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Dinuclear nickel(II) complexes of reduced asymmetric compartmental ligands †

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The reaction of the reduced asymmetric compartmental proligand 2-{[(2-dimethylaminoethyl)ethylamino]methyl}-4-methyl-6-{[(pyridin-2-ylmethyl)amino]methyl}phenol, **HL**^{4} with nickel(II) acetate in the presence of non-coordinating anions gave dinuclear nickel(II) complexes. The crystal structures of $[Ni_2\mathbf{L}^6(OAc)(\mu\text{-}OAc)(OH_2)(CH_3OH)][PF_6]$, **2**, $[Ni_2\mathbf{L}^4(\mu\text{-}OAc)_2(CH_3OH)][PF_6]$, **3**, $[Ni_2\mathbf{L}^4(\mu\text{-}OAc)_2(OH_2)(CH_3OH)][PF_6]$, **4**, and $[Ni_2\mathbf{L}^4(\mu\text{-}OAc)_2(CH_3OH)_2][BPh_4]$, **5**, are reported. 2-[(2-Dimethylaminoethylamino)methyl]-6-{[(2-dimethylaminoethyl)ethylamino]methyl}-4-methylphenol, **HL**^{5}, was found to react with $Ni(ClO_4)_2\cdot 4H_2O$ and $NaBPh_4$ in the presence of urea. to give $[Ni_2\mathbf{L}^5(OH)(OH_2)_2(urea)][BPh_4]_2$, **6**, the dinuclear core of which bears some resemblance to that of the active site in urease. The crystal structure reveals the presence of a hydroxo-bridge and an O-bonded molecule of urea.

Introduction

X-Ray crystallographic studies on urease isolated from different sources [*Klebsiella aerogenes*[1,2] and the native and inhibited metalloenzyme from *Bacillus pasterii*[3–5]] have provided a detailed description of the active site (Fig. 1). The dinickel(II)

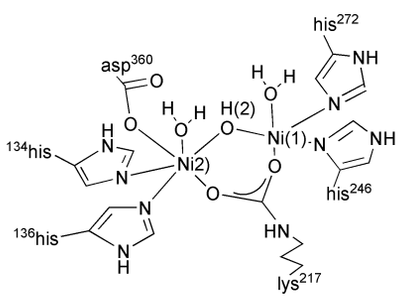
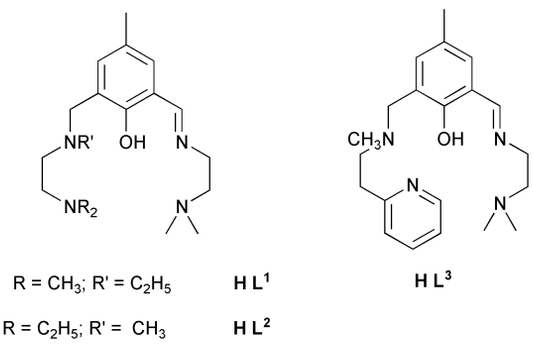


Fig. 1 Schematic depiction of the active site in urease.

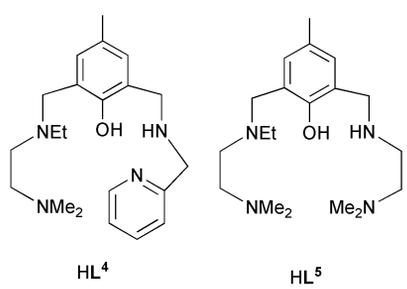
centre has each nickel(II) ion ligated by two histidine residues from the protein and a carbamylated lysine residue bridges the nickel(II) ions. Ni(2) is further ligated by an aspartate residue and two terminally coordinated water molecules and one bridging water molecule, or hydroxide ion completes the coordination environments at the metal ions. Consequently Ni(1) has a distorted square pyramidal environment and Ni(2) a pseudo-octahedral environment. The asymmetry of the metallobiosite and curiosity as to how it functions in the hydrolysis of urea have determined that urease can serve as a muse for the bio-inorganic chemist and so inspire the generation of a range of bio-resemblant coordination chemistry.

Unsymmetrical compartmental proligands such as **HL**^{1}–**HL**^{3} provide adjacent, dissimilar binding sites which can each accommodate a metal and so produce dinuclear complexes with coordination environments resembling the active site in urease.[6–9]

Reaction of **HL**^{1} and **HL**^{2} with copper(II) perchlorate has been found to give the complexes $[Cu_2OH\mathbf{L}^n](ClO_4)_2$ in which the integrity of the compartmental is retained and a hydroxo-bridge spans the Cu(II) atoms.[10] It was anticipated that in the corresponding reactions with nickel(II) perchlorate a bio-resemblant Ni–OH–Ni bridge would be formed however with **HL**^{1}–**HL**^{3} hydrolytic cleavage of the pendant imine.[10,11] As the reactions of **HL**^{1}–**HL**^{3} with nickel(II) acetate in the presence of



a coordinating anion such as the isothiocyanate anion $[NCS^-]$ had provided dinuclear nickel(II) complexes in which the ligand remains intact[12] it was proposed that the criteria for cleavage of the iminic pendant arm in metal complexes of unsymmetrical Schiff base compartmental ligands are the presence of both weakly or non-coordinating anions (ClO_4^-, BF_4^-) and nickel(II) cations. It was also suggested that the reaction proceeded through the activation of coordinated water at a nickel(II) ion or by initial formation of a hydroxo bridge at the dinickel centre.



In order to encourage hydroxo-bridge formation in dinuclear nickel(II) complexes in the presence of weakly or non-coordinating anions the asymmetric compartmental proligand **HL**^{3} was reduced to the di-aminic analogue **HL**^{4}. In an early study **HL**^{4} was reacted with $Ni(ClO_4)_2\cdot 6H_2O$ in ethanol with addition of $NaPF_6$ to facilitate crystallisation; solution of the crystal structure of the product revealed that a tetranuclear complex, $[Ni_4(\mathbf{L}^4)_2(OH)_3(OH_2)ClO_4](PF_6)_2\cdot 2CH_3OH\cdot 5H_2O$, had been formed.[13] It was suggested that, by analogy with the formation of $[Cu_2OH\mathbf{L}^n]^{2+}$ noted above, a μ-hydroxo bridged dinickel(II) species such as **1** provides the precursor for the tetranuclear assembly.

