3)	N11 91.3(3) 89.6(3)	O133 93.2(3)
	Ni12 N112 N212 N18 N119 N28 N219	distance 1.964(7) 1.976(6) 2.157(7) 2.171(7) 2.189(6) 2.194(6)	N219 100.2(3) 78.9(3) 91.5(2) 93.5(2) 157.3(2)	N28 102.4(3) 78.4(3) 93.0(2) 90.9(2)	N119 78.3(3) 102.3(3) 157.2(3)	N18 78.9(3) 100.4(3)	N212 179.0(3)
	N219 Ni13 O236 O233 N122 N222 N119 N219	2.194(0) distance 1.999(6) 2.007(6) 2.048(7) 2.063(7) 2.188(6) 2.211(7)	N219 88.5(3) 171.7(3) 99.4(3) 79.3(3) 92.6(2)	N119 172.2(3) 86.8(2) 80.3(3) 100.9(2)	N222 86.9(3) 92.6(3) 178.3(3)	N122 92.0(3) 88.7(3)	O233 93.2(3)

Table 2 Distances (Å) and angles (°) subtended around the metal ion in mononuclear complexes 1 and 3

Results and discussion

The 2,6-disubstituted pyridine moiety is a classical component of a range of ligand topologies. Previously, the potentially pentadentate ligand H_2L^1 has been described and the crystal structure of the free ligand was reported recently.⁶ Deprotonation of the two amide groups was anticipated to yield a potent dianionic ligand, and its mononuclear $[Fe(L^1)_2]^-$ and dinuclear complex $[Cu_2(L^1)_2]$ were subsequently reported.^{11,12} Structural characterization of the latter complex identified a capacity for the ligand to form helical structures with the ligand spanning across the two metal ions, and it was this potential which attracted our attention and initiated a more extensive study of the helicating properties of H_2L^1 in self-assembly reactions with metal ions.

Helicity known for the relatively simple $[Cu_2(L^1)_2]$ complex has been elaborated here with the synthesis and observation of helicity in trinuclear $[Ni_3(L^1)_2(OAc)_2(OH_2)_2]$, $[Ni_3(L^1)_2(acac)_2]$ and tetranuclear $[Cu_4(L^1)_2(dipic)_2(OH_2)_2]$ complexes. Also, examples of mononuclear complexation is extended with structural characterisation of $[Co(L^1)(HL^1)]$ and $[NiL^1]$. It is the capacity of H_2L^1 to form polynuclear helical structures with at least Cu(II), Ni(II) and, from preliminary evidence, Zn(II) that is remarkable. All of the polynuclear complexes isolated feature

Table 4 Distances (Å) and angles (°) subtended around the metal in dinuclear (2) and tetranuclear (6) copper complexes

$[Cu_2(L^1)_2]({\bf 2})$					
<i>Cu1</i> N48 N319 N41 N322 N412	distance 1.907(2) 1.944(2) 2.068(2) 2.243(2) 2.265(2)	N412 77.94(9) 103.85(8) 158.73(9) 81.35(8)	N322 111.54(10) 78.42(9) 106.83(9)	N41 80.78(9) 97.10(9)	N319 170.03(10)
Cu3 N38 N419 N31 N422 N312	distance 1.907(3) 1.924(2) 2.088(3) 2.166(3) 2.421(3)	N312 75.64(10) 103.92(10) 155.08(9) 79.87(9)	N422 108.45(11) 80.11(10) 115.83(10)	N31 80.81(11) 98.06(10)	N419 171.03(12)
[Cu ₄ (L ¹) ₂ (dipic)	$_{2}(OH_{2})_{2}](6)$				
<i>Cu1</i> N112 N122# N108 N119	distance 1.932(4) 1.980(4) 2.028(4) 2.044(4)	N119 79.70(18) 95.96(18) 159.23(17)	N108 79.64(18) 104.53(18)	N122# 174.59(18)	
Cu2 N205 N101 O201 O211 O100	distance 1.908(4) 1.960(4) 2.035(4) 2.059(4) 2.322(4)	O100 90.64(16) 97.67(17) 90.53(15) 91.51(15)	O211 79.85(17) 99.95(16) 160.67(15)	O201 80.91(17) 98.82(17)	N101 171.69(18)



