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Supramolecular metal helicate structures with incomplete metal ion coordination

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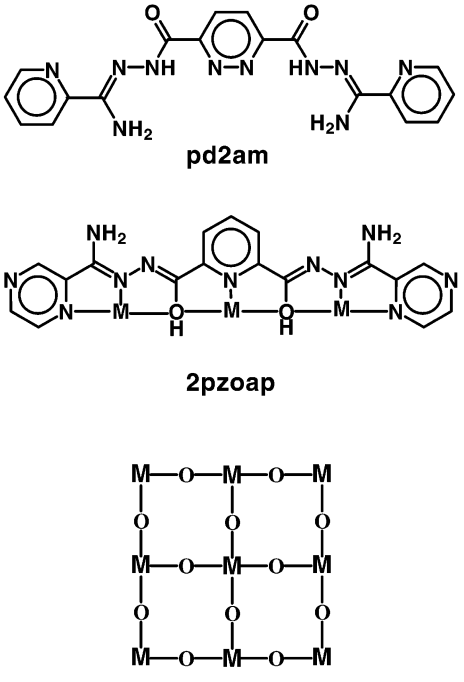
Two flexible 'polytopic' ligands take part in self assembly reactions with Ni(II) salts to produce helical structures, with 'incomplete' metal ion coordination, and the occupancy of empty coordination pockets by a water molecule and a putative fluoride ion. $[Ni_3(pd2am\text{-}H)_3(H_2O)](NO_3)_3 \cdot 2H_2O$ **1** consists of a localized $Ni_2(N–N)_3$ dinuclear centre with three N–N single bond bridges, and a distant mono-nuclear Ni(II) centre, within the same molecular ion, and $[Ni_2(2pzoap)_3F](BF_4)_3 \cdot 8.5H_2O$ **2** has a dinuclear stucture with two well separated octahedral Ni(II) sites. In both cases a single entity (H_2O **1**, F^- **2**) occupies a potential coordination pocket. Antiferromagnetic coupling is observed between the adjacent Ni(II) centres in **1**, associated with the N–N bridging interactions, but the distant metal centres in **2** are uncoupled.

Introduction

Polynucleating ligands with contiguous coordination pockets arranged in a linear fashion can align metal ion centres in chains[1–3] or grids,[4–7] depending on the chelate ring sizes involved and the coordination requirements of the metals. Self assembly processes have produced essentially flat grids of up to nine metals in rare cases.[4,8–10] Ligands with significant flexibility can produce aggregates in which the ligands twist around a group of metal centres producing helicates, in some cases, with double[11,12] and triple strands.[13,14] Interest in such systems stems in part because the aggregates are reminiscent of the natural helical structures found in DNA and proteins.[15,16]

The extended 'polytopic' ligands pd2am and 2pzoap contain multiple, contiguous coordination pockets, and in principle there are many different ways in which they could bind metal ions. In both cases built-in flexibility around the N–N single bonds allows for many rotational conformational possibilities and the potential for helicate complex formation. The linear arrangement of six five-membered chelate ring pockets in 2pzoap (Scheme 1) can coordinate three metals in a line, and self assembly with the related terminal pyridine ligand 2poap produces 3 × 3 $[Mn(II)_9(\mu\text{-}O)_{12}]^8$ and $[Cu(II)_9(\mu\text{-}O)_{12}]^9$ grids containing parallel arrangements of six heptadentate ligands, with adjacent pairs of metal ions bridged by alkoxide oxygens only. However, the ability of the metal ion to participate in bonding to all the coordination pockets depends in part on its own donor preferences, the flexibility and conformational adaptability of the ligand, competition from other Lewis acids, *e.g.* protons, and other entities capable of occupying a coordination pocket. This report describes two unusual complexes $[Ni_3(pd2am\text{-}H)_3(H_2O)](NO_3)_3 \cdot 2H_2O$ **1** and $[Ni_2(2pzoap)_3F](BF_4)_3 \cdot 8.5H_2O$ **2**, in which the incorporation of a water molecule, and a fluoride ion, in key coordination pockets has occurred, apparently preventing the formation of the typically 'expected' complexes, producing instead novel polynuclear 'incompletely metallated' helical complexes. Structures and magnetic properties are also discussed.



