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The assembly of pentanuclear nickel(II) complexes from asymmetric compartmental ligands and bearing μ_3-OH bridges†

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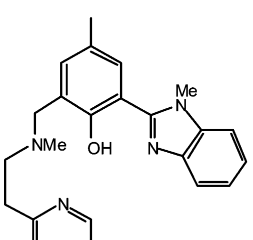
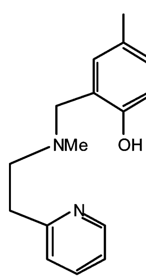
The asymmetric di-aminic compartmental ligands HL^5–HL^7 form pentanuclear nickel(II) complexes in which the core is assembled from two dinuclear [Ni_2L] units which are each linked to the third Ni atom by bridging μ_3-hydroxo groups; the crystal structure of [$Ni_5(L^5)_2(OAc)_6(OH)_2$], 1 [HL^5 is the proligand 2-{[(2-dimethylaminoethyl)ethylamino]methyl}-6-ethyliminomethyl-4-methylphenol] is reported.

Pentadentate asymmetric Schiff base compartmental proligands having two adjacent {N_2O} donor sets with the O atom available for bridging have been used to prepare a range of homodinuclear complexes.[1–5] In contrast, proligands bearing adjacent tridentate {N_2O} and bidentate {NO} donor sets, HL^1 and HL^2, generate the trinuclear nickel(II) complexes [$Ni_3(L^n)_2(OAc)_2(NCS)_2$] in which there are two μ_3-acetato-κ*O*:κ*O*:κ*O′* groups.[6] Furthermore the reaction of proligands HL^3 and HL^4 with $Ni(OAc)_2 \cdot 4H_2O$ and NaSCN in methanol give the trinuclear nickel(II) complexes [$Ni_3(L^3)_2(OAc)_2(NCS)_2$]$\cdot 2H_2O$, and [$Ni_3(L^4)_2(OAc)_2(NCS)_2$]$\cdot H_2O \cdot 2MeOH$, in each of which the pendant S-donor atom is non-coordinating and there are again two tridentate acetate bridges.[7] Reduction of the denticity of the dinucleating ligand from potentially pentadentate to potentially tetradentate generates vacant coordination sites at the metal incorporated into the donor atom diminished iminic compartment and provides an opportunity for the generation of a complex with enhanced nuclearity *via* interaction with the same donor set from a second ligand molecule. High nuclearity 3d-metal clusters derived from O- and N-donor ligands are currently of interest because of their magnetic properties.[8] Many of these clusters arise from serendipitous assemblies and so the rational synthesis of such complexes is a desirable target. This work presents the results of the interaction of $Ni(OAc)_2 \cdot 4H_2O$ with the asymmetric Schiff base compartmental proligands HL^5–HL^7 in the absence of the coordinating thiocyanate anion and reports the crystal structures of the oligonuclear products.

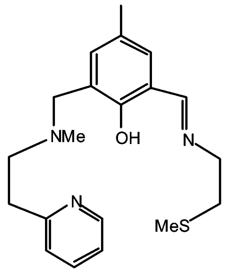
The proligands 2-{[(2-dimethylaminoethyl)ethylamino]methyl}-6-ethyliminomethyl-4-methylphenol, HL^5, 2-{[(2-diethylaminoethyl)methylamino]methyl}-4-methyl-6-[(3-methylsulfanylpropylimino)methyl]phenol, HL^6, and 2-{[(2-dimethylaminoethyl)ethylamino]methyl}-4-methyl-6-[(3-methylsulfanylpropylimino)methyl]phenol, HL^7, were prepared from 3-{[(2-dimethylaminoethyl)ethylamino]methyl}-2-hydroxy-5-methylbenzaldehyde and 3-{[(2-diethylaminoethyl)methylamino]methyl}-2-hydroxy-5-methylbenzaldehyde by reaction with 3-(methylthio)propylamine and ethylamine according to the methodology of reference 7. The complexes were prepared by the following general procedure. Nickel acetate tetrahydrate (0.713 mmol) was added to a solution of the requisite proligand, HL^5–HL^7, (0.285 mmol) in methanol (10 cm^3). The resulting solution was heated to reflux for 30 min and allowed to cool to rt giving crystals suitable for X-ray structural determination.



