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Dimetallic complexes of acyclic pyridine-armed ligands derived from 3,6-diformylpyridazine[†]

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A bis(pyridine-armed) acyclic Schiff base ligand L1 has been synthesised from 3,6-diformylpyridazine and two equivalents of 2-(2-aminoethyl)pyridine. Reduction of this ligand using NaBH₄ resulted in the formation of the amine analogue L2. Complexes of the form $[M_2L1(\mu-X)]Y_2ClO_4$ [where: M = Cu(II), $X = OH^-$ and $Y = ClO_4^- 1$, $Cl^- 2$, $Br^- 3$ or $I^- 4$; M = Co(II), $X = OH^-$ and $Y = ClO_4^- 5$; M = Ni(II), $X = SCN^- 6$ or $X = N_3^- 7$ and $Y = ClO_4^-$], and $[Cu_2L2(\mu-OH)](ClO_4)_3$ 8 were prepared and characterised. The complexes 1 and 5–7 have been characterised by single-crystal X-ray diffraction. The acyclic ligand L1 provides three nitrogen donor atoms per metal centre, including a pyridazine bridge between the metal centres, and the anion X also bridges the two metal centres. As required, coordinating solvent molecules or additional anions make up the remainder of the coordination sphere. The two copper centres of 1 are very strongly antiferromagnetic pyridazine bridging pathway and ferromagnetic 1,1-bridging azide pathway resulted in the observation of weak antiferromagnetic exchange in the dinickel(II) complex 7 ($2J = -14 \text{ cm}^{-1}$). Electrochemical examination of L1, L2 and complexes 1 and 5–8 revealed multiple redox processes. These have been tentatively assigned to a mixture of metal centred and ligand centred redox processes on the basis of cyclic voltammetry and coulometry results and comparisons with literature examples.

Introduction

Of the three diazines, pyridazine, pyrimidine and pyrazine, pyrazine has been the most widely utilised as a bridge between metal ions,¹ however, a significant number of pyridazine (or indeed phthalazine) bridged complexes are also known.^{2–5} Pyridazine-containing ligands tend to form transition metal complexes in which two metal ions are bridged by the diazine and are hence held in close proximity to one another. In the acyclic complexes further bridging groups, such as acetate, hydroxide, halogen, sulfate, nitrate, iodate, or azide, are often,⁴ but not always,^{2,5–7} also present. These 1,2-diazine-bridged acyclic, and macrocyclic,^{3,8–14} complexes are of particular interest in magnetostructural, electrochemical and catalysis studies.

This paper details the synthesis and characterisation of a new acyclic pyridazine-based Schiff base ligand L1, the amine analogue L2 (Fig. 1), and a series of dimetallic complexes, $[Cu^{I_2}L1(\mu-OH)Y_2]-ClO_4 [Y = ClO_4^-1; Y = Cl^-2; Y = Br^-3; Y = I^-4], [Co_2L1(\mu-OH)-(CH_3CN)_4](ClO_4)_3 5, [Ni_2L1(\mu-NCS)(CH_3CN)_3(H_2O)](ClO_4)_3 6, [Ni_2L1(\mu-N_3)(CH_3CN)_4](ClO_4)_3 7 and [Cu_2L2(\mu-OH)](ClO_4)_3 8. These singly-pyridazine bridged complexes are compared with the doubly-pyridazine bridged complexes obtained using a closely related Schiff base macrocyclic ligand, L3 (Fig. 1).^{3,8-14}$

Results and discussion

Synthesis of L1 and L2

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Whilst the complexes of L1 (Fig. 1) could be prepared directly, in a one-pot reaction of 3,6-diformylpyridazine and 2-(2aminoethyl)pyridine in the presence of the appropriate metal salt, it was more convenient to first prepare and isolate L1, as this

† Electronic supplementary information (ESI) available: Figs. S1–3: NMR spectra. Fig. S4: Line diagram of the least squares fit of the nitrogen atoms of L and bridging azide atoms of the two independent molecules of 7 in the asymmetric unit. Fig. S5–7: cyclic voltammetric data. Fig. S8–11: Variable temperature susceptibility and magnetic moment data. See http://www.rsc.org/suppdata/dt/b4/b403131h/



Fig. 1 The single pyridazine containing acyclic ligands L1 and L2 and the double pyridazine containing macrocyclic ligand L3.

compound is stable indefinitely whereas 3,6-diformylpyridazine is not.¹³ Both methods gave similar overall yields and product purities. Isolation of metal-free L1 meant that the amine analogue L2 (Fig. 1) could also be easily prepared. In contrast, the macrocyclic ligand L3 has, to date, only been successfully prepared as a variety of metal ion complexes, not in a metal-free form, and in these metal complexed forms the reduction of the imine bonds to amine bonds has not been reproducibly achieved.¹⁴

The L1 ligand is formed quantitatively from 3,6-diformylpyridazine and 2-(2-aminoethyl)pyridine in dry acetonitrile. A sharp C=N stretch is observed at 1643 cm⁻¹ and there is no evidence of primary amine stretches (typically 3400–3330 and 3330–3250 cm⁻¹) or of a carbonyl stretch from unreacted 3,6-diformylpyridazine (1709 cm⁻¹). The proton and carbon NMR spectral assignments were confirmed by HMQC and HMBC 2D correlation experiments. The FAB mass spectrum of L1 contained the parent ion and fragments associated with the loss of one of the alkyl arms. The melting point for this new ligand was 110 °C.

Conversion of the Schiff base ligand L1 into the diamine derivative L2 was achieved by NaBH₄ reduction in acetonitrile solution. The free amine L2 was obtained as a hygroscopic brown oil in 86% yield and this was used without further purification. If desired, the free amine could be purified by forming the dihydrochloride salt, (H₂L2)Cl₂, as a white analytically clean powder. The poor yield (21%) of this salt is attributed to its significant solubility in isopropyl alcohol making isolation difficult.

A comparison of the IR spectra of L1 and $(H_2L2)Cl_2$ shows differences which are consistent with the conversion of the imine bonds to protonated secondary amine bonds. The proton and carbon NMR spectra of the two ligands also reflect the expected changes on conversion from imine to secondary amine functional groups.

Synthesis of complexes of L1 and L2

There are numerous examples of acyclic pyridazine complexes but the diazine is not always employed in a bridging capacity. Most of the acyclic pyridazine-bridged complexes are of copper,^{4,5,15} and nickel^{5,16,17} with far fewer examples of manganese,¹⁸ iron¹⁹ or cobalt⁶ complexes. Complexation of L1, either directly in a one-pot reaction with the ligand components or *via* preformed L1, was attempted with many metal salts both in the presence and absence of a deliberately added additional bridging group.

It was found that copper, nickel or cobalt perchlorate salts, in acetonitrile, were the common component of the successful combinations, generating crystalline materials as opposed to oils or ligand degradation products. $[Cu_2L1(\mu-OH)](ClO_4)_3 1$ and $[Co_2L1(\mu-OH)-(CH_3CN)_4](ClO_4)_3 5$ were obtained as single crystals and their structures were determined *via* X-ray diffraction (Figs. 2 and 3 respectively). The product from the analogous nickel reaction was an oil regardless of the solvent used, but, by adding one equivalent of either azide or thiocyanate ions either just before or just after the addition of the nickel perchlorate, single crystals of $[Ni_2L1(\mu-NCS)-(CH_3CN)_3(H_2O)](ClO_4)_3 6$ and $[Ni_2L1(\mu-N_3)(CH_3CN)_4](ClO_4)_3 7$ were obtained, in which the added anion is present as a one-atom bridge (Figs. 4 and 5).

Infinite ladder arrays, of dicopper(II) complexes, have been observed previously in pyridazine chemistry.¹¹ This architecture is of interest, particularly for iron and cobalt, due to the possibility of it generating desirable magnetic properties. Attempts to reproduce this architecture, from 1 by the addition of two equivalents of the respective tetraethylammonium halide, resulted in complexes of the form [Cu₂L1(μ -OH)Y₂]ClO₄, where Y = Cl⁻ 2, Br⁻ 3 or l⁻ 4. Unfortunately, the limited solubility of these complexes hindered attempts to grow single crystals so no X-ray structure determinations could be attempted. Attempts to obtain structural information for 8 were also unsuccessful.

