The systematic generation of monodentate bridging ethanoates in dinuclear nickel(II) complexes of asymmetric compartmental ligands†

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The presence of five-membered chelating rings derived from the iminic and aminic pendant arms in dinuclear nickel(II) complexes of asymmetric compartmental ligands gives rise to *syn–syn* bidentate ethanoate bridging in these complexes whereas the introduction of a six-membered chelating ring at the iminic binding site induces an ethanoate shift generating a monodentate bridging ethanoate group.

Introduction

The versatility of simple carboxylate anions in binding to metal ions has been carefully reviewed.[1] The anion can adopt a wide range of bonding modes–*syn* and *anti* monodentate, symmetric and asymmetric chelating, *syn–syn*, *syn–anti* and *anti–anti* bidentate bridging and monodentate bridging. This latter mode is unusual in that two metals bind to a single carboxylate oxygen atom through both of its available lone pairs. The second oxygen atom (the "dangling" oxygen, O_d) can then interact either with one of the bridged metal ions or with a third metal ion.[2] Significant structural variations have been detected within the monodentate bridging class of carboxylates due to the flexibility of the metal to "dangling" oxygen atom interaction (Fig. 1); these range from monodentate bridging with no
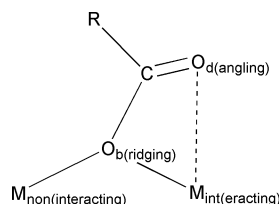

Fig. 1 The monodentate bridging mode.

interaction between O_d and a metal atom through to strong interactions between O_d and the interacting metal atom M_{int}.[2]

Homodinuclear nickel(II) complexes bearing a monodentate bridging ethanoate have been reported in which the remaining two ethanoates are bidentate bridging,[3]—$[Ni_2(OAc)_3(urea)-(tmen)_2](OTf)$ [tmen = $N,N,N'N'$-tetramethyl-1,2-diaminoethane], and $[Ni_2(OAc)_2(BPAN)(CH_3OH)](ClO_4)_2$ [BPAN = 2,7-bis[2-(2-pyridylethylamino)methyl]-1,8-naphthyridine], in which there is a single bidentate bridging ethanoate.[4] Herein we report the systematic generation of monodentate bridging ethanoates in dinuclear nickel(II) complexes derived from asymmetric compartmental proligands. The proligands provide an iminic and an aminic arm for coordination with a metal and so are donor asymmetric.[5] Furthermore by changing the spacer present in the side arm either five-membered or six-membered

chelate rings can be generated at the metal centres. Crystal structures of representative complexes are presented.

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. ^{1}H NMR and ^{13}C NMR spectra were recorded using either a Bruker ACF-250, a Bruker AM-250 or a Bruker WH-400 spectrometer. Positive ion fast atom bombardment (FAB) mass spectra were recorded using a Kratos MS80 or a VG PROSPEC spectrometer (the matrix used was 4-nitrobenzyl alcohol).

Ligand synthesis

The ligand precursors 3-{[(2-dimethylaminoethyl)ethylamino]-methyl}-2-hydroxy-5-methylbenzaldehyde (A), 3-{[(2-diethyl-aminoethyl)methylamino]methyl}-2-hydroxy-5-methylbenz-aldehyde (B) and 2-hydroxy-5-methyl-3-{[methyl-(2-pyridin-2-ylethyl)amino]methyl}benzaldehyde (C) have been described previously.[6–8]

3-{[(3-Dimethylaminopropyl)methylamino]methyl}-2-hydroxy-5-methylbenzaldehyde (D). N,N,N',-Trimethyl-1,3-propane-diamine (2.80 g, 27.3 mmol) was added drop-wise to a solution of 3-chloromethyl-5-methylsalicylaldehyde[9] (5.00 g, 27.3 mmol) and Et₃N (2.76 g, 27.3 mmol) in THF (100 cm^3) at 0 °C. After stirring at rt for 12 h the reaction mixture was filtered and the solvent removed under reduced pressure. Column chromatography of the residue gave the desired product as a yellow oil, pure by tlc [R_f(EtOAc–Et₃N 9 : 1) 0.9]. Yield: 5.13 g (71%). δ_H(250 MHz, CDCl₃, 298 K): 10.33(1H, s, CHO), 7.41(1H, s, ArH), 7.03(1H, s, ArH), 3.69(2H, s, ArCH₂N), 2.51(2H, t, NCH₂), 2.27(2H, t, NCH₂), 2.25(3H, s, ArCH₃), 2.22(3H, s, NCH₃), 2.18[6H, s, N(CH₃)₂], 1.73(2H, quin, CH₂). δ_C(62.5 MHz, CDCl₃, 298 K): 191(CHO), 160(aromatic, 4 °C), 136(aromatic, CH), 128(aromatic, CH), 124(aromatic, 4 °C), 122(aromatic, 4 °C), 60(NCH₂), 57(NCH₂), 55(NCH₂), 45[N(CH₃)₂], 41(NCH₃), 25(CH₂), 20(ArCH₃). Selected IR data (v/cm^{-1}) in CH₂Cl₂. 2956, 2860, 2772, 1678, 1609, 1471, 1398, 1284, 1225, 1150, 1040, 986, 781, 755. (MS (*m*/*z*). 264(M⁺, 16%), 192(M⁺ − C₄H₁₀N, 36), 149(M⁺ − C₆H₁₅N₂, 66),

115($M^+ - C_7H_{16}N_2O$, 9), 58(C_3H_8N, 100). Anal. Found: C, 67.43; H, 9.27; N, 10.33: Calcd for $C_{15}H_{24}N_2O_2$: C, 68.18; H, 9.09; N, 10.61%.

Representative ligand syntheses

2-[(2-Dimethylaminoethylimino)methyl]-6-[(3-dimethylamino-propyl)methylamino]-4-methylphenol HL⁵. N,N,-Dimethyl-1,2-ethanediamine (33 mg, 0.379 mmol) was added to a solution of precursor D (100 mg, 0.379 mmol) in methanol (10 cm³). The resulting solution was then refluxed for 10 min, after which the solvent was removed under reduced pressure to yield the desired product as a yellow oil. Yield: 111 mg (92%). δ_H(250 MHz, $CDCl_3$, 298 K): 8.35(1H, s, CHN), 7.15(1H, s ArH), 6.95(1H, s, ArH), 3.67(2H, t, CHNCH_2), 3.49(2H, s, ArCH_2N), 2.60(2H, t, NCH_2), 2.42(2H, t, NCH_2), 2.26(2H, t, NCH_2), 2.24[6H, s, N$(CH_3)_2$], 2.23(3H, s, ArCH_3), 2.22(3H, s, NCH_3), 2.20[6H, s, N$(CH_3)_2$], 1.73(2H, quin, CH_2). δ_C(62.5 MHz, $CDCl_3$, 298 K): 165(CHN), 157(aromatic, 4 °C), 134(aromatic, CH), 130(aromatic, CH), 127(aromatic, 4 °C), 126(aromatic, 4 °C), 60(NCH_2), 58(NCH_2), 57(NCH_2), 56(NCH_2), 55(NCH_2), 46[N$(CH_3)_2$], 45[N$(CH_3)_2$], 42(NCH_3), 26(CH_2), 20(ArCH_3). Selected IR data (v/cm⁻¹) in CH_2Cl_2. 2948, 2773, 1635, 1466, 1250, 1041, 864, 806, 780, 752. MS (m/z). 334(M^+, 6%), 219($M^+ - C_6H_{15}N_2$, 24), 205($M^+ - C_7H_{15}N_2$, 8), 72($C_4H_{10}N$, 17), 58(C_3H_8N, 100). Anal. Found: C, 67.09; H, 10.62; N, 15.91. Calcd for $[C_{19}H_{34}N_4O]\cdot1/3MeOH$: C, 67.31; H, 10.25; N, 16.24%.

