

# A tetranuclear nickel(II) complex assembled from an asymmetric compartmental ligand and bearing an intramolecular $[\text{H}_3\text{O}_2]^-$ bridge

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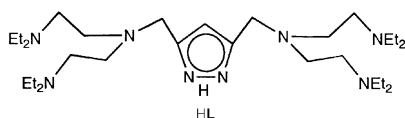
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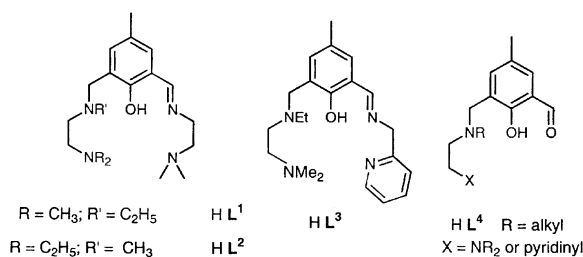
The asymmetric di-aminic compartmental ligand  $\text{HL}^5$  forms a tetranuclear nickel(II) complex in which the core is assembled from two confacial bioctahedra  $[\text{Ni}\cdots\text{Ni}, \sim 2.90 \text{ \AA}]$ ; the open faces of the bioctahedra are joined at the O atoms of two  $\mu$ -cresolato bridges  $[\text{Ni}\cdots\text{Ni}, 3.72 \text{ \AA}]$ , and the shared faces of the bioctahedra are linked by a tetradentate  $(\mu_4, \eta^2)$ -perchlorate anion and by an unusual tetradentate  $(\mu_4, \eta^2)$ - $[\text{H}_3\text{O}_2]^-$  bridge.

The hydrated hydroxide anion  $[\text{H}_3\text{O}_2]^-$  was found to act as a bridging ligand,  $[\text{O}(\text{H})\text{H}\cdots\text{OH}]^-$ , between mononuclear zinc centres in tris(pyrazolyl)borate complexes of zinc and the complexes were proposed as structural models for the oligometallobiosites present in the zinc enzymes phospholipase C and P1 nuclease.<sup>1</sup> Subsequently similar bridges have been established in dizinc(II)<sup>2</sup> and dinickel(II) complexes<sup>3</sup> of the dinucleating ligand 3,5-bis[bis(2-diethylaminoethyl)aminomethyl]pyrazole (HL). The anion has a very strong intramolecular



hydrogen bond with a short central  $\text{O}\cdots\text{O}$  contact distance (2.40–2.46  $\text{\AA}$  in the structures determined).

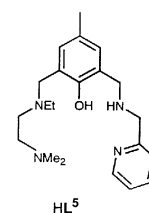
Asymmetrical compartmental proligands such as  $\text{HL}^1$ – $\text{HL}^3$  provide adjacent, dissimilar binding sites which can each accommodate a metal.<sup>4–8</sup> We have recently shown that proligands such as  $\text{HL}^1$  and  $\text{HL}^2$  generate dinuclear complexes



of both copper(II) and nickel(II) when a coordinating anion is present whereas in the presence of weakly or non-coordinating anions a different reactivity pattern is observed.<sup>8–11</sup> For example the proligands react with  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  to give complexes  $[\text{Cu}_2\text{OHL}^n](\text{ClO}_4)_2$  [ $\text{L}^n = \text{L}^1, \text{L}^2$ ] in which the integrity of the compartmental ligand is retained and the copper atoms are hydroxo-bridged, but reaction with nickel(II) perchlorate induces hydrolysis of the iminic pendant arm to generate dinuclear complexes of the resulting aldehydes,  $\text{HL}^4$ .<sup>10,12,13</sup>

