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# Pyridyl–thiazole multidentate ligands: metal-specific recognition of a combination of ligands from a mixture

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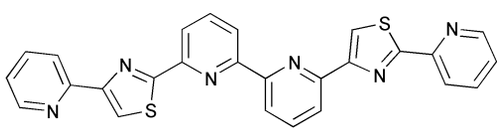
Comparison of the crystal structures of the dinuclear double helicates $[M_2(\mathbf{L}^1)_2][ClO_4]_4$ (M = Ni, Zn; $\mathbf{L}^1$ is a potentially hexadentate ligand containing a py–th–py–py–th–py sequence, where 'py' denotes pyridyl and 'th' denotes thiazolyl) illustrates how $\mathbf{L}^1$ can show two different coordination modes: in $[Zn_2(\mathbf{L}^1)_2][ClO_4]_4$ the ligands $\mathbf{L}^1$ are bis-bidentate chelates (*via* the terminal py–th fragments, with the central bipyridyl unit not coordinated) such that the metal ions are four-coordinate, whereas in $[Ni_2(\mathbf{L}^1)_2][ClO_4]_4$ the ligand coordinates in a more usual bis-terdentate manner such that the metal ions are six-coordinate. Reaction of Ni(II), Cu(II) or Zn(II) salts with a 1 : 1 mixture of the potentially hexadentate ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ (where $\mathbf{L}^2$ contains a phen–th–th–phen sequence, 'phen' denoting a 1,10-phenanthroline unit) afforded in each case a mixture of helical complexes $[M_2(\mathbf{L}^1)_2]^{4+}$, $[M_2(\mathbf{L}^1)(\mathbf{L}^2)]^{4+}$ and $[M_2(\mathbf{L}^2)_2]^{4+}$ in different proportions according to the preferences of the different metal ions for different coordination numbers, and the actual denticity of the ligand. For example the mixed-ligand complex $[M_2(\mathbf{L}^1)(\mathbf{L}^2)]^{4+}$ was formed to the same extent (*ca.* 50%) for M = Ni and M = Cu, but hardly at all for M = Zn, indicating that self–self ligand recognition operates during assembly of $\mathbf{L}^1$ and $\mathbf{L}^2$ with Zn(II) such that the homoleptic complexes $[Zn_2(\mathbf{L}^1)_2]^{4+}$ and $[Zn_2(\mathbf{L}^2)_2]^{4+}$ are favoured more than simple statistical considerations would suggest.

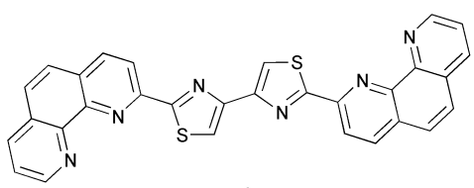
## Introduction

Double and triple helical complexes[1–5] have been of particular interest for study of the molecular recognition processes which direct the assembly process. Lehn *et al.* demonstrated that reaction of Cu(I) with a mixture of oligo(2,2′-bipyridine) ligands of different lengths resulted only in formation of the homoleptic complexes, *i.e.* no mixed-ligand species were formed and ligand self-recognition played a crucial role in the assembly process.[6] In elegant contrast to this, a mixture of two different ligands containing all-bipyridyl or all-terpyridyl binding sites with Cu(II) resulted in formation of only the heteroleptic mixed-ligand double helicate, because of the preference of Cu(II) ions for a five-coordinate geometry—*i.e.* an electronic effect.[7] Recognition between ligands in helicate formation can also arise from steric effects using ligands with bulky chiral substituents,[8] and the components of a mixture of ether-linked oligobipyridines of different lengths have been shown to undergo either self- or non-self-recognition depending upon what type of binding domains or spacer groups are present in the ligand chain.[9,10]

Previously we showed that linear polydentate ligands such as $\mathbf{L}^1$ and $\mathbf{L}^2$ (see Scheme 1) containing a combination of pyridyl, phenanthrolinyl and thiazolyl N-donor units form double helicates on complexation with first row transition metal dications (M = Co–Zn).[11–13] Although these ligands may be considered as analogues of the well-known polypyridines, inclusion of the five-membered thiazolyl rings in the backbone results in a more pronounced partitioning of the ligand into distinct bidentate and terdentate domains than is the case with polypyridines. In this paper we show how a difference in the coordination modes of two such ligands can be used as the basis for self–self recognition between them during assembly around Zn(II) ions, but not with Ni(II) or Cu(II).