† *In memoriam* Noel McAuliffe (1941–2002).

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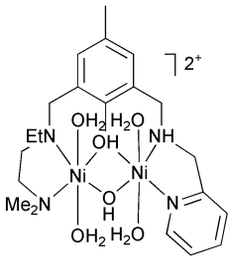


1

This paper reports an investigation of the reactions of the reduced proligands **HL**^{4} and **HL**^{5} with nickel(II) acetate and salts of non-coordinating anions thus eliminating the involvement of the anion in bridge building. The crystal structures of $[Ni_2(\mathbf{L}^4)(OAc)(\mu\text{-}OAc)(OH_2)(CH_3OH)][PF_6]$, **2**, $[Ni_2(\mathbf{L}^4)(\mu\text{-}OAc)_2(CH_3OH)][PF_6]$, **3**, $[Ni_2(\mathbf{L}^4)(\mu\text{-}OAc)_2(OH_2)(CH_3OH)][PF_6]$, **4**, $[Ni_2(\mathbf{L}^4)(\mu\text{-}OAc)_2(CH_3OH)_2][BPh_4]$, **5**, and $[Ni_2(\mathbf{L}^5)(OH)(OH_2)_2(urea)][BPh_4]_2$, **6**, are reported.

Experimental

Elemental analyses were carried out by the University of Sheffield microanalytical service. Infrared spectra were recorded as KBr discs or as liquid films between NaCl plates, using a Perkin Elmer 297 (4000–600 cm^{-1}) or a Perkin Elmer 1600 (4000–400 cm^{-1}) infrared spectrophotometer. ^1H nmr spectra were recorded using a Bruker ACF-250 spectrometer. Mass spectra (FAB and EI) were recorded using Micromass PROSPEC spectrometer (the matrix used was 4-nitrobenzyl alcohol).

Ligand synthesis

The ligand precursor 3-{[(2-dimethylaminoethyl)ethylamino]-methyl}-2-hydroxy-5-methyl benzaldehyde (A) was prepared as previously described.[10,12]

2-{[(2-Dimethylaminoethyl)ethylamino]methyl}-4-methyl-6-{[(pyridin-2-ylmethyl)amino]methyl}phenol, HL^4. 2-(aminomethyl)pyridine (204 mg, 1.89 mmol) was added to solution of precursor A (500 mg, 1.89 mmol) in ethanol (40 cm^3). The reaction mixture was then heated to reflux for 20 min and allowed to cool. $NaBH_4$ (144 mg, 3.79 mmol) was added portion wise with stirring. The reaction was then stirred at rt overnight. The solvent was removed under reduced pressure and the residue dissolved in a small volume of water. HCl (2 M) was added to acidify the solution (pH 3), which was then extracted with CH_2Cl_2 (2 × 20 cm^3). NaOH (5 M) was then added and the aqueous layer (pH 10) extracted with CH_2Cl_2 (3 × 40 cm^3). The solvent was removed under reduced pressure to yield the product as a colourless oil. Yield: 502 mg (74%).

δ_H (250 MHz, $CDCl_3$, 298 K): 8.49(1H, s, pyH), 7.55(1H, m, pyH), 7.28(1H, d, pyH), 7.07(1H, m, pyH), 6.81(1H, d, ArH), 6.66(1H, d, ArH), 3.82(2H, s, $ArCH_2$), 3.76(2H, s, $ArCH_2$), 3.66(2H, s, $ArCH_2$), 2.61–2.38(6H, m, CH_2), 2.11(3H, s, $ArCH_3$), 2.10(6H, s, NCH_3). 0.98(3H, t, CH_3). Selected IR data (ν/cm^{-1}): 2818, 1467, 1235, 1157, 1041, 780. MS (*m*/*z*): 356. Anal. Found: C, 66.52; H, 8.71; N, 14.00. Calcd for $C_{21}H_{32}N_4O\cdot 1.25H_2O$: C, 66.55; H, 9.17; N, 14.78%.

2-[(2-Dimethylaminoethylamino)methyl]-6-{[(2-dimethylaminoethyl)ethylamino]methyl}-4-methylphenol, HL^5. *N*,*N*-dimethylethylenediamine (333 mg, 3.79 mmol) was added to solution of precursor A (1.00 g, 3.79 mmol) in ethanol (70 cm^3). The reaction mixture was then heated to reflux for 20 min and allowed to cool. $NaBH_4$ (288 mg, 7.57 mmol) was added portion wise with stirring. The reaction was then stirred at rt overnight. The solvent was removed under reduced pressure and the residue dissolved in a small volume of water. HCl (2 M) was added to acidify the solution (pH 3), which was then extracted with CH_2Cl_2 (2 × 30 cm^3). NaOH (5 M) was then added and the aqueous layer (pH 10) extracted with CH_2Cl_2 (3 × 60 cm^3). The solvent was removed under reduced pressure to yield the product as a colourless oil. Yield: 911 mg (72%).

δ_H (250 MHz, $CDCl_3$, 298 K): 6.85(1H, d, ArH), 6.63(1H, d, ArH), 3.71(2H, s, $ArCH_2$), 3.61(2H, s, $ArCH_2$), 2.70–2.32(10H, m, CH_2), 2.11(3H, s, $ArCH_3$), 2.10(12H, s, NCH_3). 0.98(3H, t, CH_3). δ_C (62.5 MHz, $CDCl_3$, 298 K): 154(aromatic, 4 °C), 129, 128(aromatic, CH), 127, 126, 122(aromatic, 4 °C), 59, 56, 55, 49, 47, 46, 45(CH_2), 44, 20, 11(CH_3). Selected IR data (ν/cm^{-1}): 2970, 2820, 1592, 1474, 1234, 1043, 756. MS (*m*/*z*): 336. Anal. Found: C, 65.02; H, 11.07; N, 15.38. Calcd for $C_{19}H_{36}N_4O\cdot H_2O$: C, 64.37; H, 10.80; N, 15.80%.