Scheme 1

Experimental

Physical measurements

Infrared spectra were recorded as Nujol mulls using a Mattson Polaris FT-IR instrument. UV-Vis spectra were recorded in the solid state (mull transmittance) and in solution using a Cary 5E spectrometer. Micro-analyses were carried out by Canadian Microanalytical Service, Delta, Canada. Room temperature

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magnetic susceptibilities were measured by the Faraday method using a home-made magnetometer comprising a Mettler ME21 microbalance and Cahn 0.8 T permanent magnet, fitted with Faraday pole caps, and variable temperature magnetic data (2–300 K) were obtained using a Quantum Design MPMS5S SQUID magnetometer using field strengths in the range 0.1–0.5 T. Background corrections for the sample holder assembly and diamagnetic components of the complexes were applied.

Synthesis of ligands and complexes

Pd2am. The methyl ester of iminopicolinic acid was prepared *in situ* by reaction of 2-cyanopyridine (5.21 g, 50.0 mmol) with sodium methoxide solution, produced by dissolving sodium metal (0.11 g, 5.0 mmol) in dry methanol (100 mL). 3,6-Pyridazinedicarboxylic acid hydrazide (4.90 g, 25.0 mmol) (prepared from the reaction of dimethyl-3,6-pyridazine dicarboxylate with hydrazine hydrate in methanol) was added to the above solution and the mixture refluxed for 24 h. A yellow powder was obtained, which was filtered off, washed with water (2 × 100 mL), methanol (2 × 100 mL), and then diethyl ether (2 × 100 mL) and dried under vacuum. Yield (7.82 g, 77%), mp > 250 °C. ^{1}H NMR (300 MHz, DMSO-d$_6$, 25 °C): δ 11.0 (br s, 2H, OH), 8.64 (d, 2H, Ar), 8.39 (s, 2H, Ar), 8.23 (d, 2H, Ar), 7.94 (dd, 2H, Ar), 7.53 (dd, 2H, Ar), 7.21 (br s, 4H, NH$_2$). Mass spectrum (major mass peaks, *m*/*z*): 368 (M − 2H$_2$O), 340, 311, 224, 104, 78. IR/cm^{-1} (Nujol): 3374, 3307, 3183 (νNH); 1677 (νC=O); 1604 νC=N); 997 (νpy). Anal. calc. for $C_{18}H_{16}N_{10}O_2\cdot H_2O$: C, 51.18; H, 4.30; N, 33.16. Found: C, 51.62; H, 4.01; N, 33.08%.

2Pzoap. 2,6-Pyridinedicarboxylic acid dihydrazide (3.9 g, 0.020 mol) was added to a dry methanolic solution (100 mL) of the methyl ester of iminopyrazine-2-carboxylic acid (5.2 g, 0.050 mol), prepared *in situ* from 2-cyanopyrazine and sodium metal (stirred at room temperature for 12 h) and the mixture refluxed for 24 h with the formation of a yellow powder. The solid was filtered off washed with water, methanol and ether and dried under vacuum. Yield (6.3 g, 79%), mp 259 °C (decomp.). Mass spectrum (major mass peaks, *m*/*z*): 369 (M − 2H$_2$O), 341, 340, 312, 262, 250, 207, 168, 130, 79. IR/cm^{-1} (Nujol): 3413 (νOH); 3317, 3156 (νNH); 1685 (νC=O); 1632, 1610 (νC=N). Anal. calc. for $C_{17}H_{15}N_{11}O_2\cdot 0.5H_2O$: C, 49.27; H, 3.89; N, 37.18. Found: C, 49.19; H, 3.66; N, 37.08%.