The IR spectra were recorded as KBr discs. In the IR spectrum of 7 there is a strong sharp band at 2070 cm⁻¹ due to the asymmetric stretching vibration of the azide group. This is in a similar position to that reported for 1,1-bridging azides in some other dinickel systems,^{20,21} however, it is difficult to be definitive about the binding mode as both uncoordinated and 1,3-bridging azides²² absorb in this region, with only the near linear M-NNN-M 1,3-bridging mode being readily identified, at ca. 2200 cm^{-1.23} The X-ray structure determination proves that the azide in 7 is indeed bound in the 1,1-bridging mode (Fig. 5). The IR spectrum of 6 has one strong band due to a thiocyanate C=N stretch at 2095 cm⁻¹, yet the X-ray structure determination (Fig. 4) shows the presence of a 1,1-N-bridging thiocyanate ion only, with no evidence of disorder (e.g. partial occupancy 1,1-S-bridge). There is clear evidence in the literature that thiocyanate bands below 2000 cm^{-1} are due to the 1,1-N-bridging mode of thiocyanate.^{13,24,25} We suggest that on preparing the KBr disc there has been complete anion exchange, resulting in the observation of a band due to free or non-bridging thiocyanate anion. A second IR spectrum, carried out in Nujol, showed the expected band at 1977 cm⁻¹ (typical values for the C=N stretch for thiocyanate acting as a 1,1-N-bridge in dinickel complexes are $1965-1985 \text{ cm}^{-1}$).²⁵

Conductivity measurements were recorded in acetonitrile for all of the complexes except for the complexes **2–4**, which, due to a lack of solubility in acetonitrile, were recorded in DMF. The complexes **1** and **5–8** have molar conductivities near the literature range for 3:1 electrolytes.²⁶ The X-ray crystal structures of **1**, **5** and **6** show that the perchlorate ions have, at best, only a weak interaction with the metal centres and are therefore highly likely to dissociate in solution leading to the observed values. Complexes **7** and **8** are similarly expected to have weak interactions with the perchlorate range for a 1:1 electrolyte,²⁶ indicating that the chloride and bromide ions remain bound to the metal centres in DMF. The molar conductivity for **4**, however, is just short of the literature range for a 2:1 conductor,²⁶ suggesting that in this solvent the iodide anions have partially dissociated.

NMR spectra of the complexes 1 and 8

The proton NMR spectra of the complexes 1 and 8 were investigated over a variety of temperatures in deuterated acetonitrile (ESI[†]). Peaks were assigned on the basis of peak area integration, the changes in chemical shift as a function of temperature²⁷ (ESI⁺) and by comparison with literature examples.28 The complete assignment is given for the proton NMR spectrum of 1 at -40 °C (Fig. S2, ESI[†]). Signals are present for all protons except for the hydroxide proton, which is expected, even at this low temperature, to be too broad to be seen. The imine signal is not seen at room temperature and only just becomes distinguishable at lower temperatures. At -20 °C the pyridine protons have some resolved fine structure: the coupling constant between the triplet and the adjacent doublets is 7.6 Hz. The proton NMR spectrum of the amine analogue 8 shows many similar features to that of the imine complex 1 just discussed, with the exception of the alkyl region (Fig. S3, ESI⁺). On reducing the temperature from 30 to -35 °C the multiple signals attributed to the ethyl arms experience a downfield shift and move closer together. Unfortunately at -35 °C these signals are still numerous, broad and overlapping and assignment is not possible. The proton NMR was also repeated in deuterated methanol, which allowed a lower temperature (-90 °C) to be reached, in the hope that these signals would coalesce. The general trend observed for the complex in deuterated acetonitrile was not seen in methanol and therefore this region remains unassigned.

X-Ray crystal structures

Crystals of 1, 5, 6 and 7 were grown by the slow diffusion of diethyl ether vapour into an acetonitrile solution of the respective complex and the X-ray crystal structures determined. There is one complete molecule of 1 in the asymmetric unit (Fig. 2). Each copper(II) ion is bound in the square plane by a hydroxide ion and three nitrogen donor atoms, from the pyridazine, pyridine and imine moieties, with the angles subtended at the copper(II) centres varying from 78.3(2) to $100.2(2)^{\circ}$. Both the hydroxide ion and the pyridazine moiety bridge the two metal centres. All of the Cu-N bond lengths fall within a relatively narrow range [1.972(5)-2.005(5) Å] and the Cu–OH bond distances are slightly shorter [1.929(4)–1.932(4) Å] than the remainder, as expected. There are also interactions between the copper ions and some of the perchlorate oxygen atoms, with the hydrogen bonded perchlorate ion significantly closer to Cu(2) $[Cu(2)\cdots O(31) 2.381(4) Å]$ than either of the other two perchlorate anions are to Cu(1) [Cu(1) \cdots O21 2.559(4) and Cu(1) \cdots O(11) 2.510(4) Å]. When these interactions are taken into account Cu(1) is in a distorted octahedral environment and Cu(2) is in a distorted square pyramidal environment. A weak hydrogen bonding interaction is observed between one of the perchlorate oxygen atoms, O(32), and the hydroxide proton $[O(1)\cdots O(32) 2.857(6) \text{ Å}]$. The pyridine rings are twisted away from the mean plane through the pyridazine ring atoms [N(4) pyridine 24.2(3)°; N(6) pyridine $18.1(3)^{\circ}$]. The twist is facilitated by the flexibility afforded by the ethylene connections.



Fig. 2 Perspective view of 1 showing the labelling scheme, the hydrogen bonding interaction between the hydroxide proton (all other hydrogen atoms have been omitted for clarity) and one of the perchlorate anions, and the weak interactions between the perchlorate anions and the metal centres. Selected bond lengths (Å) and angles (°): Cu(1)-O(1) 1.932(4), Cu(1)-N(1) 1.989(5), Cu(1)-N(3) 2.005(5), Cu(1)-N(4) 1.980(5), Cu(1)-O(11) 2.510(5), Cu(1)-O(21) 2.559(4), Cu(2)-O(1) 1.929(4), Cu(2)-N(2) 1.994(5), Cu(2)-N(5), 2.003(5), Cu(2)-O(31) 2.381(4), Cu(1)...Cu(2) 3.393(2); O(1)–Cu(1)–N(4) 100.2(2), N(1)–Cu(1)–N(3) 78.3(2), N(5)– Cu(2)–O(31) 91.3(2), N(4)–Cu(1)–N(1) 172.7(2), N(4)–Cu(1)–O(11) 96.1(2), O(1)-Cu(2)-N(6) 99.7(2), N(4)-Cu(1)-N(3) 94.5(2), N(3)-Cu(1)-O(11) 92.1(2), N(6)-Cu(2)-N(2) 170.0(2), O(1)-Cu(1)-O(11) 87.6(2), N(4)-Cu(1)-O(21) 93.0(2), N(6)-Cu(2)-N(5) 94.5(2), N(1)-Cu(1)-O(11) 82.7(2), N(3)-Cu(1)-O(21) 86.9(2), O(1)-Cu(2)-O(31) 92.8(2), O(1)-Cu(1)–O(21) 91.2(2), O(1)–Cu(2)–N(2) 87.0(2), N(2)–Cu(2)–O(31) 95.7(2), N(1)-Cu(1)-O(21) 88.2(2), O(1)-Cu(2)-N(5) 165.2(2), O(1)-Cu(1)-N(1) 87.0(2), N(2)-Cu(2)-N(5) 78.4(2), O(1)-Cu(1)-N(3) 165.2(2), N(6)-Cu(2)-O(31) 91.4(2), Cu(2)-O(1)-Cu(1) 123.0(2).