Complexation reactions

$[Ni_2L^4(OAc)(\mu\text{-}OAc)(CH_3OH)(OH_2)](PF_6)$ 2. $Ni(OAc)_2\cdot 4H_2O$ (139 mg, 0.560 mmol) was added to a solution of **HL**^{6} (100 mg, 0.280 mmol) in methanol (10 cm^3). After stirring for 30 min, the addition of $NaPF_6$ (94 mg, 0.560 mmol) to the solution resulted in the formation of green crystals. Yield: 85 mg (39%).

Selected IR data (ν/cm^{-1}) using KBr disk: 2996, 2933, 1608, 1443, 1381, 1014, 845. MS (*m*/*z*): 589($MH^+ - CH_3OH$, 100%). Anal. Found: C, 39.24; H, 5.46; N, 7.07. Calcd for $C_{26}H_{43}F_6N_4Ni_2O_7P$: C, 39.69; H, 5.47; N, 7.12.

$[Ni_2L^4(\mu\text{-}OAc)_2(CH_3OH)(OH_2)][Ni_2L^6(OAc)_2(CH_3OH)](PF_6)_2\cdot 2H_2O$ 3/4. This was obtained as green crystals by an identical procedure to that above using **HL**^{6} (100 mg, 0.280 mmol), $Ni(OAc)_2\cdot 4H_2O$ (139 mg, 0.560 mmol) and $NaPF_6$ (94 mg, 0.560 mmol). Yield: 62 mg, 29%.

Selected IR data (ν/cm^{-1}) using KBr disk: 2989, 2899, 1604, 1478, 1043, 855, 761. MS (*m*/*z*): 589 ($MH^+ - CH_3OH$, 100%). Anal. Found for the bulk sample: C, 38.03; H, 5.06; N, 7.10. Calcd for $C_{52}H_{88}F_{12}N_8Ni_4O_{15}P_2\cdot 2H_2O$: C, 38.42; H, 5.66; N, 6.89%.

$[Ni_2L^4(\mu\text{-}OAc)_2(CH_3OH)_2](BPh_4)$ 5. $Ni(OAc)_2\cdot 4H_2O$ (139 mg, 0.560 mmol) was added to a solution of **HL**^{6} (100 mg, 0.280 mmol) in methanol (10 cm^3). After stirring for 30 min, the addition of $NaBPh_4$ (192 mg, 0.560 mmol) to the solution resulted in the formation of green crystals. Yield: 68 mg (25%).

Selected IR data (ν/cm^{-1}) using KBr disk: 3055, 2919, 1608, 1481, 1313, 1022, 733. MS (*m*/*z*): 589($MH^+ - 2\ CH_3OH$, 100%). Analysis. Found for the bulk sample: C, 59.13; H, 6.73; N, 5.50. Calcd for $C_{53}H_{70}BN_4Ni_2O_9\cdot 2H_2O$: C, 59.42; H, 6.96; N, 5.25%.

$[Ni_2L^5(OH)(OH_2)_2(urea)](BPh_4)$ 6. $Ni(ClO_4)_2\cdot 6H_2O$ (326 mg, 0.893 mmol) was added to a solution of **HL**^{7} (150 mg, 0.446 mmol) in methanol (10 cm^3). After stirring for 30 min, the addition of urea (134 mg, 2.23 mmol) followed by $NaBPh_4$ (305 mg, 0.893 mmol) to the solution resulted in the formation of green crystals. Yield: 157 mg (28%).

Selected IR data (ν/cm^{-1}) using KBr disk: 3427, 3054, 1660, 1580, 1427, 736, 707. MS (*m*/*z*): 471($MH^+ -$ (urea + $2H_2O$), 100%). Bulk sample analyses were inconsistent due to contamination with urea, even after washing with water. A representative analysis gave, Found: C, 61.11; H, 6.96; N, 8.11. Calcd for $C_{68}H_{88}B_2N_6Ni_2O_7\cdot H_2O\cdot$urea: C, 61.18; H, 7.29; N, 8.27%.

X-Ray crystallography

The X-ray crystallographic data are summarised in Table 1. Data were collected at 150(2) K, using a Siemens SMART CCD area diffractometer (graphite monochromated Mo-Kα X-radiation, λ = 0.71073 Å) with an Oxford Cryosystems low temperature system. The data were corrected for Lorentz and

Table 1 Summary of crystallographic data for $[Ni_2(\mathbf{L}^4)(OAc)(\mu\text{-}OAc)(OH_2)(CH_3OH)][PF_6]$, **2**; $[Ni_2(\mathbf{L}^4)(\mu\text{-}OAc)_2(CH_3OH)][PF_6]\cdot[Ni_2(\mathbf{L}^4)(\mu\text{-}OAc)_2(OH_2)(CH_3OH)][PF_6]\cdot 2H_2O$, **3/4**; $[Ni_2(\mathbf{L}^4)(\mu\text{-}OAc)_2(CH_3OH)_2][BPh_4]\cdot 2MeOH$, **5**; and $[Ni_2(\mathbf{L}^4)(OH)(OH_2)_2(urea)][BPh_4]_2\cdot 2H_2O$, **6**