[Ni$_3$(pd2am-H)$_3$(H$_2$O)](NO$_3$)$_3$·2H$_2$O 1. pd2am (0.40 g, 1 mmol) was added to a hot solution of $Ni(NO_3)_2\cdot 6H_2O$ (0.29 g, 1 mmol) in water (25 mL). The resulting suspension was stirred with heating until complete dissolution of the ligand occurred. The dark red solution was allowed to cool to room temperature and was filtered to remove any undissolved ligand. Red crystals suitable for X-ray diffraction formed from the filtrate after standing for 1 week (yield 0.41 g, 78%). IR/cm^{-1} (Nujol): 3395 (νH$_2$O); 3299 (νNH); 1693 (νC=O); 1093 (νpy). λ/nm (Nujol): 796, 912; λ/nm (H$_2$O): (ε/M^{-1} cm^{-1}) 821 (114), 916 (86). Anal. calc. for $[Ni_3(C_{18}H_{15}N_{10}O_2)_3](NO_3)_3\cdot 2H_2O$: C, 40.33; H, 3.07; N, 28.74. Found: C, 40.47; H, 2.97; N, 28.91%.

Repeated attempts to introduce a fourth metal into the complex failed, even with a large excess of metal salt, and each time the trinuclear derivative was obtained.

[Ni$_2$(2pzoap)$_3$F](BF$_4$)$_3$·8.5H$_2$O 2. 2pzoap (0.41 g, 1.0 mmol) was added to a solution of $Ni(BF_4)_2\cdot 6H_2O$ (2.05 g, 6.0 mmol) in MeOH–H$_2$O (5 : 3 mL) with the formation of a yellow–orange powder, which was filtered off and recrystallized from DMF–diethyl ether to give the nona-nuclear complex $[Ni_9(C_{17}H_{13}N_{11}O_2)_6](BF_4)_6\cdot 12H_2O$ (0.51 g, 82%).[17] The yellow coloured original mother liquor produced a small quantity of orange crystals of **2** (0.072 g, 12%) upon standing at room temperature. IR/cm^{-1} (Nujol): 3422 (νH$_2$O); 3339 (νNH); 1676, 1655 (νC=O); 1565 (νC=N). λ/nm (Nujol): 899, 560 sh, 460 sh. Anal. calc. for $[Ni_2(C_{17}H_{15}N_{11}O_2)_3F](BF_4)_3\cdot 8.5H_2O$: C, 34.68; H, 3.52; N, 26.17. Found: C, 34.66; H, 3.06; N, 26.16%.

Table 1 Summary of crystallographic data for **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{54}H_{48}N_{33}Ni_3O_{33.5}$	$C_{51}H_{53}B_3F_{13}N_{33}$-$Ni_2O_{10}$
M	1871.38	1685.11
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	15.211(3)	12.5079(17)
b/Å	15.363(3)	14.952(2)
c/Å	19.525(4)	19.463(3)
α/°	111.999(2)	96.740(2)
β/°	91.168(3)	96.966(2)
γ/°	109.541(2)	108.259(2)
U/Å^3	3931.1(14)	3384.2(8)
D_c/g cm^{-3}	1.581	1.654
T/K	150(2)	100(2)
Z	2	2
μ/mm^{-1}	0.819	0.67
Reflections collected: total, independent, R_{int}	48465, 13820, 0.0569	33715, 15434, 0.0274
Final R_1, wR_2[a]	0.0566, 0.1463	0.0560, 0.1485

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2$.

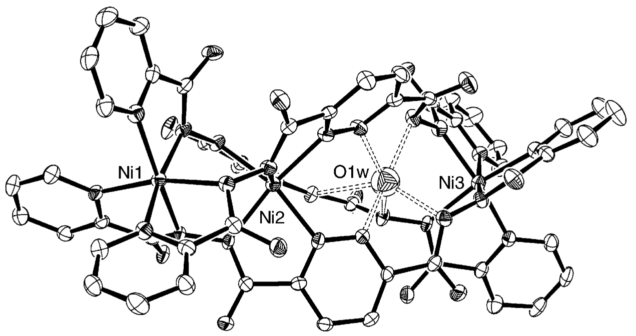

Fig. 1 Structural representation of the trinuclear cation in [Ni$_3$(pd2am-H)$_3$(H$_2$O)](NO$_3$)$_3$·2H$_2$O **1**.