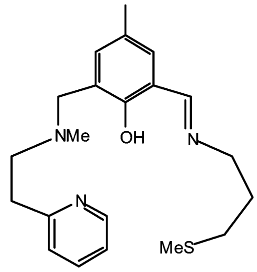
HL¹



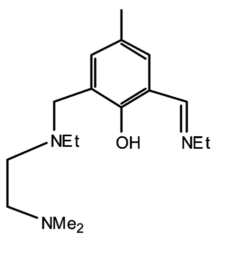
HL²



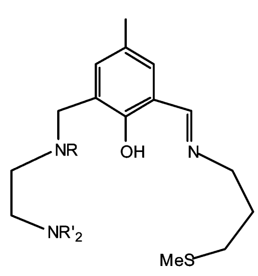
HL³



HL⁴



HL⁵



HL⁶ R = Me; R' = Et
HL⁷ R = Et; R' = Me

Solution of the structures showed that the compounds formed were the pentanuclear nickel(II) complexes, [$Ni_5(L^5)_2(OAc)_6(OH)_2$], **1**, [$Ni_5(L^6)_2(OAc)_6(OH)_2$]$\cdot 2CH_3OH \cdot 5H_2O$, **2**, and [$Ni_5(L^7)_2(OAc)_6(OH)_2$]$\cdot CH_3OH \cdot 2H_2O$, **3**. As the nature of the pentanuclear core is closely similar in all three complexes only the molecular structures of complexes **1** [$R = 0.0590$] and **2** [$R = 0.0726$] are reported here; that of complex **3** [$R = 0.0908$] is available as ESI.†

The molecular structure of one of the two molecules in the asymmetric unit **1** is shown in Fig. 1 with selected bond lengths and angles given in the caption.‡ Fig. 2 depicts the molecular structure of **2** and is presented to show the non-bonding nature and disorder of the 3-methylsulfanylpropylimino pendant arms – in the structures of both **2** and **3** these arms are disordered. The pentanuclear core of the complexes is detailed schematically in Fig. 3. The structure comprises two dinuclear [Ni_2L] units

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† Electronic supplementary information (ESI) available: the molecular structure and crystallographic details for compound **3**. See http://www.rsc.org/suppdata/dt/b2/b207631b/

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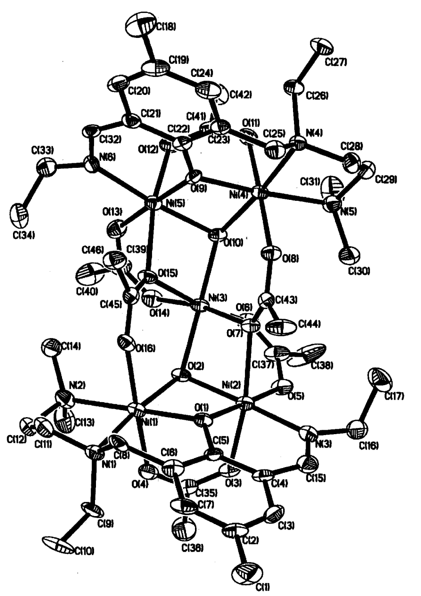