	2	**3/4**	**5**	**6**
Empirical formula	$C_{26}H_{43}F_6N_4Ni_2O_7P$	$C_{52}H_{88}F_{12}N_8Ni_4O_{15}P_2$	$C_{53}H_{70}BN_4Ni_2O_9$	$C_{68}H_{88}B_2N_6Ni_2O_7$
Formula weight	786.03	1590.08	1035.36	1240.48
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a/Å	11.771(2)	20.653(6)	11.2426(17)	11.728(4)
b/Å	16.086(3)	10.707(3)	13.318(2)	14.200(5)
c/Å	17.687(3)	31.6276(9)	18.752(3)	21.057(7)
αÅ	90	90	71.951(3)	79.907(7)
β/Å	103.915(4)	92.049(5)	82.185(3)	75.858(7)
γ/Å	90	90	88.779(3)	78.937(6)
V/Å^3	3250.9(10)	6989(3)	2644.0(7)	3306.8(19)
ρ_{calc}/Mg m^{-3}	1.606	1.511	1.300	1.246
Z	4	4	2	2
μ/mm^{-1}	1.291	1.203	0.769	0.625
Data/restraints/parameters	7829 /36 /415	16858 /16 /857	11960 /26 /673	14525 /460 /766
R	0.0613	0.0629	0.0796	0.0955
wR_2	0.1589	0.1702	0.2507	0.3084

polarisation effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined by full matrix least squares methods on F^2. Hydrogen atoms were placed geometrically and refined with a riding model and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. The programs used in the determination and refinement of the structures were Siemens SMART and SAINT for control and integration software[14] and SHELXTL as implemented on the Viglen Pentium computer.[15]

CCDC reference numbers 194355–194358.

See http://www.rsc.org/suppdata/dt/b2/b209437c/ for crystallographic data in CIF or other electronic format.

Results and discussion

In order to remove the risk of hydrolytic cleavage occurring in reactions of asymmetric compartmental ligands with nickel salts in the presence of weakly or non-coordinating anions the Schiff base proligands $H\mathbf{L}^1$ and $H\mathbf{L}^3$ were reduced. The reduced proligands were then reacted with $Ni(OAc)_2$ in the presence of $NaPF_6$ or $NaBPh_4$; $NaClO_4$was avoided as it had induced anion bridging in complex **1**.

The reaction of $H\mathbf{L}^4$ with $Ni(OAc)_2\cdot 4H_2O$ and $NaPF_6$ gave the dinuclear complex $[Ni_2(\mathbf{L}^4)(OAc)(\mu\text{-}OAc)(OH_2)(CH_3OH)][PF_6]$, **2**. The crystal structure was solved and revealed a basic dinuclear core derived from a bridging cresolate-O atom and a *syn–syn* bidentate bridging acetate anion. An ORTEP view of **2** is shown in Fig. 2 together with the numbering schemes. Selected bond lengths and angles relevant to the coordination geometries are given in the caption to the figure. In this complex each nickel(II) atom is six-coordinate. This is achieved at Ni(1) by further interaction with the articular N(Et) atom and terminal $N(Me_2)$ of one arm of the ligand and with a chelating acetate anion. At Ni(2) there is further coordination from the second ligand arm *via* the articular N(H) and pyridinyl N atoms, a water molecule and a methanol molecule. This gives the complex a donor asymmetry,[16] both donor sets are $\{N_2O_4\}$ but the precise natures of the donor atoms are quite diverse.

Chelation from the pendant nitrogen atoms provides five-membered chelate rings at each nickel(II) atom. The octahedral coordination at the nickel atoms is distorted with the greater distortion at the nickel atom, Ni(1), bearing the chelated acetate [O(4)–Ni(1)–N(1), 177.32(18); N(2)–Ni(1)–O(2), 160.28(18); O(1)–Ni(1)–O(3), 159.52(16)° and O(1)–Ni(2)–O(6), 178.27(16); O(7)–Ni(2)–N(3), 169.74(18); N(4)–Ni(2)–O(5), 175.16(18)°]. The cresolato-bridge is non-symmetric and the Ni ··· Ni separation is 3.5419(12) Å. The chelating angle, O(3)–C(22)–O(2), in the monobridging acetate is normal,

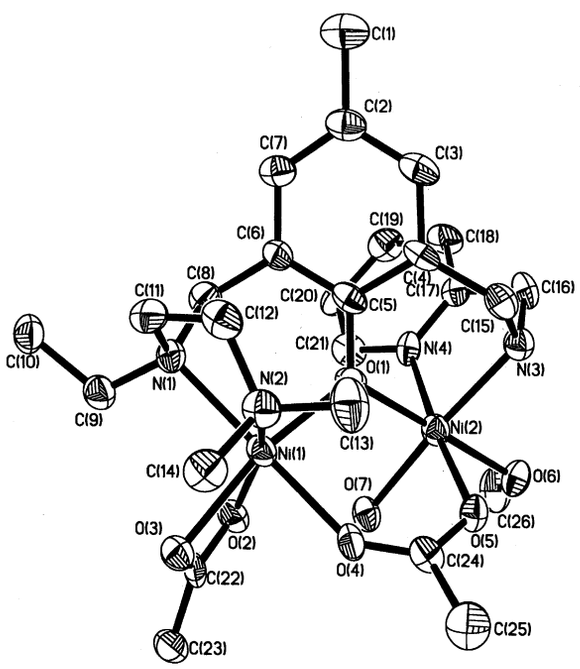


Fig. 2 An ORTEP drawing of the molecular structure of **2** showing the atom labelling; thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths and angles at the metal atoms: Ni(1)–O(1), 2.019(4); Ni(1)–O(4), 2.065(4); Ni(1)–N(2), 2.082(5); Ni(1)–O(2), 2.125(4); Ni(1)–N(1), 2.131(5); Ni(1)–O(3), 2.134(4); Ni(2)–O(1), 2.042(4); Ni(2)–N(4), 2.042(5); Ni(2)–O(5), 2.060(4); Ni(2)–O(7), 2.067(4); Ni(2)–N(3), 2.078(5); Ni(2)–O(6), 2.143(4); Ni(1)–Ni(2), 3.5419(12) Å. Ni(1)–O(1)–Ni(2), 121.40(19); O(4)–C(22)–O(5), 117.3(6); O(4)–Ni(1)–N(1), 177.32(18); N(2)–Ni(1)–O(2), 160.28(18); O(1)–Ni(1)–O(3), 159.52(16); O(1)–Ni(2)–O(6), 178.27(16); O(7)–Ni(2)–N(3), 169.74(18); N(4)–Ni(2)–O(5), 175.16(18)°.