2-{[(2-Dimethylaminoethyl)ethylamino]methyl}-6-[(3-di-methylaminopropylimino)methyl]-4-methylphenol HL⁹. N,N,-Dimethyl-1,3-propanediamine (39 mg, 0.379 mmol) and precursor A (100 mg, 0.379 mmol) were treated as described for the synthesis of HL⁵ to give the desired product as a yellow oil. Yield: 109 mg (90%). δ_H(250 MHz, $CDCl_3$, 298 K): 8.35(1H, s, CHN), 7.24(1H, s, ArH), 6.94(1H, s, ArH), 3.63(2H, s, ArCH_2N), 3.61(2H, t, NCH_2), 2.61(4H, m, 2CH_2), 2.41(2H, m, CH_2), 2.32(2H, t, CH_2), 2.26(3H, s, ArCH_3), 2.41[12H, s, 2N$(CH_3)_2$], 1.83(2H, quin, CH_2), 1.07(3H, t, CH_3). δ_C(62.5 MHz, $CDCl_3$, 298 K): 164(CHN), 157(aromatic, 4 °C), 134(aromatic, CH), 129(aromatic, CH), 127(aromatic, 4 °C), 126(aromatic, 4 °C), 58(NCH_2), 57.5(NCH_2), 57(NCH_2), 52(NCH_2), 51(NCH_2), 48(NCH_2), 46[N$(CH_3)_2$], 45.5[N$(CH_3)_2$], 29(CH_2), 20(ArCH_3), 11(CH_3). Selected IR data (v/cm⁻¹) in CH_2Cl_2. 2948, 2820, 2772, 1634, 1465, 1247, 1041, 886, 841, 810. MS (m/z). 348(M^+, 54%), 290($M^+ - C_3H_8N$, 26), 233($M^+ - C_6H_{15}N_2$, 100), 162($M^+ - C_{10}H_{25}N_3$, 30), 72($C_4H_{10}N$, 28), 58(C_3H_8N, 78). Anal. Found: C, 68.21; H, 10.84; N, 15.63. Calcd for $[C_{20}H_{36}N_4O]\cdot1/4MeOH$: C, 68.26; H, 10.39; N, 15.73%.

2-{[(2-Diethylaminoethyl)methylamino]methyl}-6-[(3-di-methylaminopropylimino)methyl]-4-methylphenol HL¹⁰. N,N,-Dimethyl-1,3-propanediamine (40 mg, 0.360 mmol) and precursor B (100 mg, 0.360 mmol) were treated as described for the synthesis of HL⁵ to give the desired product as a yellow oil. Yield: 114 mg (95%). δ_H(250 MHz, $CDCl_3$, 298 K): 8.33(1H, s, CHN), 7.16(1H, s, ArH), 6.98(1H, s, ArH), 3.62(2H, t, CHNCH_2), 3.55(2H, s, ArCH_2N), 2.70–2.45(8H, m, 4NCH_2), 2.32(2H, t, NCH_2), 2.25(3H, s, ArCH_3), 2.24(3H, s, NCH_3), 2.22[6H, s, N$(CH_3)_2$], 1.84(2H, quin, CH_2), 1.01(6H, t, 2CH_3). δ_C(62.5 MHz, $CDCl_3$, 298 K): 164(CHN), 157(aromatic, 4 °C), 134(aromatic, CH), 130(aromatic, CH), 127(aromatic, 4 °C), 126(aromatic, 4 °C), 57.5(NCH_2), 57(NCH_2), 56(NCH_2), 55.5(NCH_2), 51(NCH_2), 47(NCH_2), 45[N$(CH_3)_2$], 43(NCH_3), 29(CH_2), 20(ArCH_3) 12(2CH_3). Selected IR data (v/cm⁻¹) in CH_2Cl_2. 2972, 2819, 1634, 1467, 1284, 1040, 894, 848, 776. MS (m/z). 362(M^+, 39%), 233($M^+ - C_9H_{17}N_2$, 100), 161($M^+ - C_{13}H_{27}N_3$, 22), 72($C_4H_{10}N$, 18), 58(C_3H_8N, 37). Anal. Found: C, 67.86; H, 10.73; N, 14.58. Calcd for $[C_{21}H_{38}N_4O]\cdot3/4MeOH$: C, 67.62; H, 10.62; N, 14.51%.

2-[(3-Dimethylaminopropylimino)methyl]-4-methyl-6-{[methyl(2-pyridin-2-ylethyl)amino]methyl}phenol HL¹³. N,N,-Dimethyl-1,3-propanediamine (36 mg, 0.351 mmol) and precursor C (100 mg, 0.351 mmol) were treated as described for the synthesis of HL⁵ to give the desired product as a yellow oil. Yield: 122 mg (94%). δ_H(250 MHz, $CDCl_3$, 298 K): 8.52(1H, d, pyrH), 8.30(1H, s, CHN), 7.57(1H, m, pyrH), 7.41(1H, s, ArH), 7.14(1H, m, pyrH), 7.05(1H, m, pyrH), 6.93(1H, s, ArH), 3.64(2H, s, ArCH_2N), 3.62(2H, t, CHNCH_2), 3.07(2H, m, CH_2), 2.87(2H, m, CH_2), 2.32(2H, t, CH_2), 2.26(3H, s, ArCH_3), 2.41[9H, s, NCH_3 + N$(CH_3)_2$], 1.82(2H, quin, CH_2). δ_C(62.5 MHz, $CDCl_3$, 298 K): 165(CHN), 157(aromatic, 4 °C), 149(pyr, CH), 136(pyr, CH), 134(aromatic, CH), 130(aromatic, CH), 127(aromatic, 4 °C), 126(aromatic, 4 °C), 123(pyr, CH), 121(pyr, CH), 118(pyr, 4 °C), 58(NCH_2), 57.5(NCH_2), 57(NCH_2), 55(NCH_2), 46[N$(CH_3)_2$], 42(NCH_3), 36(CH_2), 29(CH_2), 20(ArCH_3). Selected IR data (v/cm⁻¹) in CH_2Cl_2. 2949, 2820, 1634, 1468, 1262, 1042, 902, 866, 755. MS (m/z). 369(M^+, 29%), 233($M^+ - C_8H_{11}N_2$, 50), 161($M^+ - C_{12}H_{21}N_3$, 67), 72($C_4H_{10}N$, 34), 58(C_3H_8N, 100). Anal. Found: C, 70.66; H, 9.13; N, 14.51. Calcd for $[C_{22}H_{32}N_4O]\cdot1/2MeOH$: C, 70.31; H, 8.85; N, 14.58%.

Representative complexation reactions

[Ni₂(L¹)(OAc)(NCS)₂(MeOH)] 1. Nickel ethanoate tetrahydrate (280 mg, 1.13 mmol) was added to a solution of HL¹ (200mg, 0.563 mmol) in methanol (10 cm³). The mixture was then refluxed for 30 min. After cooling, the addition of sodium thiocyanate (91 mg, 1.13 mmol) resulted in the formation of green crystals. Yield: 232 mg (64%). Selected IR data (v/cm⁻¹) using KBr disk: 3466, 2972, 2890, 2081, 2014, 1630, 1579, 1422, 1315, 1053, 1026, 941, 749. MS (m/z). 568($MH^+ - C_3H_7O_3$, 95%), 530($M^+ - C_4H_7NO_3S$, 10), 413($M^+ - C_5H_7N_2O_3S_2$, 6). Anal. Found: C, 46.28; H, 4.96; N, 12.89. Calcd for $[Ni_2(L^1)(OAc)(NCS)_2(1/2MeOH)]$: C, 46.22; H, 5.13; N, 12.69%.

[Ni₂(L⁶)(OAc)(NCS)₂(MeOH)] 5. This was obtained as green crystals in an identical procedure to that used for **1** using HL⁶ (124 mg, 0.351 mmol), nickel ethanoate tetrahydrate (175 mg, 0.702 mmol) and sodium thiocyanate (57 mg, 0.702 mmol). Yield: 102 mg (43%). Selected IR data (v/cm⁻¹) using KBr disk: 3435, 2907, 2840, 2071, 2020, 1656, 1581, 1463, 1422, 1311, 1002, 756. MS (m/z). 588($M^+ - C_3H_7O_3$, 98%), 528($M^+ - C_4H_7NO_3S$, 8). Anal. Found: C, 46.04; H, 5.30; N, 12.41. Calcd for $[Ni_2(L^6)(OAc)(NCS)_2(MeOH)]$: C, 46.02; H, 5.31; N, 12.39%.