Fig. 1 ORTEP[19] drawing of the molecular structure of $[Ni_5(\mathbf{L}^5)_2(OAc)_6(OH)_2]$, **1**, showing the crystallographic labelling. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°) at the nickel(II) atoms: Ni(1)–O(2), 2.016(4); Ni(1)–O(1), 2.047(4); Ni(1)–O(4), 2.055(4); Ni(1)–O(16), 2.100(4); Ni(1)–N(1), 2.131(5); Ni(1)–N(2), 2.189(5); Ni(2)–O(1), 2.013(4); Ni(2)–O(5), 2.034(2); Ni(2)–O(2), 2.051(4); Ni(2)–O(3), 2.075(4); Ni(2)–O(2), 2.176(3); Ni(2)–N(3), 2.042(5); Ni(3)–O(10), 2.013(3); Ni(3)–O(2), 2.018(3); Ni(3)–O(14), 2.062(4); Ni(3)–O(6), 2.061(4); Ni(3)–O(7), 2.091(4); Ni(3)–O(15), 2.098(4); Ni(4)–O(10), 2.021(3); Ni(4)–O(9), 2.037(3); Ni(4)–O(11), 2.066(4); Ni(4)–O(8), 2.089(4); Ni(4)–N(4), 2.125(4); Ni(4)–N(5), 2.163(5); Ni(1) ··· Ni(2), 2.9814(10); Ni(1) ··· Ni(3), 3.6581(10); Ni(2) ··· Ni(3), 3.0987(10); Ni(4) ··· Ni(5), 2.9709(10); Ni(3) ··· Ni(4), 3.6545(10); Ni(3) ··· Ni(5), 3.0979(10); Ni(1)–O(1)–Ni(2), 94.47(15); Ni(1)–O(2)–Ni(2), 94.28(14);. Ni(1)–O(2)–Ni(3), 130.12(17); Ni(3)–O(2)–Ni(2), 99.18(15);. Ni(3)–O(7)–Ni(2), 93.10(14); Ni(3)–O(15)–Ni(5), 93.09(14);. Ni(4)–O(9)–Ni(5), 94.94(14); Ni(4)–O(10)–Ni(5), 93.98(15);. Ni(3)–O(10)–Ni(4), 129.91(17); Ni(3)–O(10)–Ni(5), 99.63(15).

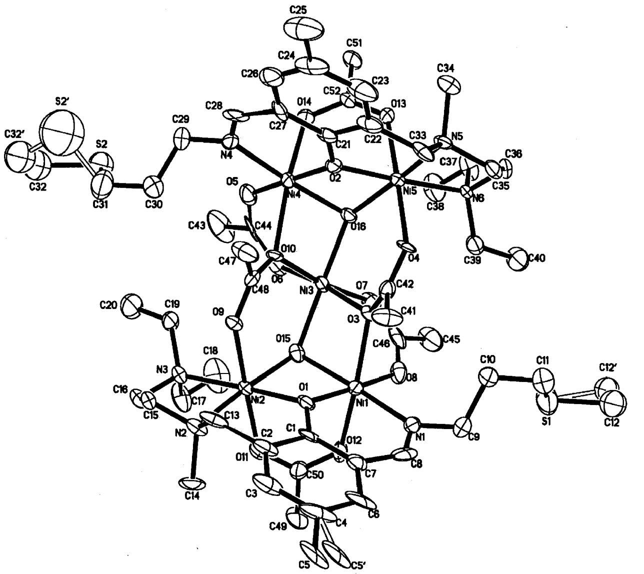


Fig. 2 ORTEP[19] drawing of the molecular structure of $[Ni_5(\mathbf{L}^6)_2(OAc)_6(OH)_2]\cdot 2CH_3OH\cdot 5H_2O$, **2**, showing the crystallographic labelling and with the solvent molecules removed for clarity. Thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