Crystallographic data collection and refinement of the structures

Data collections for **1** and **2** were made using graphite monochromatised Mo-Kα X-radiation using a Bruker SMART CCD detector diffractometer equipped with a Cryostream[18] N$_2$ flow cooling device. Series of narrow ω scans (0.3°) were performed at several ϕ-settings in such a way as to cover a hemisphere or a full sphere of data to a maximum resolution of 0.7 Å. Cell parameters were determined and refined within SMART[19] using the centroid values of approximately 1000 selected reflections with 2θ values between 20 and 45°. Raw frame data were integrated using the SAINT program.[20] The data were corrected for absorption using SADABS.[21] The structures were solved using direct methods and refined by full-matrix, least squares on F^2.[21]

Abbreviated crystal data for **1** and **2** are given in Table 1.

CCDC reference numbers 162087 and 149292.

See http://www.rsc.org/suppdata/dt/b1/b102344f/ for crystallographic data in CIF or other electronic format.

Results and discussion

Structures

[Ni$_3$(pd2am-H)$_3$(H$_2$O)](NO$_3$)$_3$·2H$_2$O 1. The structural representation of the trinuclear cation is shown in Fig. 1, and important bond distances and angles are listed in Table 2. A view of the trinuclear core is shown in Fig. 2. Three ligands bind

Table 2 Interatomic bond distances (Å) and angles (°) in **1**

Ni(1)–N(208)	2.061(4)	Ni(3)–N(303)	2.049(4)
Ni(1)–N(310)	2.074(4)	Ni(3)–N(203)	2.058(4)
Ni(1)–N(110)	2.075(4)	Ni(3)–N(201)	2.088(4)
Ni(1)–N(210)	2.090(4)	Ni(3)–N(101)	2.089(4)
Ni(1)–N(108)	2.098(3)	Ni(3)–N(103)	2.089(4)
Ni(1)–N(312)	2.101(4)	Ni(3)–N(301)	2.099(4)
Ni(2)–N(207)	2.055(3)	N(105)–N(106)	1.322(5)
Ni(2)–N(206)	2.057(3)	N(107)–N(108)	1.417(5)
Ni(2)–N(106)	2.062(3)	Ni(1)–Ni(2)	3.660(2)
Ni(2)–N(309)	2.067(3)	Ni(1)–Ni(3)	10.912(3)
Ni(2)–N(107)	2.077(3)	Ni(2)–Ni(3)	7.254(3)
Ni(2)–N(307)	2.083(4)		
N(208)–Ni(1)–N(310)	92.34(14)	N(106)–Ni(2)–N(107)	76.42(13)
N(208)–Ni(1)–N(110)	94.38(14)	N(309)–Ni(2)–N(107)	92.59(13)
N(310)–Ni(1)–N(110)	166.85(13)	N(207)–Ni(2)–N(307)	101.98(14)
N(208)–Ni(1)–N(210)	77.48(13)	N(206)–Ni(2)–N(307)	94.33(14)
N(310)–Ni(1)–N(210)	96.16(14)	N(106)–Ni(2)–N(307)	94.86(14)
N(110)–Ni(1)–N(210)	96.33(14)	N(309)–Ni(2)–N(307)	75.84(13)
N(208)–Ni(1)–N(108)	89.80(13)	N(107)–Ni(2)–N(307)	164.02(14)
N(310)–Ni(1)–N(108)	90.59(13)	N(303)–Ni(3)–N(203)	93.90(14)
N(110)–Ni(1)–N(108)	78.15(13)	N(303)–Ni(3)–N(201)	165.55(14)
N(210)–Ni(1)–N(108)	165.79(14)	N(203)–Ni(3)–N(201)	77.50(14)
N(208)–Ni(1)–N(312)	169.17(14)	N(303)–Ni(3)–N(101)	93.51(15)
N(310)–Ni(1)–N(312)	77.29(14)	N(203)–Ni(3)–N(101)	167.36(14)
N(110)–Ni(1)–N(312)	96.40(14)	N(201)–Ni(3)–N(101)	97.14(14)
N(210)–Ni(1)–N(312)	100.29(14)	N(303)–Ni(3)–N(103)	95.08(14)
N(108)–Ni(1)–N(312)	93.38(13)	N(203)–Ni(3)–N(103)	92.17(14)
N(207)–Ni(2)–N(206)	76.51(13)	N(201)–Ni(3)–N(103)	96.82(14)
N(207)–Ni(2)–N(106)	159.70(14)	N(101)–Ni(3)–N(103)	76.99(14)
N(206)–Ni(2)–N(106)	91.12(14)	N(303)–Ni(3)–N(301)	77.40(14)
N(207)–Ni(2)–N(309)	93.60(14)	N(203)–Ni(3)–N(301)	97.54(14)
N(206)–Ni(2)–N(309)	164.49(14)	N(201)–Ni(3)–N(301)	92.08(14)
N(106)–Ni(2)–N(309)	101.52(14)	N(101)–Ni(3)–N(301)	94.05(15)
N(207)–Ni(2)–N(107)	89.54(14)	N(103)–Ni(3)–N(301)	168.06(14)
N(206)–Ni(2)–N(107)	99.16(14)		