[Ni₂(L⁸)(OAc)₂(NCS)] 7. This was obtained as green crystals in an identical procedure to that used for **1** using HL⁸ (200 mg, 0.502 mmol), nickel ethanoate tetrahydrate (260 mg, 1.04 mmol) and sodium thiocyanate (85 mg, 1.04 mmol). Yield: 200 mg (59%). Selected IR data (v/cm⁻¹) using KBr disk: 3439, 2992, 2923, 2089, 1640, 1591, 1472, 1421, 1326, 1011, 760. Anal. Found: C, 50.10; H, 5.95; N, 9.93. Calcd for $[Ni_2(L^8)(OAc)_2(NCS)]$: C, 49.78; H, 5.78; N, 10.37%.

[Ni₂(L¹¹)(OAc)₂(NCS)] 10. Histamine (40 mg, 0.360 mmol) and precursor B (100 mg, 0.360 mmol) were treated as described for the synthesis of HL⁵ to give a mixture of the desired product HL¹¹ and the isomeric fused ring by-product¹⁰,¹¹ 4-methyl-2-(methylpyridin-2-ylmethylamino)-6-(4,5,6,7-tetrahydro-3H-imidazo[4,5-c]pyridin-4-yl)phenol. Without further purification a solution of nickel ethanoate tetrahydrate (179 mg, 0.720 mmol) in methanol (10 cm³) was added and the mixture refluxed for 30 min. After cooling, the addition of sodium thiocyanate (58 mg, 0.720 mmol) resulted in the formation of green crystals. Yield: 109 mg (46%). Selected IR data (v/cm⁻¹) using KBr disk: 3352, 3208, 2983, 2894, 2110, 1638, 1580, 1471, 1431,

Table 1 Summary of crystallographic data for [Ni₂L¹(AcO)(NCS)₂(MeOH)] **1** [Ni₂L⁶(AcO)(NCS)₂(MeOH)] **5** [Ni₂L⁸(AcO)₂(NCS)]·H₂O **7·H₂O** [Ni₂L¹¹(AcO)₂(NCS)]·H₂O **10·H₂O** and [Ni₂L¹²(AcO)₂(NCS)] **11**

	1	5	7·H₂O	10·H₂O	11
Empirical formula	C₂₆H₃₅N₆Ni₂O₄S₂	C₂₆H₃₅N₆Ni₂O₄S₂	C₂₈H₄₁N₅Ni₂O₆S	C₂₆H₄₀N₆Ni₂O₆S	C₂₉H₃₃N₅Ni₂O₅S
Formula weight	677.14	677.14	693.14	682.12	681.08
Space group	$P\bar{1}$ (C_i^1, No. 2)	$P2_1/n$ ($P2_1/c\ C_{2h}^5$ No. 14)	$P2_1/n$ ($P2_1/c\ C_{2h}^5$ No. 14)	$P\bar{1}$ (C_i^1, No. 2)	$P\bar{1}$ (C_i^1, No. 2)
a/Å	10.715(7)	10.0082(9)	12.6287(12)	9.7658(6)	8.9671(9)
b/Å	11.517(7)	17.3828(16)	14.3404(13)	11.7532(8)	12.3749(13)
c/Å	12.583(8)	17.2816(16)	18.0340(16)	13.8662(10)	14.4668(15)
α/°	84.718(12)	90	90	84.8920(10)	97.539(20)
β/°	71.358(12)	97.940(2)	107.076(2)	85.6140(10)	98.507(2)
γ/°	87.245(13)	90	90	70.0750(10)	100.836(2)
V/Å³	1464.8(15)	2977.7(5)	3122.0(5)	1488.53(17)	1488.53(17)
ρ_{calc}/Mg m⁻³	1.535	1.510	1.475	1.522	1.470
Z	2	4	4	2	2
μ/mm⁻¹	1.385	1.447	1.321	1.385	1.337
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
T/K	150(2)	150(2)	150(2)	150(2)	150(2)
R	0.0607	0.0574	0.0592	0.0427	0.0578
$wR2$	0.1405	0.1640	0.1632	0.1632	0.1868

1343, 1076, 1021, 825. MS (*m/z*). 605(M⁺ − C₂H₃O₂, 70%), 546(M⁺ − C₄H₆O₄, 14). Anal. Found: C, 45.33; H, 5.81; N, 12.04. Calcd for [Ni₂(L¹¹)(OAc)₂(NCS)]·MeOH: C, 46.55; H, 6.03; N, 12.07%.

[Ni₂(L¹²)(OAc)₂(NCS)] 11. This was obtained as green crystals in an identical procedure to that used for **1** using HL¹² (200 mg, 0.513 mmol), nickel ethanoate tetrahydrate (255 mg, 1.03 mmol) and sodium thiocyanate (83 mg, 1.03 mmol). Yield: 225 mg (64%). Selected IR data (ν/cm⁻¹) using KBr disk: 3411, 2912, 2858, 2094, 1645, 1583, 1489, 1471, 1416, 1230, 1000, 813, 785, 762. MS (*m/z*). 623(M⁺ − C₃H₇O₃, 81%), 562(M⁺ − C₄H₃NO₂S, 9), 310(M⁺ − C₁₀H₁₁N₃O₃S₂Ni₂, 37). Anal. Found: C, 50.48; H, 4.93; N, 9.95. Calcd for [Ni₂(L¹²)(OAc)₂(NCS)]·1/2MeOH: C, 50.79; H, 5.02; N, 10.04%.

X-Ray crystallography

The details of the X-ray crystal data, and of the structure solution and refinement for complexes **1**, **5**, **7·H₂O**, **10·H₂O** and **11** are given in Table 1. Data collected, with graphite mono-chromated Mo-Kα X-radiation, were measured on a Siemens SMART CCD area diffractometer with an Oxford Cryosystems low temperature system. The data were corrected for Lorentz and 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 terminal methyl C atom, C(25) in **5** was only refined isotropically. In the structure of **7·H₂O** the water molecule was found to be disordered and O(1W) was refined to an occupancy of 44 : 56%. The programs used in the determination and refinement of the structures were Siemens SMART and SAINT for control and integration software[12] and SHELXTL as implemented on the Viglen Pentium computer.[13]

CCDC reference numbers 152075 and 169968–169971.

See http://www.rsc.org/suppdata/dt/b1/b107928j/ for crystallographic data in CIF or other electronic format.

Results and discussion

A range of donor asymmetric compartmental proligands bearing one iminic and one aminic arm have been prepared and used to generate dinuclear nickel(II) complexes. The nature of the terminal nitrogen donor atom in the pendant arms has been varied to give combinations derived from pyridine, imidazole and tertiary amino (NR₂) groups. Changing the spacer present

in the side arm allows either five-membered or six-membered chelate rings to be generated at the metal centres and so a series of complexes having adjacent [5,5], [5,6], [6,5] and [6,6][14] binding compartments was constructed providing opportunity to investigate the effect of changing the nature of the compartment on the bonding capacity of the ligand. The ligands used are depicted in Figs. 2, 5 and 8.
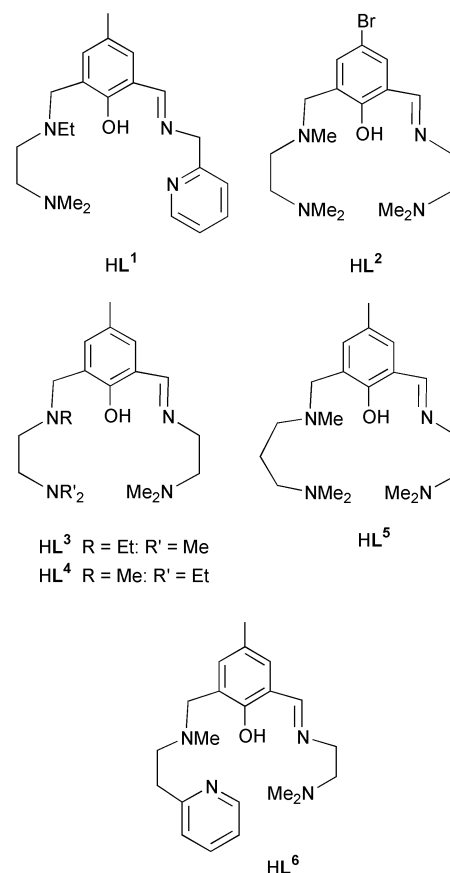

Fig. 2 Ligands used for the generation of bidentate bridging ethanoates.