$\mathbf{L}^1$




$\mathbf{L}^2$

**Scheme 1**

## Results and discussion

### Syntheses and crystal structures of $[M_2(\mathbf{L}^1)_2][ClO_4]_4$ (M = Ni, Zn)

We showed before that the hexadentate ligand $\mathbf{L}^2$ partitions itself into two thiazolyl–phenanthroline terdentate domains in complexes with Cu(II) and Zn(II), both of which are conventional dinuclear double helicates with six-coordinate metals.[11,12] In contrast, the double helicate $[Cu_2(\mathbf{L}^1)_2]^{4+}$ contains four-coordinate metal ions, because the ligand $\mathbf{L}^1$, although potentially hexadentate, is coordinated in a bis-bidentate manner *via* the terminal thiazolyl–pyridine sites, with the central bipyridyl unit of each ligand not coordinated.[12] The difference in coordination behaviour between these two ligands can be ascribed to the different position of the thiazolyl units in the backbone.

A variation on this theme is shown by the crystal structures of the two new complexes $[M_2(\mathbf{L}^1)_2][ClO_4]_4$ (M = Ni, Zn), both



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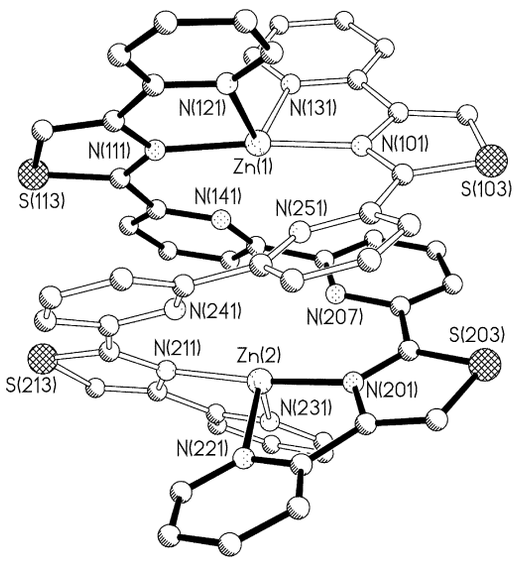


**Fig. 1** Crystal structure of the complex cation of $[Zn_2(\mathbf{L}^1)_2][ClO_4]_4 \cdot 2MeNO_2$, with the ligands shaded differently for clarity.

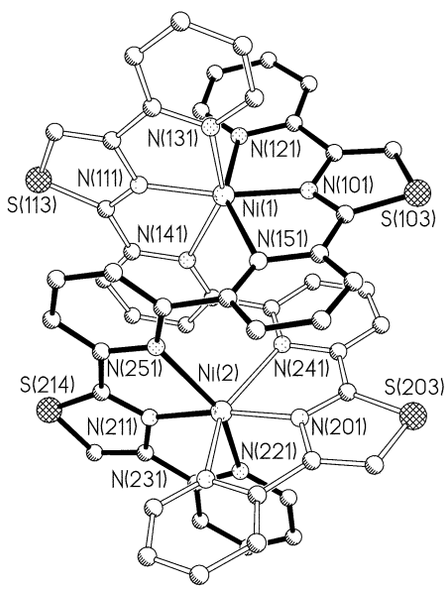


**Fig. 2** Crystal structure of the complex cation of $[Ni_2(\mathbf{L}^1)_2][ClO_4]_4 \cdot 2MeNO_2 \cdot H_2O$, with the ligands shaded differently for clarity.