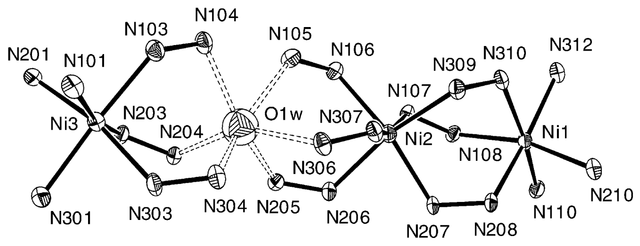

Fig. 2 View of the trinuclear core of $[Ni_3(pd2am\text{-}H)_3(H_2O)](NO_3)_3\cdot 2H_2O$ **1**.

to three octahedral nickel(II) centres in a spiral structure with two six-coordinate metals occupying contiguous coordination pockets at one end of the ligand and bridged by three single bond (N–N) diazine groups, in a manner reminiscent of a series of spiral (2 : 3) metal : ligand complexes of the ligand pahap (picolinamide hydrazone).[22] The next ligand pocket has no metal, and is occupied by a water molecule with quite short O–N contacts (O–N 2.151–2.358 Å), and the last, external ligand pocket holds a single six-coordinate nickel ion. Ni–N distances are quite short, falling in the range 2.049–2.098 Å. The Ni(1)–Ni(2) distance is 3.659(2) Å, and the twist of the two nickel centres about the triple N–N bridge (average Ni–N–N–Ni torsional angle 40.5°) is comparable with the equivalent situation in the complex ion $[Ni_2(pahap)_3]^{3+}$.[22] Water O(1w) is effectively behaving as a substitute metal centre (Fig. 1) and occupies a site with six nitrogen donors at coordinating distances, which might be considered reasonable for a six-coordinate metal ion. However, the N–O(1w)–N angles (72–114°) indicate that, on the assumption that O(1w) has an optimized positional occupancy, the coordination site donor assembly is quite distorted. The O(1w)–Ni(3) distance (3.437 Å) is comparable with the Ni(1)–Ni(2) distance. The Ni(1)–Ni(3) distance is very long (10.91 Å) placing this system well into the nanoscale range, with the external long dimension being close to 18 Å.

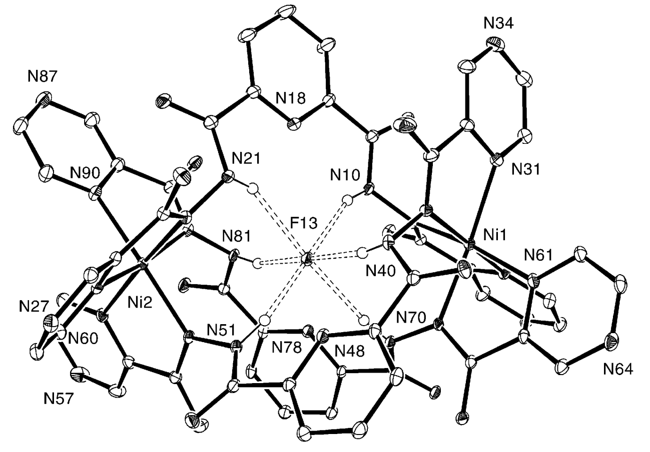

Fig. 3 Structural representation of the dinuclear cation in $[Ni_2(2pzoap)_3F](BF_4)_3\cdot 8.5H_2O$ **2**.