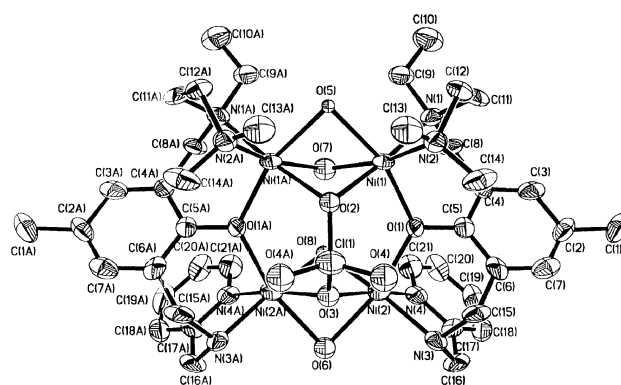
In order to prepare dinuclear nickel(II) complexes in the presence of weakly or non-coordinating anions and so encourage hydroxo-bridge formation the asymmetric compartmental ligand  $\text{HL}^3$  was reduced to the di-aminic analogue  $\text{HL}^5$  which was then reacted with  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in ethanol with addition of  $\text{NaPF}_6$  to facilitate crystallisation. Crystals suitable

for X-ray structural analysis were recovered from the ethanolic reaction mixture. Solution of the structure<sup>14</sup> revealed that complex **1**,  $[\text{Ni}_4(\text{L}^5)_2(\text{OH})_3(\text{OH}_2)\text{ClO}_4](\text{PF}_6)_2 \cdot 2\text{CH}_3\text{OH} \cdot 4\text{H}_2\text{O}$ ,



having unusual bonding features had been formed—the yield was 36%. The molecular structure of the dication  $[\text{Ni}_4(\text{L}^5)_2(\text{O}(\text{H})_3(\text{OH}_2)\text{ClO}_4)]^{2+}$  is given in Fig. 1 with selected bond lengths and angles listed in the caption to the figure.

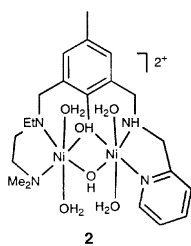
The complex lies on a crystallographic mirror plane and the tetranuclear array is assembled from two confacial bioctahedra  $[\text{N}(1), \text{N}(2), \text{O}(1)\text{—Ni}(1)\text{—O}(2), \text{O}(5), \text{O}(7)\text{—Ni}(1\text{A})\text{—N}(1\text{A}), \text{N}(2\text{A}), \text{O}(1\text{A})$  and  $\text{N}(3), \text{N}(4), \text{O}(1)\text{—Ni}(2)\text{—O}(3), \text{O}(6), \text{O}(8)\text{—Ni}(2\text{A})\text{—N}(3\text{A}), \text{N}(4\text{A}), \text{O}(1\text{A})]$  with  $\text{L}^5$  serving as a dinucleating and doubly face-capping anionic ligand. The shared faces of the bioctahedra  $[\text{O}(2), \text{O}(5), \text{O}(7)$  and  $\text{O}(3), \text{O}(6), \text{O}(8)]$  are linked to each other by a bridging  $(\mu_4, \eta^2)$  tetradentate perchlorate anion  $[\text{O}(2)\text{—Cl}(1)\text{—O}(3)]$  and two  $\mu$ -cresolato