Fig. 1 Views of the $[Co(L^1)(HL^1)]$ complex (1): (a) an ORTEP drawing of one of the two independent complex cations showing atom numbering; (b) a view of part of the lattice showing π -stacking interactions between complexes involving pendant pyridine groups.

a racemic mixture of left- and right-handed double helices; notably, their structures (discussed below) are all stabilized by inter-ligand π -stacking (with inter-ring distances of 3.2–3.8 Å) of ligands which each span several metal ions. This π -stacking



Fig. 2 An ORTEP drawing of the helical $[Cu_2(L^1)_2]$ dinuclear complex (2), showing atom numbering.

would appear to be a key to the formation of robust helical complexes, although we note its presence in the lattice of the mononuclear cobalt(III) complex also.

The major product of the reaction of the cobalt(II) acetate and H_2L^1 in methanol in the presence of air is a neutral dark brown diamagnetic complex. This crystallized in low yield from a saturated aqueous solution of the reaction mixture, although column chromatography on cationic SP-Sephadex and Dowex resins confirmed it as the major species, readily isolable upon rotary evaporation, with only traces of other ionic complexes detected. Formation of a neutral complex requires one of the four amides to remain protonated, and hence as a poor presumably uncoordinated group, which would lead to a dissymmetric complex, consistent with its complex NMR spectrum. This behaviour differs from the complex formed with



Fig. 3 An ORTEP drawing of the $[NiL^1]$ mononuclear complex (3), showing atom numbering.



Fig. 4 An ORTEP drawing of the helical $[Ni_3(L^1)_2(OAc)_2(MeOH)_2]$, trinuclear complex (4), showing atom numbering.



Fig. 5 An ORTEP drawing of the helical $[Ni_3(L^1)_2(acac)_2]$ trinuclear complex (5), showing atom numbering.

iron(III), where a monoanionic complex with all four amides deprotonated and coordinated is the dominant species.¹² The characterization of the Co(III) complex was established by an X-ray crystal structure; there are two independent complexes in the unit cell, but these do not differ in any substantial way. The structure confirmed the complex as the neutral 1 : 2complex [Co(L¹)(HL¹)] with two ligands acting as tridentate ligands, one coordinated by the central pyridine and its two



Fig. 6 An ORTEP drawing of the helical $[Cu_4(L^1)_2(dipic)_2(OH_2)_2]$ tetranuclear complex (6), showing atom numbering.