prepared by reaction of $\mathbf{L}^1$ with the appropriate metal(II) perchlorate in $MeNO_2$. These new complexes gave satisfactory analytical data, and their mass spectra were also in agreement with the formation of dinuclear $M_2L_2$ species. $[Zn_2(\mathbf{L}^1)_2][ClO_4]_4$ (Fig. 1) has basically the same structure as $[Cu_2(\mathbf{L}^1)_2][ClO_4]_4$,[12] being a double helicate with each metal only four-coordinate and the central bipyridyl unit of each ligand not coordinated. This is illustrated by (i) the long distances between the Zn ions and the four non-coordinated pyridyl units (2.50–2.70 Å), and (ii) the fact that the lone pairs of these pyridyl units are clearly not directed at the metal centres, illustrated by the relatively small torsion angles within each non-coordinated bipyridyl unit (38 and 51°). The coordination geometry about the Zn(II) ions in this complex is therefore like that of an octahedron with a *cis*-oriented pair of donor atoms removed; the remaining *trans* pair of ligands [N(111) and N(101) around Zn(1); N(211) and N(201) around Zn(2)] subtend an angle of *ca.* 172° at the metal ion in each case.

The structure of $[Ni_2(\mathbf{L}^1)_2][ClO_4]_4$, also a double helicate (Fig. 2), is however significantly different, in that both metal centres are now six-coordinate. This structure shows that $\mathbf{L}^1$ can in fact act as a bis-terdentate ligand giving pseudo-octahedral Ni(II) centres, something we had not expected on the basis of the Zn(II) and Cu(II) structures. The bonds to the pyridyl units at the centre of each hexadentate ligand [N(141) and N(151) around Ni(1); N(241) and N(251) around Ni(2)] are long as such bonds go (2.30–2.37 Å), but are considerably shorter than the genuine non-bonding distances in the Cu(II) and Zn(II) structures. In addition, the fact that the pyridyl lone pairs of this central bipyridyl unit are now pointing at the Ni(II) centres results in a much greater twist between adjacent pyridyl rings (82 and 83°) such that the ligand is more obviously partitioned into two near-orthogonal terdentate compartments. Given the similar ionic radii of $Ni^{2+}$ and $Zn^{2+}$, this behaviour may be ascribed to the fact that Ni(II) has a greater electronic preference for regular octahedral coordination than do Cu(II) and Zn(II) because of its $d^8$ configuration, although there are examples of square-planar $d^8$ complexes.

### Formation of heteroleptic complexes $[M_2(\mathbf{L}^1)(\mathbf{L}^2)]^{4+}$ (M = Ni, Cu, Zn)

Since $\mathbf{L}^1$ and $\mathbf{L}^2$ both form homoleptic double helical complexes with various first-row transition metal ions (M), we investigated their ability to form double stranded *heteroleptic* (mixed-ligand) complexes with M = Ni(II), Cu(II) and Zn(II), by treating each metal ion with a 1 : 1 mixture of $\mathbf{L}^1$ and $\mathbf{L}^2$. In this experiment there are two variables: (i) the differing stereoelectronic preferences of the metal ions, and (ii) the ability of the ligands to accommodate these preferences by using (in the case of $\mathbf{L}^1$) two different coordination modes, *viz.* bis-bidentate and bis-terdentate, as shown by the crystal structures described above. Formation of heteroleptic complexes was accomplished by mixing $\mathbf{L}^1$, $\mathbf{L}^2$ and the appropriate metal ion (1 : 1 : 2 molar ratio) in acetonitrile and examining the distribution of the three possible complexes by electrospray mass spectrometry and [for the diamagnetic Zn(II) complexes] $^1$H NMR spectroscopy.