The reaction of the proligand HL¹, prepared by modification of a reported method,[6] with Ni(OAc)₂·4H₂O and NaNCS in MeOH gave the dinuclear complex [Ni₂(L¹)(AcO)(NCS)₂-(MeOH)] **1**.[7] The crystal structure of **1** was solved and an ORTEP view of this complex is shown in Fig. 3 together with the numbering scheme. Selected bond lengths and angles relevant to the coordination geometries are given in the caption to the figure. The closely octahedral nickel(II) atoms are bridged
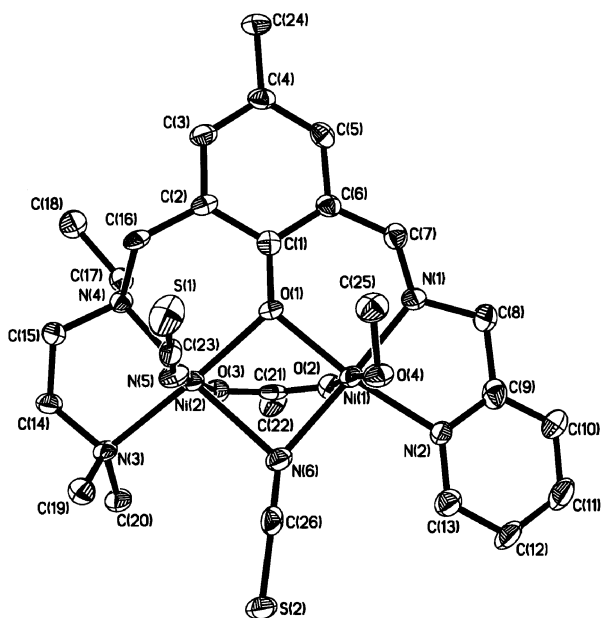
Fig. 3 An ORTEP drawing of the molecular structure of **1** showing the atom labeling; thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths and angles at the metal atoms: Ni(1)–N(1), 1.981(4); Ni(1)–O(1), 2.001(3); Ni(1)–O(2), 2.033(4); Ni(1)–N(2), 2.061(4); Ni(1)–N(6), 2.115(4); Ni(1)–O(4), 2.116(4); Ni(2)–O(3), 2.019(4); Ni(2)–O(1), 2.031(3); Ni(2)–N(5), 2.042(4); Ni(2)–N(4), 2.103(4); Ni(2)–N(3), 2.171(4); Ni(2)–N(6), 2.233(4); Ni(1)–Ni(2), 3.029 Å. Ni(1)–O(1)–Ni(2), 97.39(15); Ni(1)–N(6)–Ni(2), 88.26(17); O(4)–Ni(1)–O(2), 175.03(14); O(1)–Ni(1)–N(2), 172.35(15); N(1)–Ni(1)–N(6), 177.74(18); O(1)–Ni(1)–N(6), 87.05(15); N(1)–Ni(1)–N(2), 81.43(17); N(2)–Ni(1)–N(6), 100.52(17); O(1)–Ni(1)–N(1), 91.02(16); O(3)–Ni(2)–N(5), 174.62(16); O(1)–Ni(2)–N(3), 176.32(15); N(4)–Ni(2)–N(6), 174.20(15); O(1)–Ni(2)–N(6), 83.22(15); N(3)–Ni(2)–N(6), 100.42(16); N(3)–Ni(2)–N(4), 83.98(16); O(1)–Ni(2)–N(4), 91.40(15)°.

by the phenolic oxygen atom of $(L^1)^-$, an isothiocyanato nitrogen atom and a *syn–syn* bidentate ethanoate. Chelation from the pendant nitrogen atoms provides five-membered chelate rings, from the iminic and aminic arms, to Ni(1) and Ni(2) respectively and completes the equatorial plane at these atoms.

The six-coordination of each nickel(II) is completed by an axial oxygen atom from a methanol of solvation at Ni(1) and an axial nitrogen atom from an isothiocyanate anion at Ni(2); these ligands are sited *cis* to each other with respect to the mean molecular plane. The isothiocyanate anion, coordinated to the nickel in the aminic compartment, is on the opposite face of the molecule to the ethyl group on the articular nitrogen atom N(4). The phenolic bridge is non-symmetric with Ni_{imine}–O, 2.00 Å and Ni_{amine}–O, 2.03 Å; the Ni–N_{imine} bond is shorter, 1.98 Å, than the Ni–$N_{pyridine}$ bond, 2.06 Å—crystallographic features of the bridges in the complexes are given in Table 2. The nickel–nickel separation is 3.029 Å.
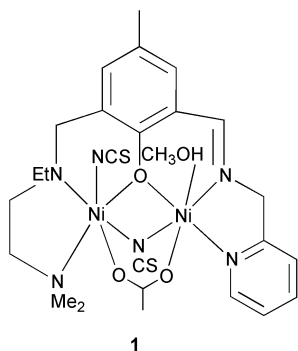
The generality of this reaction, in which both chelate rings are five-membered giving a [5,5] coordination set, is shown by

Table 2 Crystallographic features of the bridges in the complexes

Ligand from which derived (complex)	Tertiary bridge features[a]							Phenolic bridge features		
	Bridging angle/°	Axial angle at the aminic Ni atom/°	Axial angle at the iminic Ni atom/°	Aminic bridge/Å	Iminic bridge/Å	M–O_a/Å	Ni ⋯ Ni/Å	Ni(1)–O(1) iminic/Å	Ni(2)–O(1) aminic/Å	Ni(1)–O(1)–Ni(2)/Å
No bridge[b] HL^2 (15)						3.254 Ni(2)–O(5)	1.858	1.862	109.7	
5,6-chelating rings HL^8 (7)	Ni(2)–O(4)–Ni(1) 90.21	O(5)–Ni(2)–O(2) 165.86	O(3)–Ni(1)–N(5) 174.79	Ni(2)–O(4) 2.158	Ni(1)–O(4) 2.210	2.134 Ni(2)	3.094	2.000	2.034	100.2
HL^{11} (10)	89.41	161.28	O(3)–Ni(1)–N(6) 178.19	Ni(2)–O(4) 2.164	Ni(1)–O(4) 2.214	2.153 Ni(2)–O(5)	3.080	1.983	2.010	100.9
6,6-chelating rings HL^{12} (11)	Ni(2)–O(4)–Ni(1) 91.39	O(5)–Ni(2)–O(2) 162.24	O(3)–Ni(1)–N(5) 175.24	Ni(2)–O(4) 2.146	Ni(1)–O(4) 2.184	2.166 Ni(2)–O(5)	3.099	2.011	2.035	100
5,5-chelating rings HL^1 (1)	Ni(2)–N(6)–Ni(1) 88.26	N(5)–Ni(2)–O(3) 174.62	O(4)–Ni(1)–O(2) 175.03	Ni(2)–N(6) 2.233	Ni(1)–N(6) 2.115		3.029	2.001	2.031	97.4
6,5-chelating rings HL^6 (5)	Ni(2)–N(6)–Ni(1) 87.5	N(5)–Ni(2)–O(3) 170.0	O(4)–Ni(1)–O(2) 174.76	Ni(2)–N(6) 2.415	Ni(1)–N(6) 2.057		3.102	2.018	2.064	98.9

[a] Tertiary bridge features relate to the introduction of a third bridge over and above the common presence of a phenolic bridge and a bidentate ethanoate bridge at the dinuclear centre. [b] See complex $[Ni(L^2)(AcO)_2]BPh_4$ (ref. 7).

the availability of an analogous dinickel(II) complex derived from HL^2, $[Ni_2(L^2)(AcO)(NCS)_2(MeOH)]$,[7] and from the crystal structures of $[Ni_2(L^3)(AcO)(NCS)_2(MeOH)]$ **2**, and $[Ni_2(L^4)(AcO)(NCS)_2(MeOH)]$ **3**, X-ray crystallographic data and figures for which have been deposited electronically. If a six-membered chelate ring is introduced by the aminic arm as in proligands HL^5 and HL^6 a [6,5] coordination set is provided and analogous dinuclear complexes, $[Ni_2(L^n)(AcO)(NCS)_2(MeOH)]$, [$n = 5$, **4**, and $n = 6$, **5**] are obtained the structures of which confirmed the presence of a bridging thiocyanate and a bidentate bridging ethanoate as in complexes **1**–**3**. The structure of **5** is presented as a representative example of [6,5] coordination with X-ray crystallographic data and figures for complex **4** being deposited electronically.