The peripheral py–C(NH_2)C=N and the central pd–(C(O)N)$_2$ sub-units (py = pyridine, pd = pyridazine) are almost flat (torsional angles <13°), and so the overall twist of each ligand can be estimated by examining the torsional angles of the aromatic rings with respect to the N–N single bonds. Each ligand experiences a significant twist about the N–N bonds and the total torsional twist amounts to about 190°, with the peripheral pyridine (py) nitrogens effectively pointing in opposite directions.

$[Ni_2(2pzoap)_3F](BF_4)_3\cdot 8.5H_2O$ 2. The structural representation of the dinuclear cation in **2** is illustrated in Fig. 3, and important bond distances and angles are listed in Table 3. The complex has two octahedral NiN_6 centres bound to the extreme ends of the complex *via* terminal pyrazine (pz) and diazine nitrogens only. Three ligands wrap around the two metals forming a helical structure, with a large cavity in the centre of

Table 3 Interatomic bond distances (Å) and angles (°) in **2**

Ni(1)–N(1)	2.110(3)	Ni(2)–N(22)	2.052(3)
Ni(1)–N(9)	2.038(3)	Ni(2)–N(30)	2.097(3)
Ni(1)–N(31)	2.116(3)	Ni(2)–N(52)	2.050(3)
Ni(1)–N(39)	2.045(3)	Ni(2)–N(60)	2.105(3)
Ni(1)–N(61)	2.070(3)	Ni(2)–N(82)	2.042(3)
Ni(1)–N(69)	2.062(3)	Ni(2)–N(90)	2.106(3)
N(1)–Ni(1)–N(9)	76.83(11)	N(39)–Ni(1)–N(69)	93.79(11)
N(1)–Ni(1)–N(31)	102.15(11)	N(61)–Ni(1)–N(69)	77.97(11)
N(1)–Ni(1)–N(39)	173.28(11)	N(22)–Ni(2)–N(30)	76.49(11)
N(1)–Ni(1)–N(61)	93.07(11)	N(22)–Ni(2)–N(52)	99.02(11)
N(1)–Ni(1)–N(69)	87.41(11)	N(22)–Ni(2)–N(60)	174.61(11)
N(9)–Ni(1)–N(31)	87.81(11)	N(22)–Ni(2)–N(82)	93.30(11)
N(9)–Ni(1)–N(39)	96.47(11)	N(22)–Ni(2)–N(90)	91.40(13)
N(9)–Ni(1)–N(61)	168.56(11)	N(30)–Ni(2)–N(52)	90.90(11)
N(60)–Ni(2)–N(82)	90.39(11)	N(30)–Ni(2)–N(60)	100.07(11)
N(9)–Ni(1)–N(69)	96.00(11)	N(30)–Ni(2)–N(82)	169.07(11)
N(31)–Ni(1)–N(39)	76.89(11)	N(30)–Ni(2)–N(90)	99.21(11)
N(31)–Ni(1)–N(61)	99.70(11)	N(52)–Ni(2)–N(60)	76.74(11)
N(31)–Ni(1)–N(69)	170.31(11)	N(52)–Ni(2)–N(82)	94.59(11)
N(39)–Ni(1)–N(61)	93.65(11)	N(52)–Ni(2)–N(90)	166.95(13)