120.6(6)° whereas the bridging angle, O(4)–C(24)–O(5), of the *syn–syn* bridging acetate is more open, 124.9(6)°.

The reaction of $H\mathbf{L}^4$ with $Ni(OAc)_2\cdot 4H_2O$ and $NaPF_6$ also gave the dinuclear complex $[Ni_2(\mathbf{L}^4)(\mu\text{-}OAc)_2(CH_3OH)][PF_6]$, **3**, which co-crystallised with $[Ni_2(\mathbf{L}^4)(\mu\text{-}OAc)_2(OH_2)(CH_3OH)][PF_6]$, **4**, and two molecules of water. The crystal structure was solved and again showed a basic dinuclear core derived from a bridging cresolate-O atom and a *syn–syn* bidentate bridging acetate anion. This was augmented by a second *syn–syn* bidentate bridging acetate anion. An ORTEP view of **3** is shown in Fig. 3 together with the numbering schemes. Selected bond lengths and angles relevant to the coordination geometries are given in the caption to the figure. In this complex one nickel(II) atom, Ni(2) bound by the pyridinyl containing arm, is

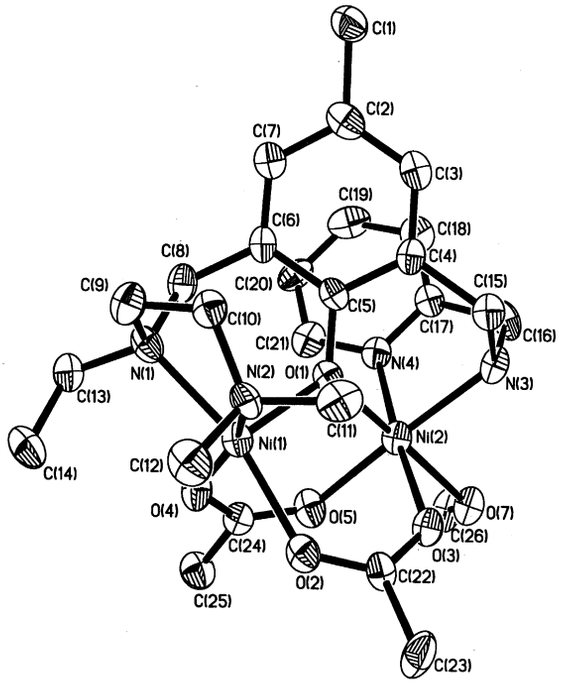


Fig. 3 An ORTEP drawing of the molecular structure of **3** showing the atom labelling; thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths and angles at the metal atoms: Ni(1)–O(1), 1.948(4); Ni(1)–O(4), 1.983(4); Ni(1)–O(2), 2.058(5); Ni(1)–N(1), 2.089(6); Ni(1)–N(2), 2.103(5); Ni(2)–O(1), 2.001(4); Ni(2)–O(5), 2.039(5); Ni(2)–N(4), 2.067(6); Ni(2)–O(3), 2.079(4); Ni(2)–N(3), 2.083(5); Ni(2)–O(7), 2.128(4); Ni(1)–Ni(2), 3.3346(14) Å. Ni(1)–O(1)–Ni(2), 115.2(2); O(4)–C(24)–O(5), 126.9(6); O(2)–C(22)–O(3), 115.9(6); O(1)–Ni(2)–O(7), 175.20(17); N(4)–Ni(2)–O(3), 175.1(2); N(3)–Ni(2)–O(5), 170.81(19); N(1)–Ni(1)–O(2), 164.99(19); N(2)–Ni(1)–O(4), 160.5(2); O(1)–Ni(2)–N(1), 96.40(19); O(1)–Ni(1)–O(4), 99.74(18); O(1)–Ni(1)–O(2), 98.42(18); O(1)–Ni(1)–N(2), 99.57(19)°.