**Fig. 1** An ORTEP drawing of the molecular structure of the dication from **1**  $[\text{Ni}_4(\text{L}^5)_2(\text{OH})_3(\text{OH}_2)\text{ClO}_4]^{2+}$  showing the atom labelling; thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths and angles at the metal atoms: Ni(1)—O(1), 2.066(8); Ni(1)—O(2), 2.060(7); Ni(1)—O(5), 2.089(7); Ni(1)—O(7), 2.144(8); Ni(1)—N(1), 2.093(12); Ni(1)—N(2), 2.120(10); Ni(2)—O(1), 2.058(8); Ni(2)—O(3), 2.060(8); Ni(2)—O(6), 2.215(8); Ni(2)—O(8), 2.014(6); Ni(2)—N(3), 2.080(10); Ni(2)—N(4), 2.013(11); Ni(1)···Ni(2), 3.720(3); Ni(1)···Ni(1A), 2.917(3); Ni(2)···Ni(2A), 2.864(3)  $\text{\AA}$ . O(2)—Ni(1)—N(1), 175.4(4); N(2)—Ni(1)—O(7), 167.4(4); O(1)—Ni(1)—O(5), 160.6(3); O(1)—Ni(1)—N(2), 103.6(4); N(2)—Ni(1)—O(5), 92.5(4); O(5)—Ni(1)—O(2), 75.6(3); O(2)—Ni(1)—O(1), 91.7(3); O(8)—Ni(2)—N(3), 171.4(4); N(4)—Ni(2)—O(3), 169.6(4); O(1)—Ni(2)—O(6), 165.8(3); O(1)—Ni(2)—N(3), 94.1(3); N(3)—Ni(2)—O(6), 97.0(3); O(6)—Ni(1)—O(8), 75.8(3); O(8)—Ni(1)—O(1), 93.7(3); Ni(1)—O(1)—Ni(2), 128.8(4); Ni(1)—O(2)—Ni(1A), 90.1(4); Ni(1)—O(5)—Ni(1A), 88.5(3); Ni(1)—O(7)—Ni(1A), 85.7(4); Ni(2)—O(3)—Ni(2A), 88.1(4); Ni(2)—O(6)—Ni(2A), 80.5(4); Ni(2)—O(8)—Ni(2A), 90.6(4)°.

bridges Ni(1)–O(1)–Ni(2) and Ni(1A)–O(1A)–Ni(2A) link the pairs of open faces (Fig. 2). The intermetallic separation of the Ni atoms at the triply bridged faces [Ni(1)⋯Ni(1A), 2.92; Ni(2)⋯Ni(2A), 2.86 Å] are considerably shorter than those of the Ni atoms in the single atom cresolato-bridges [Ni(1)⋯Ni(2), 3.72 Å]. This latter separation is itself reduced over the Ni(II)⋯Ni(II) separation of 4.45 Å found in [Ni<sub>2</sub>(L)(O<sub>2</sub>H<sub>3</sub>)](BPh<sub>4</sub>)<sub>2</sub>·2(CH<sub>3</sub>)<sub>2</sub>CO in which there is an endogenous two-atom bridge.<sup>3</sup>

There is a short central O(7)⋯O(8) contact distance of 2.45 Å indicating the presence of a very strong hydrogen bond and leading to the hydrated hydroxide anion [O(H)H⋯OH]<sup>–</sup>.<sup>15</sup> This provides an unusual (μ<sub>4</sub>,η<sup>2</sup>)-bridge between the two dinuclear nickel centres with each O atom serving as a bridging atom to a pair of Ni(II) atoms (Fig. 2). The components of this bridge have been assigned on the basis of the Ni–O distances with the water molecule being located at O(7) [Ni(1)–O(7), 2.14 Å] and the hydroxide at O(8) [Ni(2)–O(8), 2.01 Å].<sup>16</sup> It is possible that, by analogy with the formation of [Cu<sub>2</sub>OHL<sup>n</sup>]<sup>2+</sup> noted above, a μ-hydroxo bridged dinickel(II) species such as 2



provides the precursor for the tetranuclear assembly. At the hydroxo-bridges at the shared faces the Ni(1)–O(5) distance is 2.09 Å and the Ni(2)–O(6) distance is 2.22 Å. This reflects a

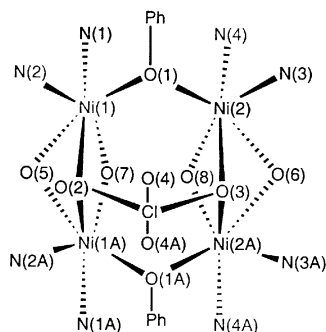


Fig. 2 Schematic representation of the tetranuclear array.

hydrogen bonding interaction of the hydroxide at O(6) with a water molecule at O(3W) [O(6)⋯O(3W), 2.66 Å]; such an interaction is absent at O(5). The oxygen atom O(7) from the hydrated hydroxide anion is hydrogen bonded to a proximal water molecule O(1W) [O(7)⋯O(1W), 2.70 Å]. All of the non-bonded water molecules are disordered as is one of the two methanol molecules.