flanking deprotonated amido groups and the other by the central pyridine, one deprotonated amido and one terminal pyridine group, with the remaining protonated amide unbound along with the other pyridine groups (Fig. 1(a)). The different modes of coordination of the two ligands requires that the two central pyridine groups lie in cis dispositions around the distorted cobalt octahedron. For one ligand, the central pyridine is flanked by two coordinated amido groups in a meridional arrangement, with the tridentate component effectively planar. However, the planes of the two pendant terminal pyridines are disposed almost at right angles to the chelate plane (89.43 and 81.24°), with one involved in π -bonding with the coordinated terminal pyridine of the other ligand, and the other involved in π -bonding to a pyridine of an adjacent complex. The other tridentate unit is also reasonably planar, with the O-C-N amide unit perpendicular to the plane of the ligated component, but the terminal pyridine attached to the free amide unit disposed roughly co-planar to the coordinated fragment of the ligand and involved in π -bonding interactions with other adjacent complexes (Fig. 1(b)). The Co-N(py) distance to the central pyridine of the meridionally-bound -N-CO-py-CO-N- fragment of 1.862 and 1.855(4) Å for Co1 and Co2, respectively, is substantially shorter than distances to other pyridine donors (1.983, 2.008(4) Å for the bound terminal pyridine of the second ligand and 1.945, 1.931(4) Å for the central pyridine of that ligand for which the other terminal pyridine is uncoordinated). This gives rise to the tight 'bite' of this fragment, reflected in intraligand angles such as N111-Co1-N18 of 81.23(18)° and N111-Co1-N117 of 81.79(17)°. This mirrors the behaviour exhibited by the pyridine-2,6-dicarboxylate ion when bound to metal ions.³⁷ Of the three bound amido groups, one (N28/N48) forms the central donor of one tridentate meridionally-bound ligand. The Co-N distance (1.878(4) Å for Co1, 1.874(4) Å for Co2) is consequently slightly shorter than distances to the other two amido groups N18/N38 (1.946(4), 1.963(4) Å) and N117/N317 (1.962(4), 1.976(4) Å) which act as equivalent terminal groups for the other tridentate ligand. The angles around the Co involving N28/N48 likewise are reduced compared with other angles. The complex is highly hydrated, and the structure features twenty water molecules in whole or partially occupied sites. The level of hydration, and the apparent role of the water molecules in stabilizing the structure, is somewhat reminiscent of biomolecules.

The other known mononuclear octahedral structure formed by H_2L^1 is with Fe(III), which forms a low-spin *mer*-[Fe(L¹)₂]⁻ anion in which each ligand is bonded symmetrically by the central pyridine (Fe–N 1.881(3) Å) and both amido nitrogens (Fe–N av. 1.955(3) Å), the terminal pyridine groups being pendants orientated in a propeller-like manner.¹² The substantially shorter distance to the central pyridine compared to the flanking amido groups also is found for the one ligand in the Co(III) complex of similar coordination mode. Very recently, the symmetrical anionic *mer*-[Co(L¹)₂]⁻ anion has been reported and defined by an X-ray structure *via* a somewhat different route from oxidation of a mixture $CoCl_2$ and H_2L^1 in strongly basic solution.³⁸ This suggests that the unsymmetrical species isolated here may be a kinetic rather than a thermodynamic product. Subsequently, we have heated the unsymmetrical complex with activated charcoal in water (2 h, 60 °C) to attempt to promote the interconversion to the symmetrical anionic form. In neutral aqueous solution, NMR spectroscopy indicates no detectable rearrangement occurs even after several hours. However, in basic solution (pH > 10) there is evidence of rearrangement, with simplification of the NMR spectrum to that consistent with the symmetrical monoanionic form observed, although this occurs slowly and is not substantially complete until ≥ 5 h.

Reaction of copper(II) acetate with H_2L^1 in a 1 : 1 molar ratio gave a green crystalline material as the major product, along with a minor dark blue microcrystalline material. From FAB mass spectrometry, the green solid was identified as a $[Cu_2L_2]$ dimeric species, whereas the minor product was characterised as a [CuL¹] monomeric complex. Changes in colour when dissolved in water (blue) and ethanol (green) suggest that solution speciation may differ somewhat from the solid state in some solvents. We have also observed that $[Cu_2(L^1)_2]$ converts in solution in the presence of added pyridine-2,6-dicarboxylic acid to the tetranuclear $[Cu_4(L^1)_2(dipic)_2(OH_2)_2]$, which suggests that dissociation and rearrangement reactions in solution are reasonably facile, but that formation of helical complexes may be thermodynamically preferred. Currently, we are investigating speciation and determining formation constants in solution separately.

The crystal structure of the $Cu_2L_2^1$ dimer has been previously reported,¹¹ and the crystals isolated in this case proved to be structurally identical to that reported. The dinuclear complex contains two $[L^1]^{2-}$ ligands coordinated to two copper(II) ions in a 5 : 5 coordination motif (Fig. 2). Somewhat surprisingly, the central pyridine distance to the copper atom is significantly longer than that of the terminal pyridines even though the former can be considered to occupy an equatorial site in a significantly distorted square-based pyramidal geometry around the copper.