which are each linked to the third Ni atom by bridging μ_3-hydroxo groups. This bridging is augmented by *syn-syn* bidentate bridging and monodentate bridging acetate anions[9] such that the central Ni(3) atom is 6-coordinate ({O6} – donor set: distorted O_h [O(10)–Ni(3)–O(2), 175.50(14); O(14)–Ni(3)–O(7), 170.10(15); O(6)–Ni(3)–O(15), 170.54(15)°]. The remaining Ni atoms are also 6-coordinate (distorted O_h). Ni(2) [O(1)–Ni(2)–O(5), 177.21(16); O(2)–Ni(2)–N(3), 174.29(16); O(3)–Ni(2)–O(7), 167.18(15)°], and Ni(5) [O(9)–Ni(5)–O(13), 178.56(15); O(10)–Ni(5)–N(6), 173.11(16); O(12)–Ni(5)–O(15), 164.79(14)°], are in $\{N_1O_5\}$ donor compartments provided by a μ_3-OH, a bridging cresolato-O atom, two bidentate acetato-O atoms, a monodentate acetato-O atom, and an imino-N atom, whilst Ni(1) [O(4)–Ni(1)–O(16), 178.27(15); O(2)–Ni(1)–N(1), 173.77(16); O(1)–Ni(1)–N(2), 173.61(16)] and Ni(4) [O(11)–Ni(4)–O(8), 178.55(15); O(10)–Ni(4)–N(4), 172.11(16); O(9)–Ni(4)–N(5), 174.01(16)°] are in $\{N_2O_4\}$ donor compartments provided by a μ_3-OH, a bridging cresolato-O atom, one bidentate acetato-O atom, a monodentate acetato-O atom, and two chelating amino-N atoms.

Discrete homopentanuclear nickel(II) clusters are relatively few.[8,10–14] Similarly nickel(II) complexes bearing a μ_3-OH ligand are scarce[15–17] and of the pentanuclear clusters only $[Ni_5(OH)(bta)_3(acac)_4(H_2O)_4]$ (acac =acetylacetonate and bta = benzotriazole or 5,6-dimethylbenzotriazole) contains such a bridge.[17] In the benzotriazole complex the Ni atoms associated with the μ_3-OH form isosceles triangles (Fig. 4) with Ni–Ni separations of 3.270, 3.269 and 3.987 Å and Ni–OH distances ranging from 2.044–2.076 Å and averaging 2.065 Å. In **1** the triangles are more distorted (Fig. 4) reflecting the nature and connectivity of the bridges – Ni(1) ··· Ni(2) and Ni(4) ··· Ni(5) are triply bridged by a μ_3-OH, a cresolato-O atom and a *syn-syn* bidentate bridging acetate; Ni(1) ··· Ni(3) and Ni(3) ··· Ni(4) are triply bridged by a μ_3-OH, a *syn-syn* bidentate bridging acetate and O_b from a monodentate bridging acetate; Ni(2) ··· Ni(3) and Ni(3) ··· Ni(5) are doubly bridged by a μ_3-OH, O_{br} from a bidentate bridging acetate and by O_d and O_b from a monodentate bridging acetate which is therefore itself triply bridging (Fig. 5).

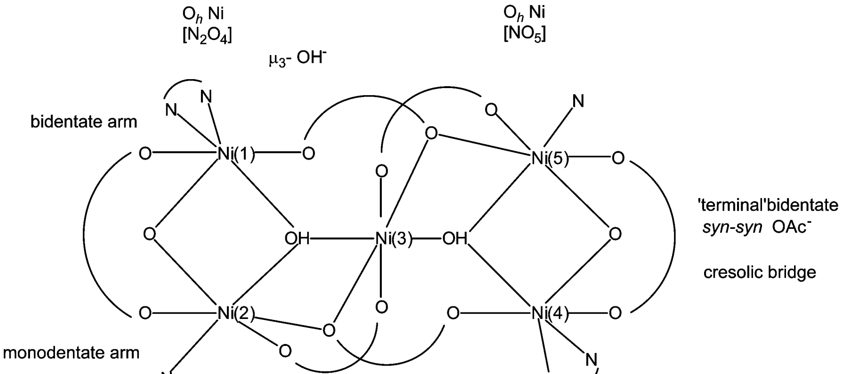
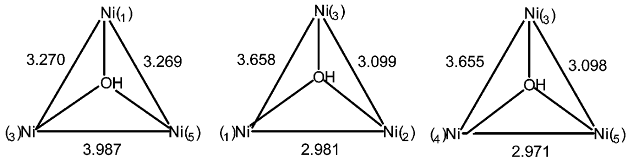


Fig. 3 Schematic presentation of the pentanuclear core.