For M = Ni, the ES mass spectrum showed an approximately 1 : 2 : 1 mixture of $[Ni_2(\mathbf{L}^1)_2]^{4+}$, $[Ni_2(\mathbf{L}^1)(\mathbf{L}^2)]^{4+}$ and $[Ni_2(\mathbf{L}^2)_2]^{4+}$ [Fig. 3(a)], which is the distribution expected on purely statistical grounds. We know from the crystal structure of $[Ni_2(\mathbf{L}^1)_2][ClO_4]_4$ above that $\mathbf{L}^1$ coordinates to Ni(II) as a bis-terdentate ligand to give six-coordinate metal centres, and we assume that $\mathbf{L}^2$ behaves similarly [on the basis of its co-ordination behaviour to Zn(II) and Cu(II) described earlier].[11,12] These ES mass spectroscopy results therefore suggest that the same coordination behaviour is maintained by each ligand separately in $[Ni_2(\mathbf{L}^1)(\mathbf{L}^2)]^{4+}$, such that the metal centres are again six-coordinate and in essentially the same coordination environment that occurs in $[Ni_2(\mathbf{L}^1)_2]^{4+}$ and $[Ni_2(\mathbf{L}^2)_2]^{4+}$. Thus, for the equilibrium in eqn. (1) with M = Ni, both sides of the equation contain the same number of ligands of each type *coordinated in the same manner*, and the same number of metal ions *in the same coordination environment*. In the absence of any strong ligand–ligand interactions this means that the reaction in eqn. (1) will have $\Delta G \approx 0$, giving a statistical mixture of products.

$$[M_2(\mathbf{L}^1)_2]^{4+} + [M_2(\mathbf{L}^2)_2]^{4+} \rightleftharpoons 2\,[M_2(\mathbf{L}^1)(\mathbf{L}^2)]^{4+} \qquad (1)$$

For M = Cu(II) a similar result was obtained, *viz.* an approximately statistical mixture of $[Cu_2(\mathbf{L}^1)_2]^{4+}$, $[Cu_2(\mathbf{L}^1)(\mathbf{L}^2)]^{4+}$ and $[Cu_2(\mathbf{L}^2)_2]^{4+}$ [Fig. 3(b)]. We found this initially somewhat surprising given the fact that the structures of $[Cu_2(\mathbf{L}^1)_2]^{4+}$ (four-coordinate metals) and $[Cu_2(\mathbf{L}^2)_2]^{4+}$ (six-coordinate metals) are quite different. The result implies that a 1 : 1 mixture of $[Cu_2(\mathbf{L}^1)_2]^{4+}$ and $[Cu_2(\mathbf{L}^2)_2]^{4+}$ has about the same stability as two equivalents of the mixed-ligand complex $[Cu_2(\mathbf{L}^1)(\mathbf{L}^2)]^{4+}$, *i.e.* the equilibrium in eqn. (1) is again evenly balanced for M = Cu. We do not know the structure of

$[Cu_2(\mathbf{L}^1)(\mathbf{L}^2)]^{4+}$, but we suggest that five-coordinate environments for the metal ions based on bis-bidentate $\mathbf{L}^1$ and bis-terdentate $\mathbf{L}^2$ is reasonable, such that each side of eqn. (1) would have 20 metal–ligand bonds. This is consistent with (i) the coordination modes of $\mathbf{L}^1$ and $\mathbf{L}^2$ to Cu(II) seen in the homoleptic complexes, and (ii) the well-known preference of Cu(II) for a five-coordinate environment, which has been exploited in self-assembly processes to give selective association of bidentate and terdentate ligand fragments.[7,14–16]

For M = Zn(II) however a quite different result was obtained, with virtually none of the mixed-ligand complex $[Zn_2(\mathbf{L}^1)(\mathbf{L}^2)]^{4+}$ observed in the mass spectrum [Fig. 3(c)]. Thus, the equilibrium in eqn. (1) with M = Zn lies largely to the left and the two homoleptic complexes are favoured—*i.e. self-recognition of the ligands is occurring*. We also examined this diamagnetic system by $^1$H NMR spectroscopy and found the same result (Fig. 4); integration of the different components of the spectra showed that only about 10% of the mixed-ligand complex was present in the equilibrium mixture. It is worth pointing out that the good agreement between the product distributions shown by the NMR and ESMS spectra in this case confirms that ESMS also provides a reliable picture of the product distribution in solution for M = Cu(II) and Ni(II).