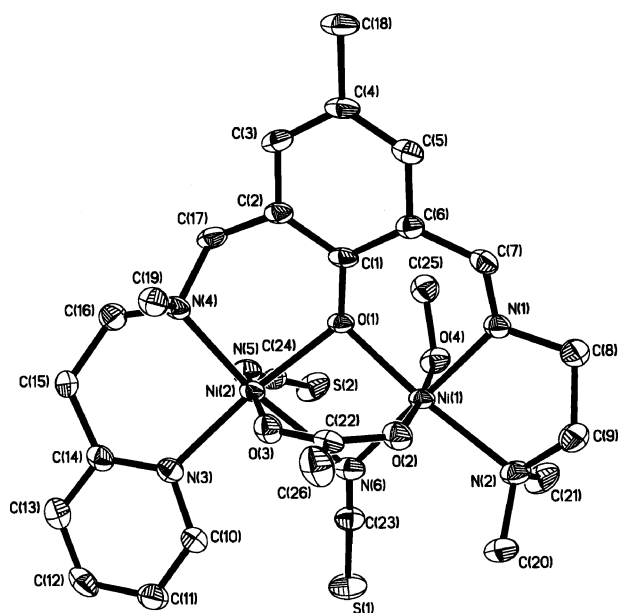An ORTEP view of complex **5** is shown in Fig. 4 together

Fig. 4 An ORTEP drawing of the molecular structure of **5** showing the atom labeling; 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)–N(1), 1.995(3); Ni(1)–O(1), 2.018(2); Ni(1)–O(2), 2.056(2); Ni(1)–N(2), 2.164(3); Ni(1)–N(6), 2.057(3); Ni(1)–O(4), 2.243(3); Ni(2)–O(3), 1.983(3); Ni(2)–O(1), 2.064(2); Ni(2)–N(5), 2.039(3); Ni(2)–N(4), 2.090(3); Ni(2)–N(3), 2.091(3); Ni(2)–N(6), 2.415(3); Ni(1)–Ni(2), 3.102 Å. Ni(1)–O(1)–Ni(2), 98.93(9); N(6)–Ni(2), 87.48(11); O(4)–Ni(1)–O(2), 174.76(11); O(1)–Ni(1)–N(2), 174.61(11); N(1)–Ni(1)–N(6), 174.81(12); O(1)–Ni(1)–N(6), 88.82(12); N(1)–Ni(1)–N(2), 82.64(12); N(2)–Ni(1)–N(6), 96.52(13); O(1)–Ni(1)–N(1), 91.97(11); O(3)–Ni(2)–N(5), 169.97(12); O(1)–Ni(2)–N(3), 172.53(11); N(4)–Ni(2)–N(6), 170.64(11); O(1)–Ni(2)–N(6), 78.65(10); N(3)–Ni(2)–N(6), 96.20(11); N(3)–Ni(2)–N(4), 92.86(12); O(1)–Ni(2)–N(4), 92.54(10)°.

with the numbering scheme. Selected bond lengths and angles relevant to the coordination geometries are given in the caption to the figure. As in **1** the closely octahedral nickel(II) atoms are bridged by the phenolic oxygen atom of the ligand, an isothiocyanato nitrogen atom and a *syn–syn* bidentate ethanoate. Chelation from the pendant nitrogen atoms provides a five-membered chelate ring from the iminic arm and a six-membered chelate ring from the aminic arm, to Ni(1) and Ni(2) respectively, and completes the equatorial plane at these atoms. The six-coordination of each nickel(II) is completed as in complex **1**. The phenolic bridge is non-symmetric with Ni_{imine}–O, 2.02 Å and Ni_{amine}–O, 2.06 Å; the Ni–N_{imine} bond is shorter, 1.995(3) Å, than the Ni–NMe_2 bond, 2.164(3) Å. The nickel–nickel separation is 3.102 Å.

It would appear that this structural type, having a *syn–syn* bidentate bridge and a monodentate thiocyanate bridge, as illustrated in the formula diagram for complex **1**, is promoted

by the presence of a five-membered chelating ring at the iminic pendant arm.

In contrast to the above the reaction, proligands HL^7 and HL^8 (Fig. 5), which provide [5,6] coordination sets, with
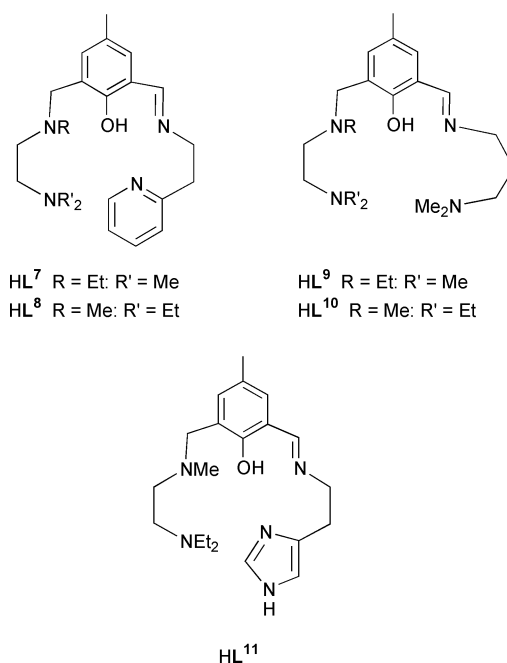

Fig. 5 Ligands used for the generation of monodentate bridging ethanoates having [5,6] coordination sets, aminic (five-membered) and iminic (six-membered).

$Ni(OAc)_2 \cdot 4H_2O$ and NaNCS, *under the same reaction conditions as those used for the preparation of* **1**, gave the dinuclear complexes $[Ni_2(L^n)(AcO)_2(NCS)]$ ($n = 7$, **6**, $n = 8$, **7**). The introduction of a six-membered chelate ring, on complexation by the iminic arm provided by the compartmental proligand, leads to a different product stoichiometry in the resulting dinuclear complexes.