Reaction of H_2L^1 with nickel(II) in solution yielded both a minor red 1:1 Ni : L¹ species and a dark brown major 3:2Ni : L^1 species. The latter complex was paramagnetic, as clear from the observation of a complex wide-scan ¹H NMR spectrum spanning ca. 140 ppm, and octahedral coordination was implied. The minor red complex proved to be diamagnetic, consistent with square-planar coordination of the nickel(II) ion. The amide hydrogen triplet present in the 1H NMR spectrum of the free ligand at 9.10 ppm is absent in the complex, consistent with deprotonation of both amides and their complexation to the nickel ion; this is supported by collapse of the doublet of the adjacent methylene found at 4.74 ppm in the free ligand to a singlet. Four-coordination of nickel(II), with both amides and the central pyridine bound, permits only one of the terminal pyridine groups to bind, with the other being an unbound pendant. The ¹H NMR spectrum would be anticipated to be unsymmetrical as a result; that this is not observed suggests rapid chemical exchange between coordinated and uncoordinated terminal pyridines is occurring.

The crystal structure of the complex confirmed the squareplanar nature of the coordination, and the presence of a pendant terminal pyridine group (Fig. 3). The geometry of the ligand is not optimal for forming square planar complexes. The small bite angles within the planar -N-CO-py-CO-N- unit are reflected in compressed N-Ni-N angles of 82.2(1) and 82.6(1)°. The terminal $-N-CH_2$ -py chelate ring is also somewhat compressed at 84.5(1)°, whereas the single angle not restrained by chelation is significantly expanded, at 110.7(1)°. That one terminal pyridine remains uncoordinated is unusual, as nickel(II) complexes are often five- or six-coordinate. The cause appears to relate to the sp² nature of the amide group holding the pyridine donor out of range of efficient coordination. The central pyridine bond to the Ni atom is significantly shorter, at 1.834(2) Å, than that of the coordinated terminal pyridine, at 1.930(2) Å, reflecting the demands of the rigid -N-CO-py-CO-N- unit. Further, the amido group located between the two coordinated pyridine groups has a bond distance N8-Ni of 1.835(2) Å, which is significantly shorter than that to the other amido group N19-Ni of 1.933(2) Å. The former distance reflects the constraints of the two neighbouring five-membered rings of which it forms a central part, as does the bent N1-Ni-N12 bond of 166.5(1)°, which shows almost as much distortion as the N8-Ni-N19 bond of 164.8(1)° in the central planar -N-CO-py-CO-Nunit. Differences extend beyond the immediate coordination sphere; for example, the distance from amido N8 to the adjacent methylene C7 is 1.448(3) Å compared to the slightly longer N19-C20 distance of 1.469(4) Å where the terminal pyridine in unbound. Despite the bond distance and angle distortions in the square planar complex, distortions of the NiN₄ donor set from planarity is minimal. In the mean square plane defined by the atoms Ni1, N1, N8, N12 and N19, deviations of each atom from this plane are only 0.0144(9), -0.0204(10), 0.0184(13), -0.0252(13) and 0.0127(10) Å, respectively.

The major product of the reaction of H_2L^1 with nickel(II) acetate was the trinickel complex $[Ni_3(L^1)_2(OAc)_2(MeOH)_2]$, where a 6 : 6 : 6 coordination motif operates with each nickel atom in a distorted octahedral environment (Fig. 4). The most surprising feature revealed by the crystal structure of this complex is that the amido groups are all involved in bridging between nickel centers, via each deprotonated amido group using both lone pairs of electrons on the nitrogen donor. In simple nickel(II) polymers such as nickel oxide, bridging oxides lead to antiferromagnetic properties at room temperature;³⁹ the effect the bridging amido groups on magnetic properties in the present system is the target of current separate investigations. The complex is soluble in both aqueous and non-aqueous solvents. In CDCl₃, the complex is paramagnetic at room temperature, as shown by the ¹H NMR spectrum, which displayed a chemical shift range from -1 to +142 ppm. The spectrum proved too complicated for facile analysis due to overlapping resonances that were also sufficiently broad to prohibit coupling experiments.