The asymmetric unit for 5 consists of one half of the complex with the other half generated by reflection (Fig. 3). Both cobalt(II) centres are in a distorted octahedral donor environment, with angles subtended at the cobalt(II) centres varying from 74.0(1)-105.9(1)°. Five of the six donors are nitrogen atoms, consisting of pyridazine (which spans the two metal centres), pyridine and imine in-plane donors, and two coordinated acetonitrile molecules in the axial positions. The Co-N(acetonitrile) bonds are longer [2.160(4) and 2.180(4) Å] than the Co-N(ligand) bond lengths [2.108(3)-2.124(3) Å]. The relative weakness of the Co-N(acetonitrile) bonds is consistent with the fact that virtually all of these solvent molecules are lost on storage of the crystals under vacuum. The sixth, and only non-N donor, is a hydroxide ion which bridges the two metal centres. There is a weak hydrogen bonding interaction between one of the perchlorate oxygen atoms [O(11)] and the hydroxide proton $[O(1)\cdots O(11) 3.22(1) \text{ Å}]$, bringing this perchlorate ion closer to the complex. Again the pyridine rings are kinked [20.2(2)°] in relation to the mean plane through the pyridazine ring atoms.

There is one independent molecule of 6 in the asymmetric unit (Fig. 4). The two nickel(II) centres are in a distorted octahedral donor environment, with angles subtended at the nickel(II) centres varying from 78.2(6)-101.1(7)°. For Ni(1) all donors are nitrogen atoms, consisting of pyridazine, thiocyanate (both of these moieties bridge the two metal centres), pyridine and imine in-plane donors and two coordinated acetonitrile molecules in the axial positions. For Ni(2) the donor set is the same except that it has a coordinated water molecule in place of one acetonitrile molecule. There is no significant difference between the Ni-N(acetonitrile) bond distances [1.990(17)-2.057(18) Å] and the Ni-N(ligand) bond lengths [2.008(16)–2.069(14) Å]. The Ni(2)–O(1) 2.068(12) Å distance is similar. The Ni-N(acetonitrile) bonds on average are shorter than the corresponding Co-(acetonitrile) bonds of the dicobalt(II) complex 5 and the related macrocyclic complexes of L3 with axially coordinated acetonitrile molecules.8 This observation is consistent with our inability to remove these solvent molecules from 6 on storage under vacuum.

 Table 1
 A comparison of selected structural parameters of two of the octahedral complexes

	$[Co_{2}L1(\mu\text{-OH})\text{-}\\(CH_{3}CN)_{4}]^{3^{+}}$	$[Ni_{2}L1(\mu\text{-NCS})\text{-} (CH_{3}CN)_{3}(H_{2}O)]^{3+}$
M–N(acetonitrile)/Å	2.160(4)-2.180(4)	1.995(15)-2.068(16)
M–N(L1)/Å	2.108(3)-2.124(3)	2.028(16)-2.072(14)
M–X–M/°	120.9(2)	115.2(7)
M…M/Å	3.477(2)	3.606(3)



Fig. 3 Perspective view of 5 showing both the labelling scheme and the hydrogen bonding interaction between the hydroxide proton and one of the perchlorate anion oxygen atoms (O11), all other hydrogen atoms, solvent molecules and other perchlorate ions have been omitted for clarity (A denotes the symmetry generated half of molecule using the relationship x, 0.5 - y, z). Selected bond lengths (Å) and angles (°): Co(1)–O(1) 1.999(2), Co(1)–N(1) 2.108(3), Co(1)–N(4) 2.118(3), Co(1)–N(3) 2.124(3), Co(1)–N(30) 2.160(4), Co(1)–N(40) 2.180(4), Co(1)····Co(1A) 3.477(2); O(1)–Co(1)–N(1) 88.7(1), O(1)–Co(1)–N(4) 105.9(1), N(1)–Co(1)–N(4) 165.3(1), O(1)–Co(1)–N(3) 162.1(1), N(1)–Co(1)–N(3) 74.0(1), N(4)–Co(1)–N(30) 91.3(1), O(1)–Co(1)–N(30) 90.2(1), N(1)–Co(1)–N(30) 92.4(1), N(4)–Co(1)–N(30) 93.6(1), N(3)–Co(1)–N(30) 86.2(1), O(1)–Co(1)–N(40) 96.4(1), N(1)–Co(1)–N(40) 86.7(1), N(4)–Co(1)–N(40) 92.7(1), N(3)–Co(1)–N(40) 173.3(1), Co(1)–O(1)–Co(1A) 120.9(2), N(1A)–N(1)–Co(1) 120.8(1).

The oxygen atoms on one of the perchlorate anions [Cl(3)] are disordered over two sites in the ratio 0.52 [O(32), O(33), O(34)]: 0.48 [O(35), O(36), O(37)]. There are hydrogen bonding interactions between the O(32) and O(36) oxygen atoms on this perchlorate ion and O(11) on another perchlorate ion [Cl(1)] with the protons on the coordinated water molecule O(1) [O(1) \cdots O(11) 2.88(2), O(1) \cdots O(32) 2.86(6) and O(1) \cdots O(36) 2.69(4) Å] (Fig. 4). Again the pyridine rings are kinked [23.9(9) for N5(pyridine) and 18.5(10)° for N6(pyridine)] in relation to the mean plane of the pyridazine ring atoms (Fig. 4).

There are two independent molecules of 7 in the asymmetric unit with only minor spatial orientation differences between the overall structures (ESI \dagger). One of the independent molecules is shown in Fig. 5. All four of the nickel(II) centres are in distorted octahedral donor environments, however due to the poor quality and lack of completeness of the data further analysis is not possible. The overall structure of the cation is, however, clear (Fig. 5).

A comparison of the two well defined structures containing distorted octahedral metal ions, $[Co_2L1(\mu-OH)(CH_3CN)_4]^{3+}$ and $[Ni_2L1(\mu-NCS)(CH_3CN)_3(H_2O)]^{3+}$, reveals close similarities (Table 1). Compared to the corresponding parameters in the thiocyanate bridged nickel(II) complex, the hydroxide bridged cobalt(II) complex has a significantly smaller M…M separation and a significantly larger M–X–M angle (as a consequence of the different one-atom bridge X), but similar M–N(ligand) distances and slightly longer M–N(acetonitrile) distances.

 Table 2
 Cyclic voltammetric data in acetonitrile–0.1 M [Bu₄N]ClO₄

Compound Scan rate/V s ⁻¹		Reduction			Oxidation $\overline{E_{1/2}/V(\Delta E_p/V) \text{ or } E_{pa}{}^a/V}$		
		$\overline{E_{1/2}}/V$ ($\Delta E_p/V$) or $E_{pc}{}^a/V$					
L1	0.2			-1.88 (0.18)			
L2	0.2						2.02
1	0.2	-0.41	-1.19	-1.87(0.19)	-0.42^{b}	0.80^{c}	1.96
8	0.2	-0.71	-1.26	-1.96	-0.53^{b}	-0.07^{c}	1.76
5	0.1	-0.71(0.25)	-0.85(0.11)	-1.64(0.13)	0.49 (0.33)	0.79 (0.20)	
6	0.1	-0.70(0.27)	-1.30(0.11)	-1.67(0.08)		× /	1.69
7	0.1	-0.74(0.11)	-1.01(0.15)	-1.49(0.17)			1.51

C(61) C(41) C(60))C(40) N(60) C(3) C(4) N(40) C(15) C(2) C(18) C(6) S(30) N(4) N(3) C(8) C(9) C(19 C(17) C(30) <u>۱</u> C(20) NIXO C(11) N(5) C(21) (14) N(50) C(22 C(12) C(13) 0(37) C(50) CI(3 Ø0(36) 0(12) 0(35) C(51) 0(11))CI(1) 0(13) 0(14)