The contrast between the behaviour of the Cu(II) and Zn(II) systems is striking, bearing in mind that (i) $[Cu_2(\mathbf{L}^1)_2]^{4+}$ and $[Zn_2(\mathbf{L}^1)_2]^{4+}$ have similar four-coordinate structures arising from bis-bidentate coordination of $\mathbf{L}^1$, and (ii) $[Cu_2(\mathbf{L}^2)_2]^{4+}$ and $[Zn_2(\mathbf{L}^2)_2]^{4+}$ have similar six-coordinate structures arising from bis-terdentate coordination of $\mathbf{L}^2$. Despite this, the heteroleptic complexes $[Cu_2(\mathbf{L}^1)(\mathbf{L}^2)]^{4+}$ and $[Zn_2(\mathbf{L}^1)(\mathbf{L}^2)]^{4+}$ have markedly different stabilities, with the Zn(II) complex being disfavoured relative to the Cu(II) complex. There are two possible reasons for this. Firstly, it is possible that $[Cu_2(\mathbf{L}^1)(\mathbf{L}^2)]^{4+}$ and $[Zn_2(\mathbf{L}^1)(\mathbf{L}^2)]^{4+}$ have significantly different structures, with the Zn(II) complex being disfavoured for steric reasons. This seems unlikely in view of the structural similarity of the Cu and Zn homoleptic complexes with both $\mathbf{L}^1$ and $\mathbf{L}^2$; it is far more likely that the two heteroleptic complexes also have similar structures containing five-coordinate metal centres (as explained above for $[Cu_2(\mathbf{L}^1)(\mathbf{L}^2)]^{4+}$) in which each ligand maintains the co-ordination mode it displayed in its homoleptic complexes. This leads to the second possibility, which is that there is a difference in stability of the two isostructural, heteroleptic complexes arising from electronic factors. This can be accounted for, as mentioned earlier, by taking into account the particular preference of Cu(II) for a five-coordinate environment arising from a mixed-ligand set comprising terdentate and bidentate components.[7,14–16] For example, the additional electronic stabilisation provided by the Jahn–Teller effect in square-based pyramidal five-coordinate structures of Cu(II) has recently been shown to exert a strong influence on the formation of some Cu(II)-based polynuclear grid-like complexes.[14] We suggest that a similar effect is operating here, accounting for the greater