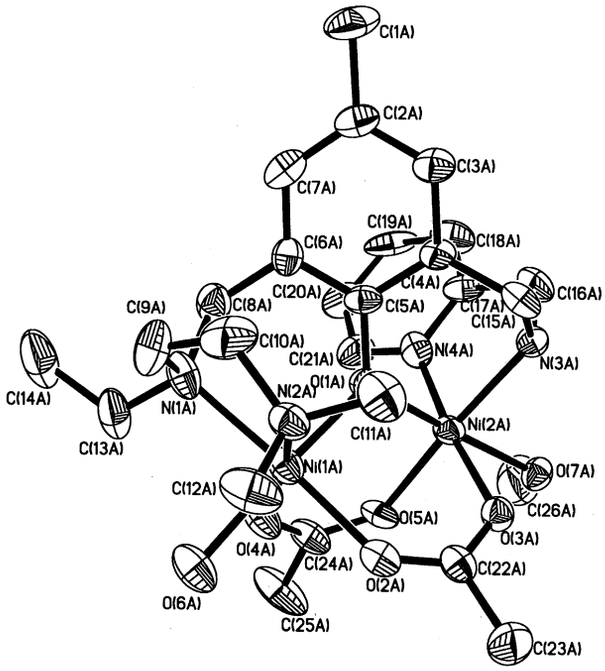


Fig. 4 An ORTEP drawing of the molecular structure of **4** showing the atom labelling; thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths and angles at the metal atoms: Ni(1A)–O(1A), 1.992(4); Ni(1A)–O(4A), 2.051(5); Ni(1A)–O(2A), 2.065(5); Ni(1A)–N(1A), 2.161(6); Ni(1A)–O(6A), 2.171(5); Ni(1A)–N(2A), 2.175(6); Ni(2A)–O(5A), 2.014(5); Ni(2A)–O(1A), 2.023(5); Ni(2A)–N(4A), 2.027(6); Ni(2A)–N(3A), 2.058(5); Ni(2A)–O(3A), 2.074(5); Ni(2A)–O(7A), 2.145(4); Ni(1A)–Ni(2A), 3.4171(14) Å. Ni(1A)–O(1A)–Ni(2A), 116.7(2); O(4A)–C(24A)–O(5A), 117.9(7); O(2A)–C(22A)–O(3A), 127.1(7); O(2A)–Ni(1A)–N(1A), 173.5(2); O(1A)–Ni(1A)–O(6A), 171.63(19); O(4A)–Ni(1A)–N(2A), 167.4(2); O(1A)–Ni(2A)–O(7A), 175.39(18); O(3A)–Ni(2A)–N(4A), 174.0(2); N(3A)–Ni(2A)–O(5A), 169.7(2)°.

six-coordinate and the second nickel(II) atom, Ni(1) is five coordinate. At Ni(2) there is further coordination from the ligand arm *via* the articular N(H) and pyridinyl N atoms and a methanol molecule. At Ni(1) there is further interaction with the articular N(Et) atom and terminal $N(Me_2)$ of the second arm of the ligand. No significant electron density was found at the vacant site and so the geometry is square pyramidal [τ = 0.075;[17] O(4)–Ni(1)–N(2), 160.5(2); N(1)–Ni(1)–O(2), 164.99(19)°]. This gives the complex a coordination number [5,6] and geometric asymmetry[16] with donor sets $\{N_2O_3\}$ and $\{N_2O_4\}$.

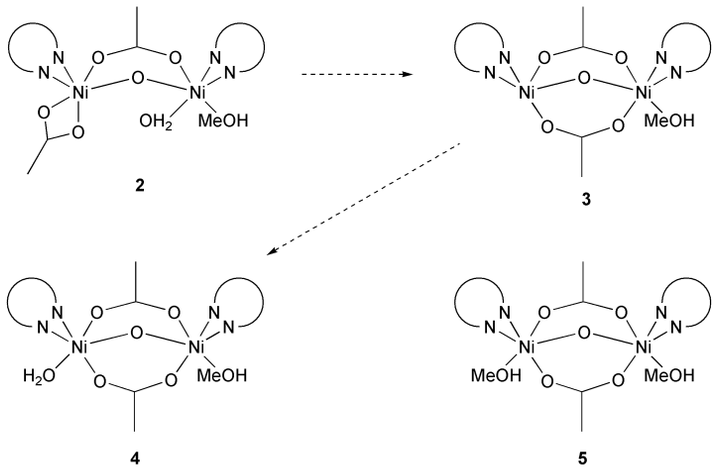
Chelation from the pendant nitrogen atoms provides five-membered chelate rings at each nickel(II) atom and the octahedral coordination at Ni(2) is more regular than at the nickel atoms in **2**, [O(1)–Ni(2)–O(7), 175.20(17); N(4)–Ni(2)–O(3), 175.1(2); N(3)–Ni(2)–O(5), 170.81(19)°]. The cresolato-bridge is non-symmetric and the Ni ··· Ni separation is 3.3346(14) Å, shorter than that in **2**.

An ORTEP view of **4** is shown in Fig. 4 together with the numbering schemes. Selected bond lengths and angles relevant to the coordination geometries are given in the caption to the figure. The vacant site noted in **3** is occupied by a water molecule in the molecular structure of **4**. There is a basic dinuclear core derived from a bridging cresolate-O atom and a *syn–syn* bidentate bridging acetate anion again augmented by a second *syn–syn* bidentate bridging acetate anion.

Each nickel(II) atom is six-coordinate and this is achieved at Ni(1A) by further interaction with the articular N(Et) atom and terminal $N(Me_2)$ of one arm of the ligand and with a water molecule. At Ni(2A) there is further coordination from the second ligand arm *via* the articular N(H) and pyridinyl N atoms and a methanol molecule. The complex is thus donor asymmetrical, both donor sets are $\{N_2O_4\}$ but the precise natures of the donor atoms are quite diverse. Chelation from the pendant nitrogen atoms provides six-membered chelate rings at each nickel(II) atom and the octahedral coordination at the nickel atoms is distorted [O(2A)–Ni(1A)–N(1A), 173.5(2); O(1A)–Ni(1A)–O(6A), 171.63(19); O(4A)–Ni(1A)–N(2A), 167.4(2)° and O(1A)–Ni(2A)–O(7A), 175.39(18); O(3A)–Ni(2A)–N(4A), 174.0(2); N(3A)–Ni(2A)–O(5A), 169.7(2)°]. The cresolato-bridge is non-symmetric and the Ni ··· Ni separation is 3.4171(14) Å, intermediate to the separations in **2** and **3**.

$[Ni_2(\mathbf{L}^4)(\mu\text{-}OAc)_2(CH_3OH)_2][BPh_4]$, **5**, was isolated when $[BPh_4]^-$ was used as the counter ion in the reaction of $\mathbf{HL}^4$ with $Ni(OAc)_2{\cdot}4H_2O$. The crystal structure was solved and showed similarity to that of **4**. The molecular structure is shown in Fig. 5 together with the numbering schemes. The significant difference from **4** is that methanol molecules are coordinated to Ni(2) and Ni(1) where previously a water molecule and a methanol molecule were coordinated. The atoms C(9), N(2) and C(20) of one aminic arm are disordered and were refined to occupancies of 61.5% : 38.5%.

It is intriguing that complexes **2**–**4** are crystallised from solutions prepared under the same reaction conditions in the presence of $[PF_6]^-$ anions. This suggests that there is a similar speciation in solution with only subtle changes in the solubility of the complexes or the conditions of crystallisation, for example variable temperature drop in the laboratory overnight, leading to the analysed product. The reactions were carried out in different laboratories at different times of the year; **3**/**4** was crystallised in one laboratory during the autumn and **5** in a refurbished laboratory during the following spring. To explain our results requires a detailed knowledge of the speciation in



Scheme 1 Schematic representations of the dinickel(II) cores present in **2**–**5**.