Fig. 4 Perspective view of 6 showing both the labelling scheme and the hydrogen bonding interactions between the coordinated water molecule and two of the perchlorate anions (all other hydrogen atoms and one noninteracting perchlorate ion have been omitted for clarity). Selected bond lengths (Å) and angles (°): Ni(1)-N(1) 2.069(14), Ni(1)-N(50) 1.990(17), Ni(2)-N(30) 2.130(14), Ni(1)-N(3) 2.008(16), Ni(2)-N(2) 2.058(14), Ni(2)-N(60) 2.052(17), Ni(1)-N(5) 2.060(18), Ni(2)-N(4) 2.052(16), Ni(1)-N(30) 2.130(14), Ni(1)-N(40) 2.057(18), Ni(2)-N(6) 2.054(17), Ni(2)-O(1) 2.068(12), Ni(1)···Ni(2) 3.606(11); N(50)-Ni(1)-N(3) 92.6(6). N(3)-Ni(1)-N(30) 165.8(6), N(6)-Ni(2)-O(1) 91.6(6), N(50)-Ni(1)-N(40) 175.3(7), N(40)-Ni(1)-N(30) 85.6(6), N(4)-Ni(2)-O(1) 90.8(5), N(3)-Ni(1)-N(40) 92.1(6), N(5)-Ni(1)-N(30) 101.1(7), N(60)-Ni(2)-O(1) 175.4(6), N(50)-Ni(1)-N(5) 89.6(7), N(1)-Ni(1)-N(30) 87.9(6), N(2)-Ni(2)-N(30) 87.4(6), N(3)-Ni(1)-N(5) 92.9(7), N(2)-Ni(2)-N(6) 171.9(7) N(6)-Ni(2)-N(30) 100.7(7), N(40)-Ni(1)-N(5) 90.7(7), N(2)-Ni(2)-N(4) 78.4(6), N(4)-Ni(2)-N(30) 165.8(6), N(50)-Ni(1)-N(1) 88.6(6), N(6)-Ni(2)-N(4) 93.5(7), N(60)-Ni(2)-N(30) 88.3(6), N(3)-Ni(1)-N(1) 78.2(6), N(2)-Ni(2)-N(60) 88.4(6), O(1)-Ni(2)-N(30) 88.0(5), N(40)-Ni(1)-N(1) 91.8(6), N(5)-Ni(1)-N(1) 170.8(6), N(50)-Ni(1)-N(30) 89.7(6), N(6)-Ni(2)-N(60) 91.7(6), N(4)-Ni(2)-N(60) 92.2(6), N(2)-Ni(2)-O(1) 88.7(5), Ni(1)-N(30)-Ni(2) 115.1(7)



Fig. 5 Perspective view of one of the two independent molecules of 7 in the asymmetric unit (hydrogen atoms and perchlorate ions have been omitted for clarity). Due to the poor quality and lack of completeness of the data further analysis is not possible but the overall structure of the cation is clear.

As expected, the complex $[Cu_2L1(\mu-OH)](ClO_4)_3$ has a similar hydroxide bridging angle $[122.9(2)^\circ]$ to that of the cobalt complex $[120.9(2)^\circ]$ as each complex possesses the same one-atom bridging group. The ligand also adopts a similar conformation in each complex. The length of the alkyl arm containing the pyridine donor is such that for the nitrogen of the pyridine unit to bind to the metal centre, the alkyl arm is buckled out of plane and the pyridine ring plane is thus kinked with respect to the pyridazine ring plane. For reasons unknown it is more pronounced on one side of the molecule (for **1**, **6** and **7**) than the other. The magnitude of this effect is similar for each complex.

Electrochemistry

Cyclic voltammetric data for ligands L1 and L2, and complexes 1, 8, 5, 6 and 7 are given in Table 2. Ligand L1 exhibits a quasi-reversible one-electron reduction process which is assigned to reduction of the imine to a secondary amine.²⁹ This assignment is based on the observation that pyridazine ring reduction is likely to occur at a more negative potential than the solvent limit³⁰ and chemical reduction of L1 (with NaBH₄) results in amine L2 and not a hydropyridazine derivative. For the amine derivative, L2, the only redox process is an irreversible oxidation which can reasonably be assigned to either pyridazine ring oxidation or amine oxidation. Amine oxidation in dibenzylamine occurs at 1.49 V vs. Ag/AgNO₃,³¹ while Yan, Yang and Cao have shown that pyridazine is electrochemically irreversibly oxidized at ~2.2 V vs. Ag/AgNO₃,³² The electron donating groups present in L2 will lower the oxidation potential of pyridazine in this ligand.

Cyclic voltammograms of the Cu–imine complex 1 in acetonitrile show multiple redox processes (Fig. 6). Scanning from -0.10 V to more negative potentials reveals three reduction steps; an irreversible oxidation process is seen on scanning in the positive direction from the same initial potential. When the negative going scan is reversed at -1.50 V, a sharp oxidation peak is observed at $E_{\rm pa} = -0.42$ V. An irreversible oxidation process at $E_{\rm pa} = 0.80$ V (not shown) appears when the negative-direction scan is reversed at -0.70, -1.50 or -2.20 V.

Coulometry accompanying controlled potential electrolysis establishes that the reduction process at $E_{pc} = -0.41$ V involves two electrons (0.98 equivalents of 2e⁻) and is assigned to the reduction of both Cu(II) centres by one electron. The voltammetric response suggests that this is followed by loss of a Cu(I) ion from the complex to give a new mono Cu(I) derivative of L1 and [Cu(CH₃CN)₄]⁺. The latter complex is further reduced *via* a one-electron process at $E_{pc} = -1.19$ V to give Cu(0) which deposits on the electrode and is subsequently stripped off at $E_{pa} = -0.42$ V. This reforms the Cu(I) acetonitrile complex which is then irreversibly oxidised at 0.80 V. The electrochemical behaviour of Cu(ClO₄)₂ in acetonitrile supports this interpretation.³³ By comparison with the electrochemistry of the free ligand, the quasi-reversible reduction couple at $E_{Va} = -1.87$ V and the irreversible oxidation of the complex at $E_{pa} = 1.96$ V are assigned to ligand-centred processes.

Cyclic voltammograms of the amine analogue **8** show similar processes to those of **1** (Fig. 6), and similar assignments are likely with the exception of the irreversible reduction at $E_{pc} = -1.96$ V which is tentatively assigned to reduction of the pyridazine ring.



Fig. 6 Cyclic voltammograms of Cu–imine complex 1 (—) and Cu–amine complex 8 (—) at 0.2 V s⁻¹ in acetonitrile. Arrows indicate the starting point and initial direction of the scans.

Comparison of the electrochemistry of the acyclic complexes **1** and **8** with that reported for the macrocyclic complex $[Cu_2L3(CH_3-CN)_2](ClO_4)_4$,¹¹ reveals that the potentials for Cu(11) reduction are more negative for the acyclic complexes, and the reduction products are less stable. These differences are the expected consequences of complexes **1** and **8** having one not two pyridazine bridges and lacking the stabilising effect of the macrocyclic ligand.

The cyclic voltammograms of complex 5, the Co(II) analogue of 1, show three quasi-reversible reduction processes (ESI⁺). Controlled potential bulk electrolysis confirms that the first two reductions together correspond to the addition of two electrons per complex (0.93 equivalents of 2e⁻). These processes are tentatively assigned to predominantly metal centred reductions, i.e. the formation of Co(II)Co(I) followed by $Co(I)_2$. As expected the potentials are considerably more negative than those of the doubly pyridazine bridged macrocyclic complex $[Co_2L3(CH_3CN)_4](ClO_4)_4(E_{\frac{1}{2}} = -0.11)$ and -0.33 V).¹² The third reduction process at $E_{\frac{1}{2}} = -1.64$ V is assigned to a ligand based reduction. Complex 5 also exhibits two quasi-reversible oxidation processes which are tentatively assigned to predominantly metal centred oxidations, giving Co(III)Co(II) followed by Co(III)₂. Consistent with these assignments, the oxidation processes in the acyclic complex occur at less positive potentials than the analogous oxidation processes of the macrocyclic complex $[Co_2L3(CH_3CN)_4](ClO_4)_4$ ($E_{\frac{1}{2}} = 0.87$ and 1.06 V).¹²

Dinickel(II) complexes 6 and 7 show similar voltammetry (ESI[†]). Each complex undergoes four quasi-reversible reduction steps and an irreversible oxidation process. Controlled potential electrolysis of 6 indicates that the first two closely-spaced reductions correspond to a total of four electrons per complex. The origins of the reduction processes for the nickel complexes are uncertain. Whilst pyridazine is well known to stabilise low oxidation states of metal ions,^{3,9,11,12,34,35} it seems unlikely that it could stabilise Ni(0) in this acyclic ligand arrangement. On the other hand, pyridazine ring reductions are not usually expected to occur at these potentials. Likewise, the irreversible oxidation processes of 6 and 7 may be metal-or ligand-based.