(a) (b)

Fig. 4 A comparison of the Ni_3 triangles in (a) $[Ni_5(OH)(bta)_3(acac)_4(H_2O)_4]$ and (b) complex **1**.

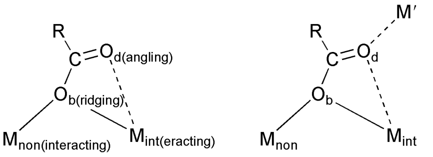
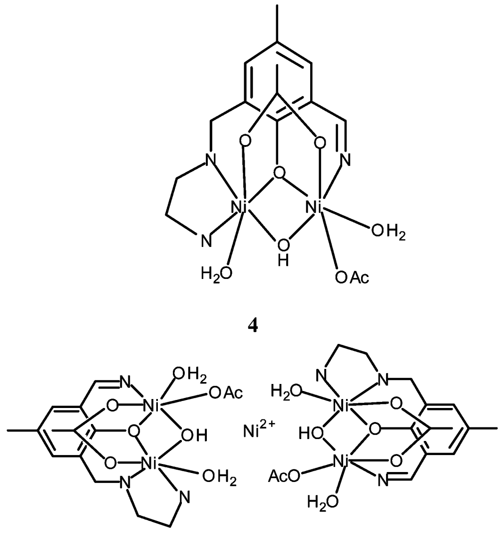


Fig. 5 The monodentate bridging mode (left) and the triply bridging mode derived from it (right).

The Ni atom pairs, Ni(1) Ni(2), and Ni(4) Ni(5) are not coplanar and there is a slight tetrahedral distortion (24°). The topology of the core is resemblant of that found in the benzotriazole complex, and is described as a distorted tetrahedral arrangement of Ni atoms centered on a fifth Ni atom.[14] The μ_3-OH atoms both lie 0.69 Å out of the respective Ni_3 planes. The Ni–OH distances lie between 2.013 and 2.051 Å, within the range found in previous structures.[14–17]

We have previously commented that the precursor for the assembly of a tetranuclear nickel(II) complex of an asymmetric compartmental ligand in which the nickel(II) atoms were bridged by an intramolecular $(\mu_4,\eta^2{:}\eta^2)$-$[H_3O_2]^-$ anion and a tetradentate $(\mu_4,\eta^2{:}\eta^2)$-perchlorate anion could have been a μ-hydroxo bridged dinickel(II) complex.[18] It is similarly plausible that the reaction giving **1** should proceed (Scheme 1) *via* an intermediate such as **4**, with two molecules of **4** and a molecule of $Ni(OAc)_2{\cdot}4H_2O$, self-assembling to produce **1**.



Scheme 1 A proposal for the self-assembly of the pentanuclear core.

Acknowledgements

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Notes and references

‡ Crystal data for **1**: $C_{92}H_{152}N_{12}Ni_{10}O_{32}$ M = 2525.36, triclinic, $P\bar{1}$, a = 16.1749(15), b = 20.2038(18), c = 22.630(2) Å, α = 63.50(2)4, β = 85.667(2), γ = 89.991(2)°, U = 6595.1(10) Å^3, Z = 2, μ = 1.272 mm^{-1}, T = 150(2) K, R_1 = 0.0590 (wR_2 = 0.1590, for all 31542 data, 1319 parameters).

Crystal data for **2**: $C_{54}H_{114}N_6Ni_5O_{23}S_2$ M = 1573.18, triclinic, $P\bar{1}$, a = 11.5662(17), b = 11.7496(17), c = 27.030(4) Å, α = 86.069(3), β = 85.732(3), γ = 83.580(3)°, U = 3633.5(9) Å^3, Z = 2, μ = 1.402 mm^{-1}, T = 150(2) K, R_1 = 0.0719 (wR_2 = 0.2154, for all 10434 data, 806 parameters).

CCDC reference numbers 191320 (complex **1**), 191319 (complex **2**) and 191318 (complex **3**). See http://www.rsc.org/suppdata/dt/b2/b207631b/ for crystallographic data in CIF or other electronic format.

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