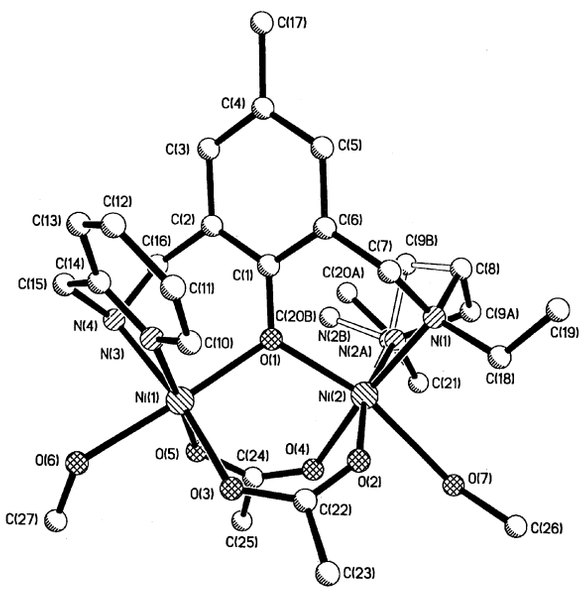


Fig. 5 An ORTEP drawing of the molecular structure of **5** showing the atom labelling; thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths and angles at the metal atoms: Ni(1)–O(1), 2.023(3); Ni(1)–N(3), 2.066(4); Ni(1)–O(3), 2.06(4); Ni(1)–O(5), 2.070(4); Ni(1)–N(4), 2.092(5); Ni(1)–O(6), 2.142(4); Ni(2)–O(2), 2.004(5); Ni(2)–O(1), 2.011(4); Ni(2)–O(4), 2.038(4); Ni(2)–N(1), 2.122(4); Ni(2)–N(2A), 2.149(6); Ni(2)–N(2B), 2.152(7); Ni(2)–O(7), 2.379(6); Ni(1)–Ni(2), 3.4268(11) Å. Ni(1)–O(1)–Ni(2), 116.31(16); O(2)–C(22)–O(3), 126.1(5); O(4)–C(24)–O(5), 125.6(6); O(1)–Ni(1)–O(6), 175.50(15); N(3)–Ni(1)–O(5), 174.28(16); O(3)–Ni(1)–N(4), 169.53(17); O(4)–Ni(2)–N(1), 172.13(18); O(2)–Ni(2)–N(2A), 166.6(3); O(2)–Ni(2)–N(2B), 169.2(52); O(1)–Ni(1)–O(7), 166.20(16)°.

solution and as this cannot be accessed a hypothesis for the formation of the complexes is advanced. Schematic representations of the dinickel(II) cores present in **2**–**5** are depicted in Scheme 1.

Complexes **2** and **3** represent extremes of the carboxylate shift — the movement of a bound carboxlate from being chelated to forming a monodentate bridge and then a bidentate bridge.[18,19] Migration of an O-atom from the chelated acetate to replace a water molecule on the second nickel atom would generate a vacant site at the first nickel atom. This could then be filled by a water molecule to generate **4**, or by a MeOH molecule to generate **5**. It is probable that in solution the coordinated solvent molecules are quite labile and so complex **5** could also from arise from **4** by solvent exchange. In the present study this complex was isolated and recovered with the $[BPh_4]^-$ cation present — this might be a consequence of solubilities varying with counterion.

Realisation of the formation a hydroxo-bridge occurred in the absence of acetate *via* the reaction of HL^5 with $Ni(ClO_4)_2 \cdot 6H_2O$, $NaBPh_4$ and urea. Poor quality crystals of $[Ni_2(L^5)(OH)(OH_2)_2(urea)][BPh_4]_2$, **6**, were recovered and the crystal structure solved. An ORTEP view is shown in Fig. 6 together with the numbering schemes. Selected bond lengths and angles relevant to the coordination geometries are given in the caption to the figure. In this complex there is a dinuclear core derived from a bridging cresolate-O atom and a hydroxide anion. The nickel(II) atom, Ni(1), bound by the ligand arm bearing an articular N(H) atom and a terminal NMe_2 group, is six-coordinate and the second nickel(II) atom, N(2), bound by the ligand arm bearing an articular N(Et) atom and a terminal NMe_2 group, is five coordinate. At Ni(1) the six coordination is completed by a water molecule and an O-bound urea molecule.

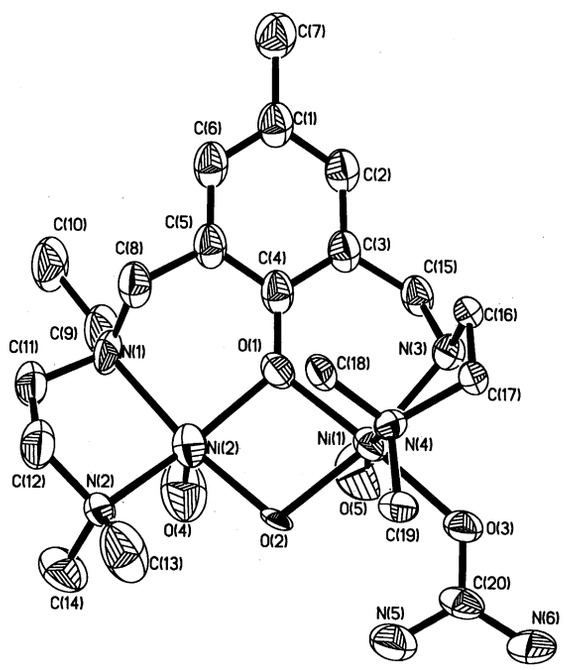
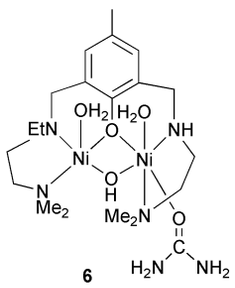