Each of the two ligands in the trinickel complex binds to all three metal ions. The central pyridine group of each ligand occupies trans axial locations around the central nickel. Each amido group binds in the plane of the metal ions in a bridging mode to both the central nickel and different terminal nickel atoms. The terminal pyridine then occupies an axial location to the same metal ion as the adjacent amido group binds. This leads to each ligand being wrapped as the separate arms of a double helix around the central metal framework; symmetry in the crystal is such that distances and angles in the two ligands are close replicates. There is a right- and left-handed form of the helix. The final two equatorial coordination sites on each terminal nickel ion are occupied by an acetate and a methanol group, completing their octahedra. Thus the central nickel lies in a NiN₆ environment of four amido and two axial trans pyridine groups, whereas each terminal nickel lies in an NiN_4O_2 environment of two cis amido groups, two axial trans pyridine groups, and an acetate and alcohol group in cis dispositions.

The central nickel is bound by two symmetry-related -N-COpy-CO-N- units, with the Ni2-N12(py) distance of 1.977(3) Å significantly shorter than the amido bonds Ni2-N8 of 2.172(3) Å and Ni2-N19 of 2.166(3) Å. The central pyridine distance is even shorter than in the structure of the monomer (1.834(2) Å). However, the bridging amido groups are significantly elongated compared with either type of amido group (1.835(2), 1.933(2) Å) in the monomer structure. This presumably reflects both the effect of bridging to two metal centers and the structural demands of three adjacent octahedral nickel atoms. Whereas the *trans* pyridine groups appear to exhibit little distortion from linearity (N12–Ni2–N12# 175.76(17)°), the distorted octahedron is revealed by the angles to groups in the plane (for example, N12–Ni2–N8 78.65(11)° and N8–Ni2–N12# 98.35(11)°). The terminal nickel octahedra are crystallographically equivalent. Different M–L distances to *trans* pyridines (2.034(3), 2.048(3) Å), *cis* amido groups (2.197(3), 2.191(3) Å) and acetate (2.056(2) Å) and methanol (2.147(3) Å) oxygens mean a distorted octahedral environment, reflected also in some internal angles (such as N1–Ni1–N19# 100.83(11)°). Some weak π -stacking interactions (distances from 3.1–3.3 Å) involving the two sets of three pyridine rings on opposite sides of the plane containing the nickel atoms may assist in defining the helical structure.

The terminal acetate and methanol ligands suggested themselves as a target for substitution reactions. In particular, replacement of these with simple chelate ligands was anticipated as a reasonable expectation. Attempts to perform substitution reactions were pursued with chelating ligands which bind as monoanionic species and thus would replicate the overall charge in the displaced groups, namely pentane-2,4-dionate (acac), dithiocarbamate ion and β -alaninate. The latter two led to isolation of simple nickel complexes of dithiocarbamate and alaninate; however, with acac, a trimer featuring substitution of the monodentate ligands by the chelate, $[Ni_3(L^1)_2(acac)_2]$, was isolated. The structure was inferred from the FAB MS, and confirmed by a crystal structure analysis (Fig. 5). Obviously, there are close similarities with the structure of the precursor trimer as the polydentate ligand is bound in an identical manner in each, although the coordination of the symmetrical acac chelate leads to some changes. As in the precursor, both leftand right-handed helices exist in the crystal. Counter-intuitively, the structure exhibits different environments for all three nickel atoms