The crystal structure of $7 \cdot H_2O$ was solved and revealed that whilst a basic dinuclear core derived from a bridging phenolate and a bidentate bridging ethanoate was retained, a monodentate bridging ethanoate had replaced the bridging isothiocyanate. An ORTEP view of **7** is shown in Fig. 6 together with the numbering schemes. Selected bond lengths and angles relevant to the coordination geometries and the monobridging ethanoates are given in the caption to the figure. In this complex the six-coordinate nickel(II) atoms are again bridged by the phenolic oxygen atom of the deprotonated ligand and a *syn–syn* bidentate ethanoate but further bridging is now provided by a monodentate bridging ethanoate anion. Chelation from the pendant nitrogen atoms provides six-membered chelate rings from the iminic arms to Ni(1) and five-membered chelate rings from the aminic arms to Ni(2) and the six-coordination of each nickel(II) is completed at Ni(2) by the chelating oxygen atoms O(4) and O(5), and at Ni(1) by a monodentate bridging ethanoate oxygen atom O(4) and an axial nitrogen atom from an isothiocyanate anion–these ligands are *trans* to each other. If the oxygen atoms of the bidentate bridging ethanoate, O(2) and O(3) are regarded as occupying apical positions in the relevant octahedral environment at Ni(2) and Ni(1) then it is noted that the monodentate bridging ethanoate has O(5) [O_d] *trans* to O(2) [O(5)–Ni(2)–O(2), 165.9°] and O(4) [O_b] *cis* to O(5). The isothiocyanate anion has migrated to the nickel in the iminic compartment when compared to its position in complex **1** and the methanol of solvation at Ni(1) has been lost. The octahedral coordination at the nickel atoms is more distorted than that at the nickel atoms in **1** with the greater distortion occurring at the aminic site. The monobridging ethanoate bridge is non-symmetric—Ni(2)–O(4) (aminic bridge), 2.158(2) Å and
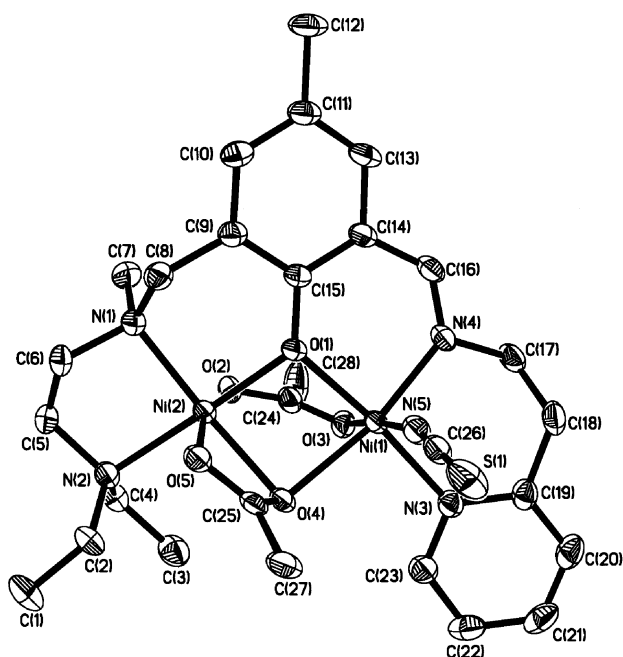
Fig. 6 An ORTEP drawing of the molecular structure of **7**·H$_2$O showing the atom labeling; thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths and angles at the metal atoms: Ni(1)–O(1), 2.000(2); Ni(1)–N(4), 2.014(3); Ni(1)–N(5), 2.068(3); Ni(1)–O(3), 2.081(3); Ni(1)–N(3), 2.074(3); Ni(1)–O(4), 2.210(2); Ni(2)–O(2), 1.995(3); Ni(2)–O(1), 2.034(2); Ni(2)–N(1), 2.060(3); Ni(2)–O(4), 2.158(2); Ni(2)–O(5), 2.134(3); Ni(2)–N(2), 2.196(3); Ni(1)–Ni(2), 3.094 Å. Ni(1)–O(1)–Ni(2), 100.19(9); Ni(1)–O(4)–Ni(2), 90.21(9); O(3)–Ni(1)–N(5), 174.79(10); O(1)–Ni(1)–N(3), 173.42(10); N(4)–Ni(1)–O(4), 168.35(10); N(4)–Ni(1)–N(3), 94.99(10); N(3)–Ni(1)–O(4), 95.36(10); O(4)–Ni(1)–O(1), 78.75(8); O(1)–Ni(1)–N(4), 90.62(9); N(1)–Ni(2)–O(4), 157.09(12); O(5)–Ni(2)–O(2), 165.86(9); O(1)–Ni(2)–N(2), 176.83(9); O(1)–Ni(2)–O(4), 79.30(9); O(4)–Ni(2)–N(2), 101.91(9); N(2)–Ni(2)–N(1), 86.61(10); N(1)–Ni(2)–O(1), 91.19(10)°.

Ni(1)–O(4) (iminic bridge), 2.210(2) Å—as is the phenolic bridge symmetric—Ni(2)–O(1) (aminic bridge), 2.034(2) Å and Ni(1)–O(1) (iminic bridge), 2.000(2) Å—and the bonds between Ni–N$_{imine}$ (2.01 Å) and Ni–N$_{pyridine}$ (2.07 Å) are slightly longer than those found in **1**. The Ni · · · Ni separation is 3.094 Å, slightly longer than that found in **1**, 3.029 Å. The chelating angle, O(5)–C(24)–O(4), in the monobridging ethanoate is normal, 118.9° whereas the bridging angle, O(3)–C(26)–O(2), of the *syn–syn* bridging ethanoate is more open, 125.5°. In the monobridging ethanoate interaction with the nickel atoms the plane of the chelating ethanoate (O(5)–Ni(2)–C(24)–O(4)) lies at 67.8° to the plane of the Ni(1)–O(4)–Ni(2) bridge. There is a non-coordinated water molecule, which is disordered (44 : 56), present in the lattice. [A second structure of **7**·H$_2$O, **7a**, has been determined in which the -NEt$_2$ is disordered, the terminal carbon being refined at 50 : 50%, but the lattice solvent is not.] In the case of complex **6** derived from HL^7 the overall structural features are comparable with those of **7** and the X-ray crystallographic data and figures for complexes **6** and **7a** have been deposited electronically.

From the above it can be seen that a simple modification in ligand design, the introduction of a six-membered ring at the imino-compartment of the compartmental ligands has, as illustrated by the formula diagram for complexes **6** and **7**, promoted the generation of a monodentate, bridging ethanoate. Different coordination environments for the nickel(II) atoms, as compared with those for complex **1**, have been noted even though the reaction conditions producing the complexes were the same. The opportunity to systematically generate monodentate bridging ethanoates in dinuclear nickel(II) complexes was therefore further investigated using a range of compartmental ligands.

6 R = Et, R' = Me
7 R = Me, R' = Et
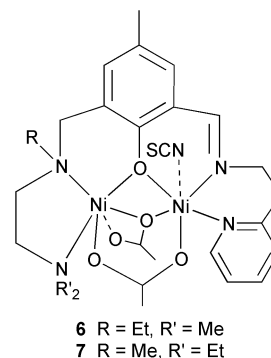
The complexes [Ni$_2$(L^n)(AcO)$_2$(NCS)] were prepared from proligands HL^9 [**8**], HL^{10} [**9**], and HL^{11} [**10**], in which the aminic arm was aliphatic and provided a five-membered chelate ring. The iminic arm, providing a six-membered chelating ring, was terminated by a dimethylamino group (HL^9, HL^{10}) and histamine (HL^{11}). In all cases a monodentate bridging ethanoate was found to be present in the structure and the coordination geometries at the metals paralleled those in complex **7** suggesting that it is the entire compartment generating the six-membered ring that is responsible for the reaction product. The crystal structure of **10** is presented as representative of these complexes having [5,6] coordination with X-ray crystallographic data and figures for complexes **8** and **9** being deposited electronically.

The structure of **10**·H$_2$O revealed that the ethanoate bonding mode was again monodentate bridging. An ORTEP view of **10** is shown in Fig. 7 together with the numbering schemes. Selected bond lengths and angles relevant to the coordination geometries and to the monobridging ethanoates are given in the
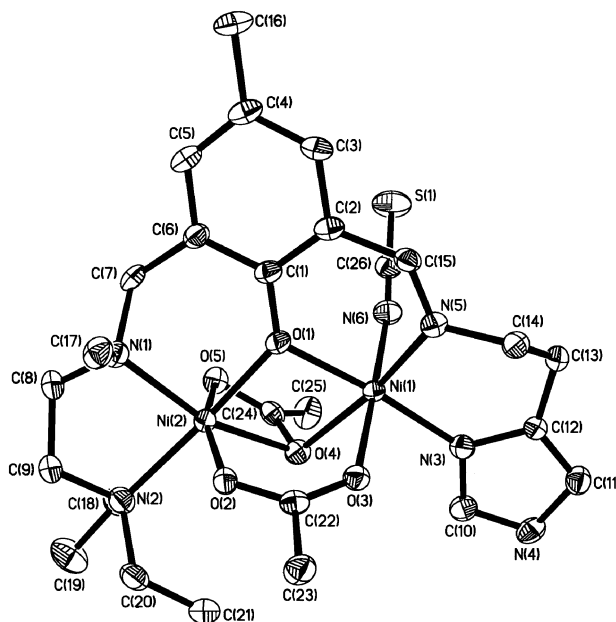