Magnetochemistry

Variable temperature magnetic susceptibility measurements were made on powdered samples of **1**, **5**, **6** and **7** in the range 300 to 4.2 K (Table 3 and ESI[†]).

The magnetic behaviour of **1** is typical of very strongly antiferromagnetically coupled systems containing a small amount of para-

Table 3 Results of fitting variable-temperature data to the Bleaney–Bowers equation (ρ is fraction of monomer)

	g	-2J/cm ⁻¹	ρ
1	2.10	1146 ~20	0.004
5 7	2.20	14	0.12

magnetic impurity. The best fit was calculated from the modified Bleaney–Bowers equation for exchange coupled pairs of copper(II) ions.³⁶ A one *g*-value Bleaney–Bowers equation was used to model the observed data.‡ A reasonable fit was obtained for the region 300–150 K. The resulting parameters are summarised in Table 3.

Very strong antiferromagnetic exchange $(-2J = 1146 \text{ cm}^{-1})$ is observed for 1: essentially it is diamagnetic, which is mirrored in the small degree of chemical shift and broadening seen in the proton and carbon NMR spectra (ESI†). Highly effective magnetic exchange between the two copper centres in 1 can conceivably occur *via* either the hydroxide bridge, or the pyridazine bridge or a combination of both pathways. In related systems^{34,37} the single atom hydroxide bridge is the predominant spin exchange pathway and it is expected to be in this case as well, however, pyridazine also mediates magnetic exchange and in the absence of other pathways can be quite effective¹¹ therefore a contribution from this pathway is also expected.

The magnetic behaviour of 7 is typical of weakly antiferromagnetic coupled systems containing a larger than usual paramagnetic impurity (12.2%). The data fitted well to a S = 1 dimer model using the Bleaney-Bowers equation (Table 3). Dinickel systems bridged only by a 1,1 azide ion typically exhibit ferromagnetic behaviour.^{21,38,39} In this case, due to the ability of the pyridazine bridge to mediate antiferromagnetic exchange, the overall exchange is weakly antiferromagnetic. This observation can be quantified somewhat by invoking the anticomplimentary arguments used more commonly for unsymmetrically di-bridged Cu--Cu species such as those found in Cu(µ-OPh)(µ-1,1-N₃)Cu and in Cu(µ-OR)(µpyrazolate)Cu combinations.^{40,41} The nature of the orbital overlap in the Ni(d_{xy})- μ -1,2-pyridazine pathway is akin to that of Cu(d_{xy})- μ -1,2-pyrazolate⁴¹ and yields a dominant $J_{\text{antiferro}}$ contribution to J. The 1,1-azide pathway acts in a counter complimentary manner to the pyridazine pathway, its J_{ferro} contribution acting to decrease the net antiferromagnetic coupling. Furthermore, MO calculations on symmetrical di- μ -1,1-N₃ Ni(II) complexes³⁹ suggest that a minimum $J_{\text{antiferro}}$ contribution should occur at a Ni–N–Ni angle of ~110°. close, perhaps coincidentally, to the approximate value obtained from the poor X-ray analysis of 7 (114°). These arguments are generally supportive of the low negative J value (-7 cm^{-1}) observed.

There are few, if any, other dinickel complexes containing 1,1bridging azide and a pyridazine or phthalazine bridge combination. Thompson and Tandon¹⁷ mentioned the need for such compounds in order to define an antiferromagnetic regime for 1,1-N₃⁻ bridging. The approximate Ni–Ni distance of 3.57 Å and Ni–N–Ni angle of 114°, obtained from the poor X-ray analysis of **7**, give a guide to the requisite geometry for antiferromagnetic coupling.¹⁷ Interestingly, a phthalazine/Cl⁻ bridge combination (Ni–Ni 3.68 Å, Ni–Cl–Ni 101.6°) yielded g = 2.227, 2J = -26 cm⁻¹, with rather stronger antiferromagnetic coupling than in **7**.⁴²

Unfortunately, due to large monomeric impurities, reasonable fits to the Bleaney–Bowers equation could not be obtained for **5** and **6**. For **5**, the position of χ_{max} suggests a stronger coupling than in the related macrocycle dicobalt complex.⁸ At room temperature this sample contains high-spin Co(II) ions [298 K: $\mu = 4.2 \mu_B$ per Co(II)] and -2J is estimated to be *ca*. 20 cm⁻¹. From the magnetic moment data for **6** at room temperature it can be seen that, as expected, the complex contains high-spin nickel(II) centres with magnetic

[‡] Strictly a different g value should be used for each Cu centre but one value was chosen as the χ -values were very small and there were only small changes with temperature.

moments slightly higher than the spin only value [290 K: μ = 2.98 $\mu_{\rm B}$ per nickel]; weak overall coupling is again evident.

Conclusions

The incorporation of 3,6-diformylpyridazine into Schiff-base ligand systems in recent years has allowed a renewed and varied investigation of the pyridazine moiety and its ability to act as a bridge in transition metal complexes, both in macrocyclic complexes and, more recently, in acyclic complexes. The reactions of transition metal perchlorate salts with the new acyclic pyridazine-containing L1 and L2 ligands have led to dimetallic complexes in which the two incorporated metal(II) ions are bridged in the equatorial plane by the pyridazine unit and an anion (hydroxide, thiocyanate or azide). Single-crystal X-ray structure determinations carried out on four of these complexes proved this to be the case. Strong antiferromagnetic exchange was exhibited by the dicopper(II) complex 1, which is typical of hydroxide-bridged systems, the pyridazine bridge playing a minor role in the exchange. Competition between the pyridazine (antiferromagnetic) and 1,1-bridging azide group (ferromagnetic) resulted in the observed overall weak antiferromagnetic exchange for the dinickel(II) complex 7. Electrochemical investigation of the complexes revealed quasi- or irreversible processes, in contrast to the reversible processes observed in the related macrocyclic complexes. The electrochemical potentials of these processes in the acyclic complexes, when compared with the corresponding Cu(II) and Co(II) L3 macrocyclic complexes, revealed that the potentials at which the equivalent reductions and, in the case of cobalt, oxidations, occur are substantially more negative for the acyclic complexes. This decreased stabilisation of the lower oxidation states is attributed to the presence of one less pyridazine ring in the acyclic complexes as compared to the related macrocyclic complexes, and to the lack of the macrocyclic ring.

Experimental

Starting materials and reaction procedures

As reported previously except for the following.^{11,13} 3,6-Diformylpyridazine was synthesised according to the published procedure.¹³ 2-(2-Aminoethyl)pyridine (Aldrich, 95%) was distilled under vacuum before use and *o*-aminophenol (Riedel-de Haen) was used without further purification. The magnetic measurements were carried out on a Quantum Design MPMS5 SQUID Instrument as described earlier.⁸ Other measurements were carried out as described previously.¹³

CAUTION! Whilst no problems were encountered in the course of this work, perchlorate mixtures are potentially explosive and should therefore be handled with appropriate care.