The central nickel atom displays average Ni–N(py) (1.970(6) Å) and Ni–N(amido) (2.178(7) Å) distances comparable to average distances for the precursor structure (1.977(3) and 2.169(3) Å, respectively). For the two terminal Ni atoms, average Ni–N(py) (2.060(7) Å), Ni–N(amido) (2.202(7) Å) and Ni–O (2.002 Å) distances compare less closely with those in the precursor (2.041(3), 2.194(3), and 2.102 Å, respectively). Of course, this is a result of changing the type of O-donor ligands, but there are secondary influences from introduction of a chelate ligand which are reflected in distances and angles. The O–Ni–O angle, for example, is opened out to 93.2(3)° in the acac chelate but near that of a perfect octahedral angle at 89.48(10)° in the acetato-methanol precursor.

It is notable that the 3 : 2 M : L coordination motif observed with nickel(II) in the above two examples may be formed with some other metal ions. With zinc(II), FAB MS spectrometry has identified a species apparently of the same type. Unfortunately, we have not as yet been able to crystallize this complex, and so this observation still awaits confirmation. What is notable is that, by providing additional types of ligands, the assembly of even larger helical clusters is possible, as shown through isolation of a $Cu_4L_2^1$ species also including other chelating ligands.

Recently, trinuclear M₃L₂ species were also reported as copper(II) complexes of potentially pentadentate ligands 2,6-bis(pyridine-2-carboxamido)pyridine (H_2L^3) and 2,6-bis-(pyrazine-2-carboxamido)pyridine (H₂L⁴),⁴⁰ of formula [Cu₃- $(L)_2(\mu_2-OAc)_2$]. Here, the ligands have the amide functionality 'reversed' compared with the present system, as a result of synthesis from 2,6-diaminopyridine rather than the diacid analogue. The structures reveal the central pyridine of each ligand binds to the central copper atom, with amide and terminal pyridine sets bonding to terminal copper atoms, and acetate groups bridging between a central and terminal copper atom. Each copper lies in a distorted octahedral environment, with the structure displaying a form of helicity via the ligands twisting about the amide groups, although the methylene groups in H_2L^1 allow greater ligand backbone flexibility in systems we report.



The tetranuclear $[Cu_4(L^1)_2(dipic)_2(OH_2)_2]$ was first detected serendipitously, from the reaction of Cu(II) with a batch of H_2L^1 contaminated with unreacted 2,6-bis(methoxycarbonyl)pyridine that undergoes metal catalysed hydrolysis of the diester. Subsequently, direct reaction of equimolar amounts of H_2L^1 and pyridine-2,6-dicarboxylic acid with copper(II) acetate was attempted, but did not yield the polymer, presumably because the overall reaction in this case would produce eight moles of acetic acid per cluster compared with four moles in the successful reaction involving the diester. The greater acidity in the former case lowering pH sufficiently to inhibit complexation. This was solved by employing a two-stage reaction involving solvent and concomitant evolved acid removal in the initial step, as described in the Experimental section, leading to isolation of the tetranuclear complex in high yield. Despite being a neutral polymer, the double helix complex is surprisingly soluble in water, perhaps related to the presence of terminal coordinated water molecules in the complex. The structure of the helical complex is shown in Fig. 6. The complex is inherently chiral, and both right- and left-handed helices coexist in the crystal. At this stage, no attempts to separate the forms has been undertaken. Notably, a tetracopper(II) complex of H₂L³ was also reported recently to arise through serendipitous chemistry, although in that case one of the three ligands present in the $[Cu_4(L^3)_2(L^3-O)]$ complex had the central pyridine oxidized to an N-oxide; details of the structure have not appeared.40