Fig. 6 An ORTEP drawing of the molecular structure of **6** showing the atom labelling; thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths and angles at the metal atoms: Ni(1)–O(1), 2.016(5); Ni(1)–O(2), 2.032(4); Ni(1)–O(3), 2.038(6); Ni(1)–N(3), 2.054(6); Ni(1)–N(4), 2.110(6); Ni(1)–O(5), 2.153(7); Ni(2)–O(2), 1.940(5); Ni(2)–O(1), 1.960(5); Ni(2)–O(4), 2.041(7); Ni(2)–N(2), 2.069(7); Ni(2)–N(1), 2.091(7); Ni(1)–Ni(2), 3.0495(18) Å. Ni(1)–O(1)–Ni(2), 100.2(2); Ni(1)–O(2)–Ni(2), 100.3(2); N(4)–Ni(1)–O(5), 172.8(3); O(1)–Ni(1)–O(3), 171.7(2); N(3)–Ni(1)–O(2), 168.8(2); N(1)–Ni(2)–O(2), 167.1(2); N(2)–Ni(2)–O(1), 152.8(2); O(4)–Ni(2)–N(1), 100.3(3); O(4)–Ni(2)–O(2), 91.7 (3); O(4)–Ni(2)–O(1), 104.1(3); O(4)–Ni(2)–N(2), 103.0(3)°.

At Ni(2) five coordination is completed by a water molecule and the geometry is distorted square pyramidal [τ = 0.24;[17] O(2)–Ni(2)–N(1), 167.1(2); N(2)–Ni(2)–O(1), 152.8(2)°]. This gives the complex a coordination number [5,6] and geometric asymmetry with donor sets $\{N_2O_3\}$ and $\{N_2O_4\}$.

Chelation from the pendant nitrogen atoms provides five-membered chelate rings at each nickel(II) atom and the octahedral coordination at Ni(1) is distorted, [N(4)–Ni(1)–O(5), 172.8(3); O(1)–Ni(1)–O(3), 171.7(2); N(3)–Ni(1)–O(2), 168.8(2)°]. The cresolato-bridge is non-symmetric and the Ni ··· Ni separation is 3.0495(18) Å, reduced from the values found for **2**–**5** and reflecting the reduced connectivity of the bridges. The angles at the monoatomic bridges are similar, 100.2(2)° [Ni(1)–O(1)–Ni(2)] and 100.3(2)° [Ni(1)–O(1)–Ni(2)]. Both water molecules lie on the same side of the Ni(2)–O(1)–Ni(1)–O(2) molecular plane and the urea molecule is *cis*- to the water molecule at Ni(1).



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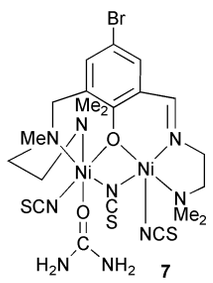
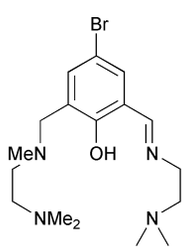


7

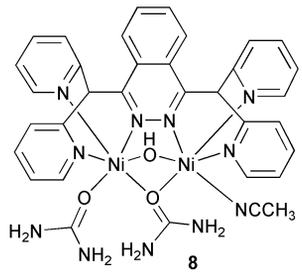
Complexes incorporating urea have been synthesised and used as models to help elucidate possible binding modes of the substrate to the dinickel(II) centre in urease.[20] Several model complexes have been prepared with urea bound to a nickel at the dinuclear through its carbonyl oxygen atom (η^1(O)-coordinated). Koga *et al*., prepared and structurally characterised $[Ni_2\mathbf{L}^6(\mu\text{-}CH_3COO)(CH_3COO)(urea)]BPh_4$, **7** from the Schiff base compartmental ligand H**L**^{6}.[7] Like complex **6** it is coordination number [5,6] and geometry asymmetric but with donor sets $\{N_4O_1\}$ and $\{N_4O_2\}$. The geometry at Ni_{iminic} is square pyramidal and that of N_{aminic} pseudo-octahedral, the Ni ··· Ni separation is 3.155 Å.



H **L**^{6}

In complex $[Ni_2\mathbf{L}^7(\mu\text{-OH})(\mu\text{-urea})(urea)(NCCH_3)](ClO_4)_3$, **8**, derived from 1,4-bis(2,2′dipyridylmethyl)phthalazine (**L**^{7}), there is one O-bound urea molecule and a second urea molecule that forms a unique single atom bridge (μ^2-κO) between the two metal ions *via* its carbonyl-O atom.[21] The μ^2-κO bridging mode had not been previously encountered for urea. The Ni ··· Ni separation is 3.079(4) Å compared to 3.6 Å in urease and 3.0495(12) Å in complex **6**.

Complex **8** has been found to effect the hydrolysis of urea upon heating *via* a two-step reaction.[21] In the first step a molecule of ammonia is eliminated from urea with concomitant formation of cyanate. When the cyanate-bearing product is further heated in the presence of water the cyanate is hydrolysed. Together these results established a precedence for the hydrolysis of urea *via* a cyanate intermediate as an alternative mechanism for the urease-catalysed hydrolysis of urea.



8

We have not yet been able to detect any hydrolysis of urea using complex **6** despite its having biosite resemblance through the bridging hydroxide and coordinated water molecules. It has been suggested that the unique single atom (μ^2-κO) bridging mode of urea detected in **8** might be of relevance to the enzyme urease in that the urea molecule would be better activated by coordination to two nickel atoms rather than simply to one — at this point the bonding mode of urea which permits the catalytic reaction in urease is not known.[21] The lack of reactivity with complex **6**, in which there is only a η^1(O)-coordinated urea, can be regarded as providing circumstantial support for this hypothesis.

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