Fig. 7 An ORTEP drawing of the molecular structure of **10**·H$_2$O showing the atom labeling; thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths and angles at the metal atoms: Ni(1)–O(1), 1.983(2); Ni(1)–N(3), 2.018(3); Ni(1)–N(5), 2.037(3); Ni(1)–O(3), 2.085(2); Ni(1)–N(6), 2.089(3); Ni(1)–O(4), 2.214(2); Ni(2)–O(2), 1.998(2); Ni(2)–O(1), 2.010(2); Ni(2)–N(1), 2.063(3); Ni(2)–O(4), 2.164(2); Ni(2)–O(5), 2.153(2); Ni(2)–N(2), 2.193(3); Ni(1)–Ni(2), 3.080 Å. Ni(1)–O(1)–Ni(2), 100.92(10); Ni(1)–O(4)–Ni(2), 89.41(8); O(3)–Ni(1)–N(2), 178.19(10); O(1)–Ni(2)–N(3), 174.55(10); N(5)–Ni(2)–O(4), 170.91(9); N(5)–Ni(2)–N(3), 94.88(11); N(3)–Ni(2)–O(4), 93.86(10); O(4)–Ni(2)–O(1), 80.91(9); O(1)–Ni(2)–N(5), 90.27(10); O(5)–Ni(2)–O(2), 161.28(9); O(1)–Ni(1)–N(2), 176.03(10); N(1)–Ni(1)–O(4), 158.48(10); O(1)–Ni(1)–O(4), 81.57(9); O(4)–Ni(1)–N(2), 102.40(10); N(2)–Ni(1)–N(1), 86.87(11); N(1)–Ni(1)–O(1), 89.31(10)°.

caption to the figure. The coordination nature of the dinuclear core is very similar to that in **7·H₂O**; chelation from the pendant nitrogen atoms provides a six-membered chelate ring from the iminic arm to Ni(1) and a second five-membered chelate ring from the aminic arms to Ni(2). Each nickel(II) atom is six-coordinate with the octahedral coordination at the nickel atoms distorted. The monobridging ethanoate bridge is non-symmetric—Ni(2)–O(4) (aminic bridge), 2.164(3) Å and Ni(1)–O(4) (iminic bridge), 2.214(2) Å—as is the phenolic bridge—Ni(2)–O(1) (aminic bridge), 2.010(2) Å and Ni(1)–O(1) (iminic bridge), 1.983(2) Å; the bond between Ni–N$_{imine}$ (2.04 Å) is slightly longer than that found in **1** whilst the Ni–N$_{imidazole}$ distance (2.02 Å) is comparable. The Ni · · · Ni separation is 3.080 Å, slightly shorter than that found in **7·H₂O**, 3.094 Å. The chelating angle, O(5)–C(24)–O(4), in the monobridging ethanoate is normal, 120.0° whereas the bridging angle, O(3)–C(22)–O(2), of the *syn–syn* bridging ethanoate is more open, 126.5°. In the monobridging ethanoate interaction with the nickel atoms the plane of the chelating ethanoate (O(5)–Ni(2)–C(24)–O(4)) is at 67.1° to the plane of the Ni(1)–O(4)–Ni(2) bridge. There is a non-coordinated water molecule present in the lattice. The overall structural features of complexes **8** and **9** are closely similar to those of **10**.

A group of proligands in which both pendant arms would provide six-membered chelate rings at both metals (Fig. 8) was
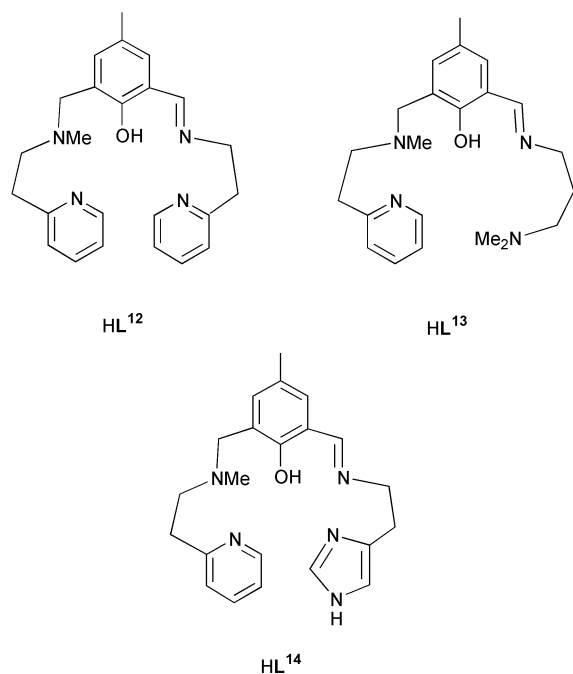

Fig. 8 Ligands used for the generation of monodentate bridging having [6,6] coordination sets, aminic (6-membered) and iminic (6-membered).

then prepared together with their dinickel(II) complexes. In **HL¹²** both pendant termini were pyridinyl groups, in **HL¹³** the aminic arm bore a pyridinyl group and the iminic arm a dimethylamino group and in **HL¹⁴** the aminic group terminated with a pyridinyl group and the iminic arm with a histidinyl group. The dinuclear complexes [Ni₂(L^n)(AcO)₂(NCS)] [**11**, n = 12; **12**, n = 13; **13**, n = 14] were recovered in each case and all exhibited the anticipated coordination spheres; the structure of **11** is discussed as a representative example of [6,6] coordination with X-ray crystallographic data and figures for complexes **12** and **13** being deposited electronically.

In the structure of **11** the two six-coordinate nickel(II) atoms are again bridged by the phenolic oxygen atom of the deprotonated ligand, a *syn–syn* bidentate ethanoate and a monodentate bridging ethanoate anion. An ORTEP view of **11** is shown in Fig. 9 together with the numbering schemes. Selected bond
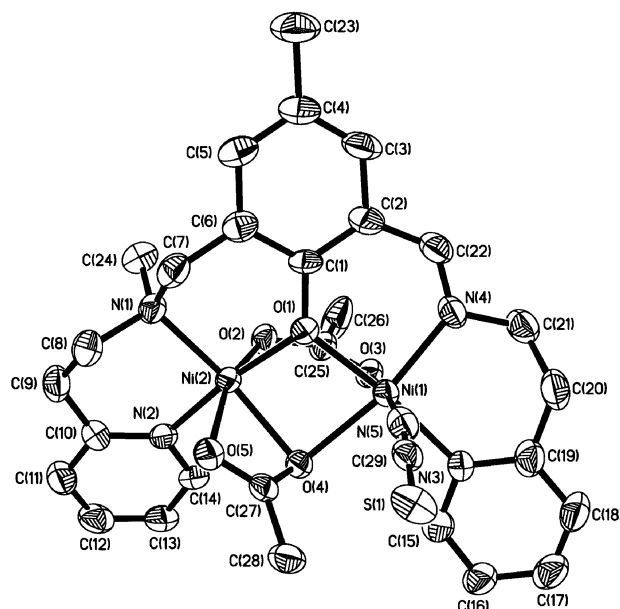

Fig. 9 An ORTEP drawing of the molecular structure of **11** showing the atom labeling; thermal ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths and angles at the metal atoms: Ni(1)–O(1), 2.011(3); Ni(1)–N(4), 2.015(4); Ni(1)–N(5), 2.082(4); Ni(1)–O(3), 2.094(3); Ni(1)–N(3), 2.091(4); Ni(1)–O(4), 2.184(3); Ni(2)–O(2), 2.014(3); Ni(2)–O(1), 2.035(3); Ni(2)–N(1), 2.064(4); Ni(2)–O(4), 2.146(3); Ni(2)–O(5), 2.166(3); Ni(2)–N(2), 2.218(4); Ni(1)–Ni(2), 3.099 Å. Ni(1)–O(1)–Ni(2), 99.99(13); Ni(1)–O(4)–Ni(2), 91.39(11); O(3)–Ni(1)–N(5), 175.24(13); O(1)–Ni(1)–N(3), 173.59(12); N(4)–Ni(1)–O(4), 167.22(14); N(4)–Ni(1)–N(3), 94.85(15); N(3)–Ni(1)–O(4), 94.41(12); O(4)–Ni(1)–O(1), 79.45(11); O(1)–Ni(1)–N(4), 91.50(14); O(5)–Ni(2)–O(2), 162.24(12); O(1)–Ni(2)–N(2), 172.84(12); N(1)–Ni(2)–O(4), 156.48(13); O(1)–Ni(2)–O(4), 79.48(11); O(4)–Ni(2)–N(2), 93.60(12); N(2)–Ni(2)–N(1), 93.65(14); N(1)–Ni(2)–O(1), 93.51(13)°.