The copper(II) environments in $[Cu_4(L^1)_2(dipic)_2(OH_2)_2]$ display a 5 : 4 : 4 : 5 coordination motif, with the outer copper ions having a square pyramidal CuN2O3 geometry including an axial terminal water molecule in each, whereas the inner two have square planar CuN_4 geometry. The two $[L^1]^{2-1}$ ligands each span three copper ions. The central pyridine and two adjacent amido nitrogens bind to an inner copper, with each terminal pyridine subsequently coordinated to different copper ions, one to a terminal copper and the other to the second inner copper ion. Whereas the central amido-pyridineamido unit attached to the one copper is essentially planar, the terminal pyridines are twisted via the tetrahedral methylene groups to occupy a coordination site for another copper in a different plane; Cu...Cu separation is defined in part by the length of this pendant arm. Each terminal copper then completes its coordination sphere with a tridentate pyridine-2,6-dicarboxylate and a water molecule. The terminal copper lies in a distorted five-coordinate environment, due partly to Jahn-Teller distortion, which leads to the terminal water group

being relatively long at 2.322(4) Å, and partly to the small 'bite' of the planar dipic dianion. Whereas Cu-O(carboxylate) distances are relatively normal at 2.035(4) and 2.059(4) Å, the Cu-N distance of the central pyridine is significantly contracted at 1.908(4) Å compared with that of the pendant pyridine at 1.960(4) Å. The O-Cu-N angles in the dipic ligand are also significantly contracted at 80.91(17) and 70.85(17)° compared with O-Cu-N angles involving the terminal water group [90.64(16) and $97.67(17)^{\circ}$]. Of these angles, notably the angle to the pendant is opened out, and the N-Cu-N angle $(171.69(18)^{\circ})$ bent down towards the central copper, presumably reflecting a compensation for this bridging pyridine pendant between achieving square-based pyramidal geometry around the external copper itself and adequate Cu...Cu separation. The central square planar copper also shows considerable tetrahedral distortion from planarity, with opposed N-Cu-N angles of 174.59(18) and 159.23(17)°; the latter involves the terminal pyridine from the second $[L^1]^{2-}$ ligand, reflecting compensations similar to those discussed for the terminal copper ions. The Cu–N distances range form 1.932(4) to 2.044(4) Å, the shortest distance associated with the central pyridine, resulting from similar considerations to those applying with dipic. The two sets of four pyridine rings on each side of the chain of metal ions are π -stacked, with inter-ring distances in the range 3.2–3.8 Å. The terminal Cu1-central Cu2 internuclear distance is 3.552(9) Å, whereas the internal central Cu1 · · · central Cu1 internuclear distance is 3.072(13) Å.

The coordinated water groups in [Cu₄(L¹)₂(dipic)₂(OH₂)₂] offer the potential for ligand substitution chemistry in the same way that the unidentate ligands in $[Ni_3(L^1)_2(OAc)_2(MeOH)_2]$ were clearly demonstrated above as sites for substitution. In the present case, however, chelation cannot be introduced, as the two water molecules lie in separate sites at opposite ends of the molecule. Spectrophotometric titration of a solution of the copper(II) tetramer with thiocyanate in aqueous solution displayed an absorbance change with an isosbestic point maintained initially, consistent with sequential substitution of the two water groups by thiocyanate. Unfortunately, we were unable to crystallize the substituted product for structural characterisation. However, the concept has been demonstrated for the copper(II) polymer, complementing more detailed study of the nickel(II) polymer. That selective substitution of unidentate ligands can be achieved attests to the robustness of the helical structures reported here.

Further examples demonstrating the facility of helicate formation with polyamide–polypyridine ligands continue to appear. Oligoamides derived from 2,6-diaminopyridine and 2,6-pyridinedicarboxylic acid ($H_{2n+2}L^5$) have been reported recently to form double helices with Cu(II) that are dinuclear when n = 1, and hexanuclear when n = 3. Cu ··· Cu distances are 3.74 Å in the dinuclear species, and in the range 3.58–3.61 Å for the hexanuclear complex.⁴¹ The corresponding Cu ··· Cu distances in [Cu₄(L¹)₂(dipic)₂(OH₂)₂] are 3.05 and 3.55 Å for central–central and central–terminal coppers, respectively.

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