The work described above describes the first example of a tetranuclear nickel(II) complex assembled from an asymmetric compartmental ligand and bearing a tetranucleating intramolecular [H<sub>3</sub>O<sub>2</sub>]<sup>–</sup> bridge. *Caution!* Although we have experienced no difficulties with the perchlorate salt it should nevertheless be regarded as hazardous and treated with care.

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## Notes and references

- M. Ruf, K. Weis and H. Vahrenkamp, *J. Am. Chem. Soc.*, 1996, **118**, 9228–9294.
- F. Meyer and P. Rutsch, *Chem. Commun.*, 1998, 1037–1038.
- F. Meyer, E. Kaifer, P. Kircher, K. Heinz and H. Pritzkow, *Chem. Eur. J.*, 1999, **5**, 1617–1630.
- D. E. Fenton and H. Okawa, *Chem. Ber./Recl.*, 1997, **130**, 433–442.
- J. D. Crane, D. E. Fenton, J. M. Latour and A. J. Smith, *J. Chem. Soc., Dalton Trans.*, 1991, 2979.
- M. Lubben, R. Hage, A. Meetsma, K. Byma and B. L. Feringa, *Inorg. Chem.*, 1995, **34**, 2217.
- J. Reim and B. Krebs, *J. Chem. Soc., Dalton Trans.*, 1997, 3793.
- S. Uozumi, M. Ohba, H. Okawa and D. E. Fenton, *Chem. Lett.*, 1997, 673–674.
- S. Uozumi, H. Furutachi, M. Ohba, H. Okawa, D. E. Fenton, K. Shindo, M. Murata and D. J. Kitko, *Inorg. Chem.*, 1998, **37**, 6281–6287.
- H. Adams, D. E. Fenton, S. R. Haque, S. L. Heath, M. Ohba, H. Okawa and S. E. Spey, *J. Chem. Soc., Dalton Trans.*, 2000, 1849–1856.
- H. Adams, S. Clunas, D. E. Fenton and S. E. Spey, *J. Chem. Soc., Dalton Trans.*, in press.
- H. Adams, S. Clunas and D. E. Fenton, *Inorg. Chem. Commun.*, 2001, **4**, 667–670.
- S. R. Haque, PhD Thesis, University of Sheffield, 1999.
- Crystal data for [Ni<sub>4</sub>(L<sup>5</sup>)<sub>2</sub>(OH)<sub>3</sub>(OH<sub>2</sub>)ClO<sub>4</sub>](PF<sub>6</sub>)<sub>2</sub>·2CH<sub>3</sub>OH·4H<sub>2</sub>O (**1**), C<sub>44</sub>H<sub>83</sub>ClF<sub>12</sub>N<sub>8</sub>Ni<sub>4</sub>O<sub>16</sub>P<sub>2</sub>, *M* = 1540.41, monoclinic, *a* = 11.337(6), *b* = 22.608(11), *c* = 11.892(6) Å, *α* = 90, *β* = 90.706(9), *γ* = 90°, *U* = 3048(3) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.679 Mg m<sup>–3</sup>, space group *P2<sub>1</sub>/m*, *μ*(Mo-K $\alpha$ ) = 1.419 mm<sup>–1</sup>, *F*(000) = 1596. 12274 Reflections measured, 4109 independent [*R*<sub>int</sub> = 0.1430] which were used in all calculations. The final *R*<sub>1</sub> [1700 *F* > 3 $\sigma$ (*F*)] was 0.0787 and *wR*<sub>2</sub> (all data) was 0.2138. CCDC reference number 172114. See <http://www.rsc.org/suppdata/cc/b1/b109019b/> for crystallographic data in CIF or other electronic format.
- J. Emsley, *Chem. Soc. Rev.*, 1980, **9**, 91–124.
- A. M. Barrios and S. J. Lippard, *Inorg. Chem.*, 2001, **40**, 1250–1255.