lengths and angles relevant to the coordination geometries and to the monobridging ethanoates are given in the caption to the figure. The coordination nature of the dinuclear core is very similar to that in **7·H₂O** and **10·H₂O** but chelation from the pendant nitrogen atoms provides a six-membered chelate ring from the iminic arm to Ni(1) and a second six-membered chelate ring from the aminic arm to Ni(2). Each nickel(II) atom is six-coordinate with the octahedral coordination at the nickel atoms again distorted. The monobridging ethanoate bridge is non-symmetric—Ni(2)–O(4) (aminic bridge), 2.146(3) Å and Ni(1)–O(4) (iminic bridge), 2.184(3) Å—as is the phenolic bridge—Ni(2)–O(1) (aminic bridge), 2.035(3) Å and Ni(1)–O(1) (iminic bridge), 2.011(3) Å. The Ni–N$_{imine}$ bond (2.02 Å) is slightly longer than that found in **1** as is the Ni–N$_{pyridine}$ bond (2.09 Å). The Ni · · · Ni separation is 3.099 Å, comparable to those found in **7·H₂O** *and* **10·H₂O** The chelating angle, O(5)–C(27)–O(4), in the monobridging ethanoate is normal, 119.5° whereas the bridging angle, O(3)–C(25)–O(2), of the *syn–syn* bridging ethanoate is more open, 127.1°. In the monobridging ethanoate interaction with the nickel atoms the plane of the chelating ethanoate (O(5)–Ni(2)–C(27)–O(4)) is at 61.2° to the plane of the Ni(1)–O(4)–Ni(2) bridge. The overall structural features of complexes **12** and **13**, data for which has been deposited electronically, are closely similar to those of **11**.

The flexibility given to the ligands by the saturated aminic arms appears to be an important feature in the molecular assembly. It allows formation of the distorted octahedral site at Ni(2) by accommodating the chelating monobridged μ²,η¹,η²-ethanoate—this group subtends an angle of ≈62° at the Ni atom. The Ni$_{aminic}$ sites [Ni(2)] are more distorted than the Ni$_{iminic}$ sites [Ni(1)] and this is exemplified in the *trans*-axial angles in **7·H₂O** where angles of 157.1, 165.9 and 176.8° are found at Ni(2) compared with 174.8, 173.4 and 168.3 at Ni(1).

The ethanoate containing O_d and O_b binds to the opposite face of the molecule to the alkyl function of the articular N-alkyl group.

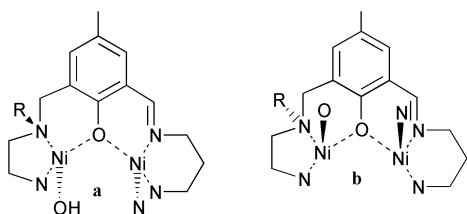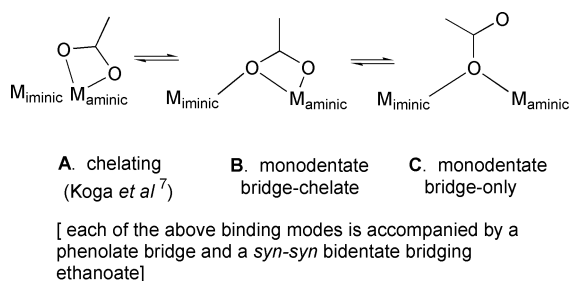The schematic diagrams in Fig. 10 illustrate the potential

Fig. 10 Stereoisomers for the dinuclear complexes.

stereoisomers (**a**) and (**b**) that are available to complexes of this type; however it has not been possible to obtain discrete enantiomers, the structures solved have all been in centro-symmetric space groups.

The work of Okawa and co-workers[7] has shown that the reaction of HL^2 with $Ni(OAc)_2$ in the presence of the non-coordinating BPh_4^- anion gives the complex $[Ni_2(L^2)(AcO)_2]$-BPh_4 (**15**) in which one ethanoate is chelated to the Ni atom in the aminic compartment with bridging between the two Ni atoms being provided by the phenolic oxygen atom of $(L^2)^-$, and a *syn–syn* bidentate ethanoate. The Ni $\cdots$ Ni separation in this complex is ≈ 3.25 Å and the Ni(1)–O(1)–Ni(2) angle is $109.7°$.[7] In the current work where the BPh_4^- anion has been replaced by an NCS^- anion the basic bridging core of one phenolic oxygen and a bidentate ethanoate remains the same and the additional chelating ethanoate is replaced by a mono-dentate bridging ethanoate in complexes where there is a six-membered chelate ring at the Ni in the iminic compartment [5,6 and 6,6], and by a monodentate NCS^- bridge in complexes where there is a five-membered chelate ring at the Ni in the iminic compartment [5,5]. There is an accompanying reduction in the Ni $\cdots$ Ni separation to ≈ 3.10 Å [5,6 and 6,6] and ≈ 3.03 Å [5,5] and in the Ni(1)–O(1)–Ni(2) angle to $\approx 100.5°$ and $98.1°$ respectively.

To explain our results requires a detailed knowledge of the speciation in solution. This cannot be accessed and so an hypothesis for the formation of the complexes is advanced bearing in mind Lippard's remarks on the "carboxylate shift".[1] It is proposed that complex **A**, having the dinuclear core provided by the bridging phenolate and bidentate ethanoate and with the additional ethanoate group chelated to the aminic Ni atom, is formed on addition of $Ni(OAc)_2$ to the requisite proligand. After addition of the co-ordinating NCS^- anion an equilibrium could exist in solution between different binding modes (Scheme 1).

A. chelating (Koga *et al*[7])   **B**. monodentate bridge-chelate   **C**. monodentate bridge-only

[each of the above binding modes is accompanied by a phenolate bridge and a *syn-syn* bidentate bridging ethanoate]

Scheme 1 Possible binding equilibrium.

The X-ray structures reveal that the [5,6] and [6,6]-chelation modes favour product **B** and so in solution **A** $\rightleftharpoons$ **B** dominates, with addition of the NCS^- occurring at the Ni_{iminic} atom. In this

mode the monodentate bridge-chelated ethanoate would have a greater stability than a simple monodentate bridged ethanoate. When the chelation mode is [5,5] then the X-ray structures show the presence of a monodentate bridging NCS^- anion. The equilibrium in solution now favours **C** and so addition of the anion could lead to bridge interconversion, the NCS^- anion being the favoured monodentate donor and the second NCS^- anion would replace the MeOH of solvation at the N_{aminic} atom, this being the solvent which is least well bound.

Conclusions

Although it is possible that non-crystalline material recovered from the reactions, or residual mother liquors from the crystal-lisation process, could contain complexes of a different com-position the results above indicate that in dinuclear nickel(II) complexes of asymmetric compartmental ligands it is the provision of an iminic pendant arm capable of generating a six-membered chelate ring at the metal that leads to the systematic generation of complexes in which there is a monodentate, bridging ethanoate present. The generality of this reaction has so far been tested for ligands in which the donor atoms of the pendant arms are nitrogenous being derived from pyridine, imidazole and tertiary amino (NR_2) groups.

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13 Siemens SHELXTL version, an integrated system for solving and refining crystal structures from diffraction data (Revision 5.1), Siemens Analytical X-ray Instruments Ltd, Madison, WI, 1996.
14 The coordination set is defined by the number of atoms in the chelate ring at the metal hence the generation of six-membered chelate rings at both nickel atoms provides a [6,6] coordination set. The chelate ring from the aminic arm is listed before that from the iminic arm.