L1. To a stirred yellow solution of 3,6-diformylpyridazine (0.780 g, 5.7 mmol), in dry acetonitrile (60 cm³), was added a clear colourless solution of 2-(2-aminoethyl)pyridine (1.400 g, 11.4 mmol) in dry acetonitrile (40 cm³). The resulting clear golden yellow solution was stirred overnight during which time the colour intensified. The solution was then reduced to dryness in vacuo to give the impure ligand L as a light fawn solid in quantitative yield. This was usually used without further purification, but could be purified by recrystallisation from dichloromethane or benzene by vapour diffusion of pentane; mp 110 °C. Found: C, 69.6; H, 6.2; N, 24.5. C₂₀H₂₀N₆ requires: C, 69.7; H, 5.9; N, 24.4%. IR (KBr disk, inter alia) v_{max}/cm⁻¹: 3043, 3013, 2927, 2881, 2857, 1643, 1588, 1568, 1474, 1431, 765. $\delta_{\rm H}$ (300 MHz, solvent CDCl₃, reference TMS): 8.61 (2H, s, H6), 8.56 (2H, d, H14), 8.15 (2H, s, H4) 7.58 (2H, t, H12), 7.17 (2H, d, H11), 7.12 (2H, d of d, H13), 4.17 (4H, t, H8), 3.23 (4H, t, H9). $\delta_{\rm C}$ (75 MHz, solvent CDCl₃, reference CDCl₃): 159.8 (C6), 159.1 (C5), 157.3 (C10), 149.2 (C14), 136.1 (C12), 124.4 (C4), 123.4 (C11), 121.3 (C13), 60.9 (C8), 39.0 (C9) FAB m/z (fragment): 345 (C₂₀H₂₁N₆); 252 (C₁₄H₁₄N₅).

L2. To a stirred room-temperature yellow solution of L1 (0.344 g, 1 mmol), in dry acetonitrile (50 cm³), was added solid sodium

borohydride (0.076 g, 2 mmol) in small portions over 1 h causing a red colour to develop. The solution was stirred for 2 h, then brought to reflux for 5 min. After cooling to room temperature the deep red solution was acidified with 1 M hydrochloric acid (ca, 7 cm³) until pH = 1 and then the solvent was removed in vacuo. The resulting brown oily residue was dissolved in saturated sodium chloride solution (50 cm³) and to this was added 1 M sodium hydroxide (ca. 5 cm³) until pH = 10. The aqueous solution was extracted with chloroform $(4 \times 30 \text{ cm}^3)$, the organic extracts combined, dried over anhydrous sodium sulfate, filtered and the solvent removed in *vacuo* to give a deep brown oil (0.298 g, 86%). $\delta_{\rm H}$ (300 MHz, solvent CDCl₃, reference TMS): 8.51 (2H, s, H14), 7.58 (2H, s, H12), 7.48 (2H, s, H4), 7.18 (2H, s, H11), 7.13 (2H, d, H13), 4.10 (4H, s, H6), 3.01 (~10H, multiplet, H8, H9 and amine NH). $\delta_{\rm C}$ (75 MHz, solvent CDCl₃, reference solvent): 160.1 (C5), 159.8 (C10), 149.0 (C14), 136.2 (C12), 126.1 (C4), 123.1 (C11), 121.1 (C13), 52.9 (C6), 48.7 (C8), 38.2 (C9). This was usually used without further purification but if desired purification of this oil could be achieved by converting it to the dihydrochloride salt, (H₂L2)Cl₂ as follows. The oil was dissolved in dry ethanol (60 cm3), acidified with two equivalents of concentrated hydrochloric acid and the solvent removed in vacuo yielding a deep brown powder. This was washed with hot isopropyl alcohol (3×10 cm³), filtered and dried *in vacuo* to give the dihydrochloride salt as a white powder (0.087, 21%); mp 195 °C (decomp.). Found: C, 55.7; H, 6.3; N, 19.8. C₂₀H₂₆N₆Cl₂·½H₂O requires: C, 55.8; H, 6.3; N, 19.5%. IR (KBr disk, inter alia) v_{max}/cm⁻¹ 3250, 2946, 2762, 2668, 2452, 1593, 1476, 1436, 1057, 1004, 769 $\delta_{\rm H}$ (300 MHz, solvent D₂O, reference DSS): 8.39 (2H, d, H14), 7.79 (2H, t, H12), 7.76 (2H, s, H4), 7.36 (2H, d, H11), 7.30 (2H, t, H13), 4.60 (4H, s, H6), 3.54 (4H, t, H8), 3.22 (4H, t, H9). $\delta_{\rm C}$ (75 MHz, solvent D₂O, reference DSS) 158.5 (C5), 157.5 (C10), 151.2 (C14), 141.8 (C12), 131.4 (C4), 127.2 (C11), 126.0 (C13), 52.0 (C6), 49.8 (C8), 35.4 (C9). FAB m/z (fragment): 349 (L2H⁺).

 $[Cu_2L1(\mu-OH)](ClO_4)_3$ (1). To a stirred yellow solution of L1 (0.300 g, 0.877 mmol) in dry acetonitrile (27 cm³), was added a blue solution containing Cu(ClO₄)₂·6H₂O (0.650 g, 1.754 mmol) in dry acetonitrile (26 cm³). The resulting intense blue-green solution was stirred for 4 h after which it was reduced in volume to ca. 20 cm³. 1 was isolated as a mixture of cyan powder and intense purple single crystals by vapour diffusion of diethyl ether into the reaction solution. This mixture was filtered off, mechanically separated and the two samples dried in vacuo. The powder and crystals were shown to be identical by elemental analysis (0.460 g, 58%). Found: C, 30.6; H, 2.5; N, 10.8. C₂₀H₂₁N₆Cl₃O₁₃Cu₂ requires: C, 30.5; H, 2.7; N, 10.7% IR (KBr disk, inter alia) v_{max}/cm⁻¹: 3512, 3061, 2955, 2916, 2856, 1633, 1606, 1565, 1480, 1440, 1096, 799, 629. $\delta_{\rm H}$ (300 MHz, 233 K, solvent CD₃CN, reference external TSP): ~10.85 (2H, br, H6), ~9.35 (2H, br, H14), 8.15 (2H, s, H4), 8.23 (2H, t, H12), 7.99, 7.85 (2H, d, H11, H13), ~5.0 (4H, br, H8), 3.48 (4H, s, H9). δ_C (75 MHz, solvent CD₃CN, reference external TMS): 166.2 (C3), 159.4 (C10), 149.4 (C8), (140.7, 140.4) (C1, C7), 132.9 (C9), 51.0 (C4), 34.8 (C5). FAB m/z (fragment): 822 ([Cu₂L1(μ -OH)(H₂O)₂(ClO₄)₃]⁺); 724 $([Cu_2L1(\mu-OH)(H_2O)_2(ClO_4)_2]^+); 688 ([Cu_2L1(\mu-OH)(ClO_4)_2]^+);$ 671 ($[Cu_2L1(ClO_4)_2]^+$); 588 ($[Cu_2L1(\mu-OH)(ClO_4)]^+$). $\Lambda_m(CH_3CN) =$ 347 mol⁻¹ cm² Ω^{-1} (cf. 340–420 mol⁻¹ cm² Ω^{-1} for a 3 : 1 electrolyte in CH₃CN).²⁶ λ_{max} (CH₃CN) = 542 nm (ε = 224 dm³ mol⁻¹ cm⁻¹). $\lambda_{max}(H_2O) = 541 \text{ nm} (\varepsilon = 153 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}); \mu = 0.4 \mu_B \text{ per Cu}$ [Gouy and Evans method (CH₃CN)].

General procedure for copper halide derivatives 2-4

To a stirred blue–green solution of 1 was added the appropriate tetraethylammonium halide which resulted in the formation of a fine dark green (2 or 3) or brown (4) precipitate. This mixture was stirred overnight after which time the precipitate was filtered off, washed with dry acetonitrile (10 cm³) and dried *in vacuo*.

 $[Cu_2L1(\mu-OH)Cl_2]ClO_4$ (2). Yield: 0.030 g, 51%. Found: C, 36.4; H, 3.3; N, 13.0. $C_{20}H_{21}N_6Cl_3O_5Cu_2$ requires: C, 36.5; H, 3.2; N, 12.8%. IR (KBr disk, *inter alia*) v_{max}/cm^{-1} : 3407, 3072, 2926, 1630,

Downloaded by University of Sussex on 05 May 2012 Published on 26 May 2004 on http://pubs.rsc.org | doi:10.1039/B403131H 1608, 1588, 1569, 1484, 1446, 1095, 897, 771, 623; $\Lambda_{\rm m}({\rm DMF}) =$ 78 mol⁻¹ cm² Ω^{-1} (*cf.* 65–90 mol⁻¹ cm² Ω^{-1} for a 1 : 1 electrolyte in DMF);²⁶ $\lambda_{\rm sh}({\rm DMF}) \sim 600$ nm.