the molecule, which is occupied by a putative fluoride ion (it is crystallographically difficult to distinguish between a fluoride ion and an oxygen atom, but the structural refinement is improved slightly with fluorine at this site). Elemental anyalyses are consistent with this situation assuming neutral ligands (*vide infra*). Ni–N distances fall within the range 2.037–2.117 Å, typical for octahedral Ni(II), and the Ni–Ni separation is 7.792 Å. The F^- ion is poised within reach of six diazine nitrogens and three pyridine nitrogens. Contacts to the pyridine nitrogen atoms are quite long (3.14–3.30 Å), but the six diazine nitrogen contacts are much shorter (2.73–2.95 Å) and clearly involve hydrogen bonds (Fig. 3; N–H–F angles 149–165°). The fluoride ion is therefore somewhat loosely bound in a pseudo-octahedral environment, but effectively stabilizes the vacant coordination 'hole' in the structure.

N–N diazine bond lengths (1.39–1.42 Å) are consistent with the expected N–N single bonds. Bond distances within the H_2N-C–N–N–C–O sub-unit of each ligand are consistent with a C=O double bond, a C–NH_2 single bond, and an (O)C–N_2 single bond, and so the ligands are neutral with protons on nitrogen atoms N(10), N(21), N(40), N(51), N(70) and N(81), which point inwards to the central core. The pzC(NH_2)N and py(C(O)N)$_2$ sub-units in the three ligands are roughly flat, but the twisting of the external pyrazine sub-units relative to the central pyridine around the N–N single bonds leads to a pronounced ligand twist, with an overall twist of about 180°. Since each pyrazine nitrogen occupies a triangular face of the metal octahedra, the pyrazine rings, and thus each of the ligands, are each offset by approximately 120°.

Self assembly mechanism

The combination of the three contiguous diazine (N_2) fragments in pd2am would be expected to accommodate four metals easily, based on previous studies with related ligands and ligand fragments. However, since repeated attempts to introduce four metal atoms failed, there must be some fundamental feature of the structural arrangement or the mechanism of self assembly which prevents this happening. It is reasonable to assume that the first step in the process involves the coordination of the ends of three ligands to one Ni(II) centre *via* pyridine and diazine nitrogen atoms. The ligands then begin their twist at the flexible diazine single N–N bond fragments, and the second metal occupies site number two easily with the familiar twisted arrangement observed with pahap, and the three pyridazine nitrogens become bonded to this Ni(II) centre. Three ligands are now localized around the two metals and two possible coordination events could now occur. The third metal could occupy the next contiguous site or this site could be missed in favour of the fourth site. In order for the third site to be occupied the three pyridazine groups would have to align their second nitrogen atoms appropriately in order to attract metal number three. Because of the rigidity of the aromatic pyridazine ring this is clearly more difficult than the twist around the N–N single bond bridges and it is apparently easier for the third metal to occupy the external coordination pocket. The adventitious water finds a place in the unoccupied cavity and stabilizes the 'hole'. It is of interest to note that there are no simple dinuclear complexes of first row transition elements with three pyridazine bridges.

The case of $[Ni_2(2pzoap)_3F](BF_4)_3{\cdot}8.5H_2O$ **2** is less obvious. The 2pzoap ligand would be expected to produce a nine-metal grid structure with typical six-coordinate metal ions, as found for Mn(II)[8] and Cu(II)[9,10] with the analogous 'tritopic' ligand 2poap (terminal pyridine equivalent ligand), and the self assembly of such systems would depend on the building of the grid with ligands oriented in a linear manner (Scheme 1). In order for the grid to assemble, a group of linear precursor sub-units with a metal ion occupying each of the three tri-coordinating ligand pockets (Scheme 1) would be expected to form first. In the reaction between $Ni(BF_4)_2$ and 2pzoap the major product (82%) appears to be the Ni_9 self-assembled grid complex $[Ni_9(C_{17}H_{13}N_{11}O_2)_6](BF_4)_6{\cdot}12H_2O$ (experimental),[17] in which each ligand has lost two protons. Aqueous solutions of $M(BF_4)_2$ salts are potentially acidic, in part due to the inherent acidity of M^{2+} transition metal cations, but also because BF_4^- undergoes a dissociative equilibrium in water ($BF_4^- + H_2O \rightleftharpoons BF_3(OH)^- + HF$; $K = 2.0 \times 10^{-3}$),[23] capable of producing an acidic medium and acting as a source of F^- ions. Increased acidity would maintain the ligand in a neutral form, suppress the formation of the Ni_9 grid, and encourage incorporation of a fluoride ion by creation of a proton-rich cavity. The low yield (12%) of **2**, compared with the Ni_9 grid complex is consistent with this suggestion.