[Cu₂L1(μ-OH)Br₂]ClO₄ (3). Yield: 0.063 g, 59%. Found: C, 31.9; H, 3.1; N, 11.0; Br, 22.6. C₂₀H₂₁N₆ClBr₂O₅Cu₂ requires: C, 32.1; H, 2.8; N, 11.2; Br, 21.4%. IR (KBr disk, *inter alia*) v_{max} /cm⁻¹: 3454, 3026, 2919, 1620, 1605, 1568, 1553, 1480, 1430, 1110, 897, 798, 625; A_m (DMF) = 88 mol⁻¹ cm² Ω⁻¹ (*cf.* 65–90 mol⁻¹ cm² Ω⁻¹ for a 1 : 1 electrolyte in DMF);²⁶ λ_{max} (DMF) = 763 nm (ε = 198 dm³ mol⁻¹ cm⁻¹).

[Cu₂L1(μ-OH)I₂]ClO₄ (4). Yield: 0.037 g, 33%. Found: C, 28.6; H, 2.4; N, 9.8; I, 30.2. C₂₀H₂₁N₆ClI₂O₅Cu₂ requires: C, 28.6; H, 2.5; N, 10.0; I, 30.2%. IR (KBr disk, *inter alia*) ν_{max}/cm^{-1} : 3446, 2924, 2853, 1627, 1604, 1569, 1458, 1376, 1121, 800, 625. Λ_m (DMF) = 120 mol⁻¹ cm² Ω⁻¹ (*cf.* 65–90 mol⁻¹ cm² Ω⁻¹ for a 1 : 1 electrolyte and 130–170 mol⁻¹ cm² Ω⁻¹ for a 2 : 1 electrolyte in DMF);²⁶ λ_{max} (DMF) = 357 nm (ε = 6244 dm³ mol⁻¹ cm⁻¹).

 $[Co_2L1(\mu-OH)(CH_3CN)_4](ClO_4)_3$ (5). To a stirred yellow solution of L1 (0.243 g, 0.705 mmol), in dry acetonitrile (60 cm³), was added a light rose coloured solution of Co(ClO₄)₂·6H₂O (0.520 g, 1.410 mmol), in dry acetonitrile (40 cm³). The resulting deep red solution was stirred for 41/2 h then some of the solvent was removed in vacuo to ca. 30 cm³. Complex 5 was isolated as brick-red single crystals by vapour diffusion of diethyl ether into the solution. The crystals were filtered off and dried in vacuo to give 5.3CH₃CN (0.319 g, 70%). Found: C, 32.3; H, 3.0; N, 12.0. C₂₂H₂₄N₇Cl₃O₁₃Co₂ requires: C, 32.2; H, 2.8; N, 12.2%. IR (KBr disk, *inter alia*) v_{max}/cm⁻¹: 3540, 3071, 2998, 2938, 2310, 2281, 1629, 1606, 1569, 1483, 1446, 1093, 785, 773, 625. FAB m/z (fragment): 812 ([Co₂L1(µ-OH)(H₂O)(ClO₄)₃]⁺); 713 ([Co₂L1(µ-OH)(H₂O)(ClO₄)₂]⁺); 677 ([Co₂L1(ClO₄)₂]⁺); 577 $([Co_2L1(ClO_4)]^+); 478 ([Co_2L1]^+); \Lambda_m(CH_3CN) = 343 \text{ mol}^{-1} \text{ cm}^2$ Ω^{-1} (cf. 340–420 mol⁻¹ cm² Ω^{-1} for a 3 : 1 electrolyte in CH₃CN);²⁶ $\lambda_{\text{max}}(\text{CH}_3\text{CN}) = 369 \text{ nm} (\varepsilon = 1293 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}). \ \mu = 4.2 \ \mu_{\text{B}} \text{ per}$ Co (SQUID method at 298 K).

 $[Ni_2L1(\mu-NCS)(CH_3CN)_3(H_2O)](ClO_4)_3$ (6). To a stirred yellow solution of L1 (0.236 g, 0.685 mmol), in dry acetonitrile (40 cm³), was added an aqua-blue solution of Ni(ClO₄)₂·6H₂O (0.500 g, 1.370 mmol), in dry acetonitrile (40 cm³). The resulting intense brown solution was left to stir for 20 min, then a solution of NaSCN (0.058 g, 0.715 mmol) in dry acetonitrile (27 cm³) was added, with no apparent change. The solution was stirred for 41/2 h after which time the solvent was reduced in vacuo to ca. 50 cm³. Complex 6 was isolated as red-brown single crystals by vapour diffusion of diethyl ether into the reaction solution. The crystals were filtered off and dried in vacuo (0.264 g, 38%). Found: C, 33.6; H, 3.8; N, 14.6; S, 3.2. C₂₇H₃₁N₁₀SCl₃O₁₃Ni₂ requires: C, 33.8; H, 3.3; N, 14.6; S, 3.3%. IR (KBr disk, inter alia) v_{max}/cm^{-1} : 3073, 3005, 2940, 2315, 2286, 2094, 1967, 1646, 1586, 1570, 1085, 628 FAB m/z (fragment): 922 ([Ni₂L1(µ-NCS)(CH₃CN)₃(ClO₄)₃]⁺); 904 ([Ni₂L1(µ-NCS)(H₂O)(CH₃CN)₂(ClO₄)₃]⁺); 827 ([Ni₂L1(CH₃CN)₂- $(ClO_4)_3]^+$; 730 ([NiL1(H₂O)(CH₃CN)₃(ClO₄)₂]⁺); 718 ([Ni₂L1(μ -NCS)(H₂O)(ClO₄)₂]⁺); 596 ([NiL1(ClO₄)₂]⁺); $\Lambda_{\rm m}$ (CH₃CN) = 359 mol⁻¹ cm² Ω^{-1} (cf. 340–420 mol⁻¹ cm² Ω^{-1} for a 3 : 1 electrolyte in CH₃CN);²⁶ λ_{max} (CH₃CN) = 908 nm (ε = 36 dm³ mol⁻¹ cm⁻¹); μ = $2.98 \,\mu_{\rm B}$ per Ni (SQUID method at 290 K).

[Ni₂L1(μ -N₃)(CH₃CN)₄](ClO₄)₃ (7). To a stirred yellow solution of L1 (0.330 g, 0.95 mmol), in dry acetonitrile (40 cm³), was added solid NaN₃ (0.062 g, 0.95 mmol) and an aqua-blue solution of Ni(ClO₄)₂·6H₂O (0.700 g, 1.92 mmol) in dry acetonitrile (30 cm³). The brown mixture was stirred for 12 h after which it was reduced *in vacuo* to half of the original volume. Complex 7 was isolated as deep brown crystals by vapour diffusion of diethyl ether into the reaction solution. The crystals were filtered off and dried *in vacuo* (0.260 g, 28%). Found C, 34.4; H, 3.4; N, 18.8. C₂₈H₃₂N₁₃Cl₃O₁₂Ni₂ requires: C, 34.8; H, 3.4; N, 18.8%. IR (KBr disk, *inter alia*)

 v_{max} /cm⁻¹: 3424, 3073, 2999, 2939, 2315, 2286, 2070, 1640, 1608, 1584, 1569, 1445, 1098, 784, 769, 624. FAB *m/z* (fragment): 492 ([Ni₂L1N₂]⁺); 476 ([Ni₂L1N]⁺); 461 ([Ni₂L1]⁺); 402 ([NiL1]⁺); Λ_{m} (CH₃CN) = 336 mol⁻¹ cm² Ω⁻¹ (*cf.* 340–380 mol⁻¹ cm² Ω⁻¹ for a 3 : 1 electrolyte in CH₃CN);²⁶ λ_{max} (CH₃CN) = 515 nm (ε = 76 dm³ mol⁻¹ cm⁻¹), λ_{max} (CH₃CN) = 855 nm (ε = 21 dm³ mol⁻¹ cm⁻¹); μ = 3.05 μ_{B} per Ni (SQUID method at 300 K).

 $[Cu_2L2(\mu-OH)](ClO_4)_3$ (8). To a stirred yellow solution of L2 (0.126 g, 0.362 mmol) in dry acetonitrile (60 cm³), was added a blue solution of $Cu(ClO_4)_2$ ·6H₂O (0.268 g, 0.723 mmol) in dry acetonitrile (50 cm3). The resulting intense blue solution was stirred for 4 h after which it was reduced in vacuo to ca. 40 cm³. Complex 8 was isolated as dark green microcrystals by vapour diffusion of diethyl ether into the reaction solution (0.129 g, 45%). Found: C, 30.7; H, 3.0; N, 10.8. C₂₀H₂₅N₆Cl₃O₁₃Cu₂ requires: C, 30.4; H, 3.2; N, 10.6. IR (KBr disk, *inter alia*) v_{max} /cm⁻¹: 3550, 3256, 3230, 3206, 3079, 2939, 1636, 1609, 1570, 1543, 1483, 1445, 1316, 1105, 776, 628. $\delta_{\rm H}$ (300 MHz, 238 K, solvent CD₃CN, reference CH₃CN): 9.86 (2H, br, H14), 8.95 (2H, s, H4), 8.20 (2H, t, H12), 8.08, 7.99 (2H, d, H11, H13), ~7.6 (~4H, br, H6), 4.6 to 2.6 (8H, overlapping, H8, H9). FAB m/z (fragment) 826 ([Cu₂L2(μ -OH)(H₂O)₂(ClO₄)₃]⁺); 726 $([Cu_2L2(\mu-OH)(H_2O)_2(ClO_4)_2]^+); 688 ([Cu_2L2(\mu-OH)(ClO_4)_2]^+);$ 674 ($[Cu_2L2(ClO_4)_2]^+$); 573 ($[Cu_2L2(ClO_4)]^+$) 472 ($[Cu_2L2]^+$); $\Lambda_{\rm m}(\rm CH_3CN) = 345 \ {\rm mol^{-1} \ cm^2 \ } \Omega^{-1}$ (cf. 340–420 mol⁻¹ cm² Ω^{-1} for a 3:1 electrolyte in CH₃CN);²⁶ λ_{max} (CH₃CN) = 561 nm (ε = 216 dm³ mol⁻¹ cm⁻¹).

Electrochemistry

All electrochemical measurements were made using a EG&G Princeton Applied Research 273A potentiostat. Unless otherwise stated cyclic voltammograms were obtained in acetonitrile-0.1 M [Bu₄N]ClO₄ solutions containing 1 mmol L⁻¹ complex. Solutions were degassed using a N2 purge and a N2 atmosphere was maintained throughout all experiments. The working electrode was a 1 mm diameter Pt disk electrode and the reference electrode was Ag/Ag⁺ (0.01 mol L⁻¹ AgNO₃ in 0.1 mol L⁻¹ [Bu₄N]ClO₄-CH₃CN). Ferrocene was added at the conclusion of each experiment; the Fc⁺/Fc couple consistently occurred at $E_{\frac{1}{2}} = 0.07 \pm 0.01$ V in both CH₃CN and DMF. Controlled potential electrolysis was used to determine electron counts. A three-compartment cell contained platinum mesh working and counter electrodes and the reference electrode described above. The compartments were separated by porosity 5 glass frits. The solution in the working electrode compartment was stirred via a N2 purge.

X-Ray crystallography

X-Ray data were collected ($\lambda = 0.71073$ Å) on a Siemens P4 fourcircle diffractometer for **1**, **5**·3CH₃CN and **6**·½Et₂O, and on a Bruker SMART area detector diffractometer for **7**·2CH₃CN, and the structures solved and refined using SHELXS and SHELXL.⁴³ Details of the crystal structures are collected in Table 4 and additional notes referring to particular structures are detailed below.

1. A semi-empirical absorption correction was applied ($T_{\min} = 0.38$, $T_{\max} = 0.43$). All non-hydrogen atoms were made anisotropic. There are a number of short intermolecular distances between perchlorate oxygen (O33) and imine carbon (C15), and pyridazine ring carbons C2 and C3. These are attributed to a weak electrostatic interaction between O33 and C15, the additional two short distances being a consequence of this attractive interaction.

5·3CH₃CN. All non-hydrogen atoms were made anisotropic other than the minor occupancy atoms of each disorder (one per-chlorate ion and one MeCN disordered).

6· $\frac{1}{2}$ Et₂**O**. A semi-empirical absorption correction was applied ($T_{\min} = 0.20, T_{\max} = 0.29$). The nickel atoms and counter ions (one

Table 4 X-Ray data for structure determinations on complexes 1 and 5-7

	1	5·3MeCN	6 ·½Et₂O	7·2MeCN
Emp. formula	$C_{20}H_{21}N_6Cl_3O_{13}Cu_2$	C ₃₄ H ₄₂ N ₁₃ Cl ₃ O ₁₃ Co ₂	C29H36N10Cl3O13.5SNi2	C ₂₈ H ₃₂ N ₁₃ Cl ₃ O ₁₂ Ni ₂
$M_{ m r}$	786.86	1065.02	996.51	1007.49
T/K	155(2)	168(2)	168(2)	168(2)
Space group	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Crystal system	$P2_1/n$	$P2_1/m$	$P2_1/c$	$P2_1/n$
a/Å	13.774(4)	7.593(2)	10.573(3)	11.0655(19)
b/Å	14.918(2)	24.947(9)	32.050(9)	11.899(2)
$c/\text{\AA}$	14.287(2)	12.636(3)	13.228(2)	65.120(13)
$\beta/^{\circ}$	111.27(2)	105.48(3)	95.343(15)	91.694(5)
V/Å3	2735.6(9)	2306.6(12)	4463.2(19)	8570(3)
Ζ	4	2	4	8
$D_{\rm c}/{ m g~cm^{-3}}$	1.911	1.533	1.483	1.562
Crystal size/mm	$0.80\times0.30\times0.18$	$1.20\times0.40\times0.04$	$0.52\times0.38\times0.32$	$0.35\times0.17\times0.05$
μ/mm^{-1}	1.927	0.967	1.138	1.139
F(000)	1584	1092	2044	4128
θ Range/°	2.05-22.5	2.34–27	2-22.5	3.42-22.55
Reflections collected	4203	4767	6292	8314
Data (R_{int}) /restr./param.	3564(0.0405)/0/397	3933(0.0374)/33/359	5731(0.0857)/7/488	6114(0.0675)/1962/568
GOF	1.054	1.017	1.020	0.911
R1, wR2 ($F > 4\sigma(F)$)	0.0433, 0.0874	0.0472, 0.1128	0.1011, 0.2460	0.0951, 0.2302
R1, $wR2$ (all data)	0.0719, 0.0970	0.0726, 0.1271	0.2596, 0.3306	0.1893, 0.2674
$\Delta \rho_{\text{max/min}}/e \text{ Å}^{-3}$	0.572/-0.492	0.738/-0.525	0.975/-0.617	0.64/-0.45

perchlorate ion disordered) were made anisotropic. There is a short intermolecular distance between perchlorate oxygen O34 and imine carbon C6, which is attributed to a weak electrostatic interaction between these two atoms.

7·2CH₃CN. A semi-empirical absorption correction (SADABS) was applied ($T_{min} = 0.91$, $T_{max} = 1.00$). The nickel atoms and chloride counter ions were made anisotropic. The data is of poor quality and lacks completeness but the overall structure of the cation is clear. There is a short intermolecular distance between partial disordered perchlorate oxygen O66 and the nitrile carbon C150, which is attributed to a weak electrostatic interaction between these two atoms.

CCDC reference numbers 228409-228412.

See http://www.rsc.org/suppdata/dt/b4/b403131h/ for crystallographic data in CIF or other electronic format.

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