The structure of **2** indicates that a single nickel(II) must assemble the three ligands, in a manner similar to **1**, with the metal ion bound to six external nitrogen atoms from three ligands. With three ligands bound in a spiral manner to one metal it is impossible for the remaining donors to arrange themselves in a grid pattern, particularly if the next available donor atoms are protonated, and so the three floppy ligands are now forced to organize themselves with the available Lewis acid centres. The central pyridines and adjacent nitrogen donors are now too far away from each other to contribute to the coordination sphere of a single metal ion assembly, and since the ligand is flexible, it is easier for the other ends to associate into an N_6 sub-unit around a second nickel(II) centre. The large 'empty' cavity in the middle of the complex simply picks up an adventitious fluoride ion in the process of self assembly, which is stabilized by hydrogen bonding contacts to the diazine nitrogen atoms.

Magnetic properties

Variable temperature magnetic data were collected for **1** in the temperature range 10–300 K in a 0.5 T field. The plot of magnetic moment per mole for **1**, as a function of temperature, is illustrated in Fig. 4, and shows a marked drop from 5.2 μ_B (per mole) at 300 K to 3.8 μ_B at 10.0 K. Given the structural arrangement of the three Ni(II) centres one would expect the two contiguous metals to be antiferromagnetically coupled, while the third would not be involved in spin exchange. Consequently the data were fitted to a simple isotropic Heisenberg expression based on an equal mixture of a nickel dimer ($H = -2JS_1{\cdot}S_2$) and a mono-nuclear Curie-like component. An excellent data fit was obtained with $g = 2.14(1)$, $J = -4.6(1)\ \mathrm{cm}^{-1}$, $\theta = -0.6$ K, TIP $= 600 \times 10^{-6}\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$ ($10^2R = 0.31$) (θ = Weiss-like temperature correction; $R = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma\chi_{obs}^2]^{1/2}$). The solid line in Fig. 4 was calculated

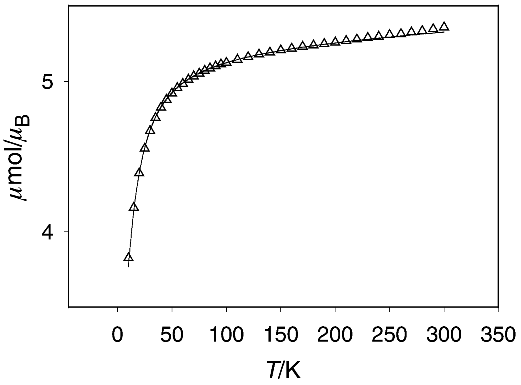

Fig. 4 Variable temperature magnetic data for $[Ni_3(pd2am\text{-}H)_3(H_2O)](NO_3)_3\cdot 2H_2O$ **1**.

using these parameters. The presence of weak antiferromagnetic coupling between Ni(1) and Ni(2) is in contrast to the behaviour of the complex $[Ni_2(pahap)_3](ClO_4)_4$, which has a similar $Ni_2(N–N)_3$ dinuclear centre, but is uncoupled, which can be associated with a somewhat smaller rotation of the metal ion orbitals around the N–N single bonds.[22]

The magnetic properties of **2** are unremarkable, and a constant magnetic moment of 4.1 μ_B (per mole) over the temperature range 2–300 K indicates completely isolated magnetic centres, which would be predicted from the structure.

Conclusion

Two unusual polynuclear spiral complexes are reported in which long, flexible 'polytopic' ligands combine with Ni(II) ions in self assembly processes to produce structures in which a solvent water molecule and a fluoride ion play an important role in the outcome of the reaction product and occupy 'empty' coordination sites, effectively stabilizing the final structural arrangement.

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