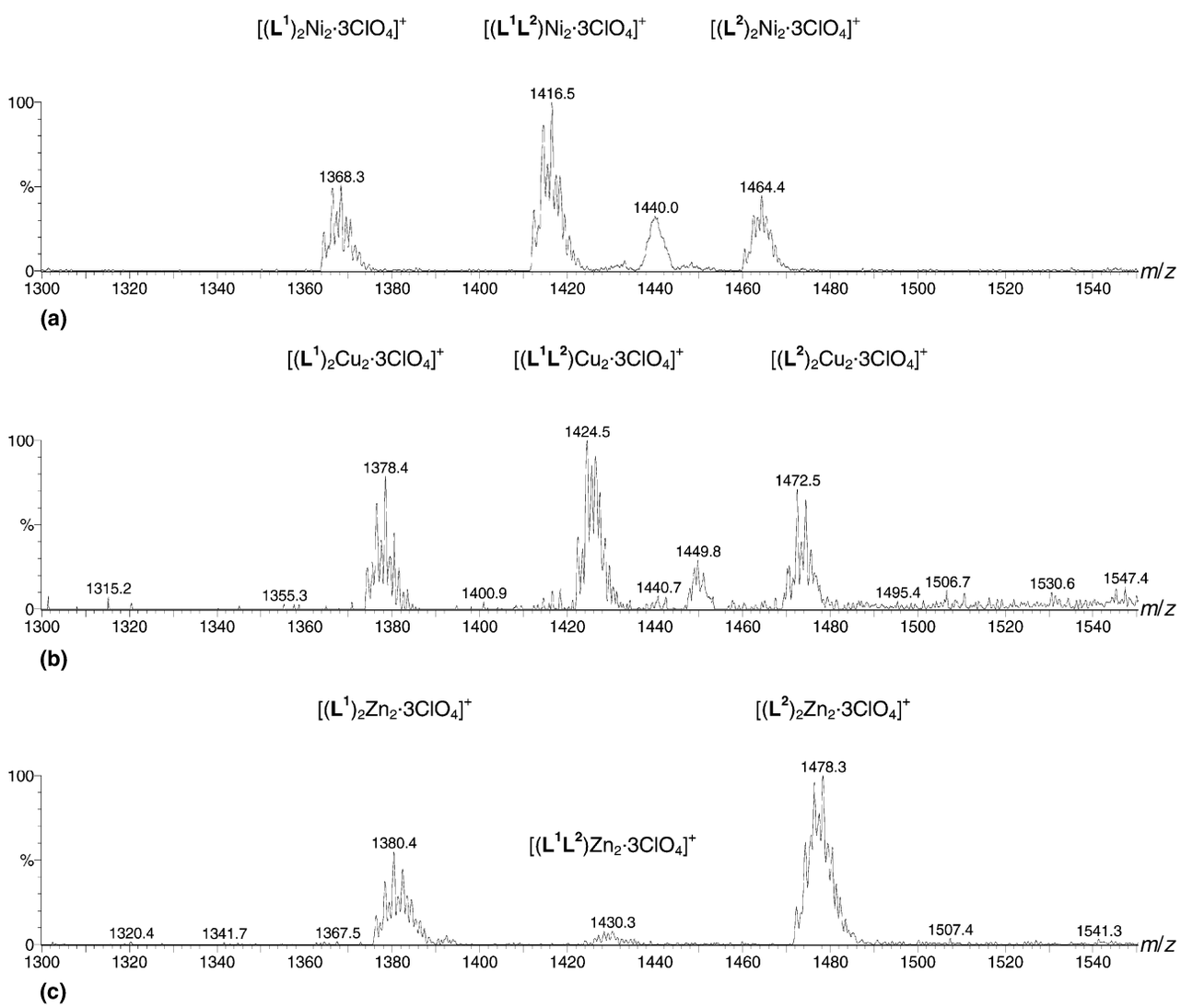


**Fig. 3** Partial ES mass spectra of the reaction mixtures generated by mixing $\mathbf{L}^1$, $\mathbf{L}^2$ and $M(ClO_4)_2{\cdot}6H_2O$ in a 1 : 1 : 2 ratio: (**a**) M = Ni; (**b**) M = Cu; (**c**) M = Zn.

extent of formation of five-coordinate $[Cu_2(\mathbf{L}^1)(\mathbf{L}^2)]^{4+}$ from a mixture of starting materials, compared to five-coordinate $[Zn_2(\mathbf{L}^1)(\mathbf{L}^2)]^{4+}$.

In conclusion, studies on the relative abundance of the three components $[M_2(\mathbf{L}^1)_2]^{4+}$, $[M_2(\mathbf{L}^2)_2]^{4+}$ and $[M_2(\mathbf{L}^1)(\mathbf{L}^2)]^{4+}$ (M = Ni, Cu, Zn) show some interesting effects. For M = Ni, the statistical distribution is as expected assuming that the three complexes are essentially isostructural and there are no significant ligand–ligand interactions in the mixed-ligand complex. For M = Cu and Zn however, the different stereoelectronic requirements of the dications lead to different extents of formation of the mixed-ligand complexes. The consequence of this is a much greater degree of self-recognition between ligands during the assembly of double helicates when M = Zn than occurs when M = Cu or Ni.

## Experimental

### General details

The following instruments were used for routine spectroscopic measurements: $^1$H NMR spectra, a Bruker Avance DPX400; electrospray mass spectra, a VG Quattro II triple quadrupole mass spectrometer. Ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ were prepared according to the previously published methods.[12]

### Syntheses of $[M_2(L^1)_2][ClO_4]_4$ (M = Ni, Zn)

**CAUTION**: perchlorate salts are potentially explosive and should be treated with due care. Those complexes described below which were isolated as perchlorates were only prepared in small amounts (10–20 mg) and we had no problems with them.

**$[Zn_2(L^1)_2](ClO_4)_4$.** To a suspension of $\mathbf{L}^1$ (0.010 g, 0.02 mmol) in nitromethane (2 cm$^3$), $Zn(ClO_4)_2\cdot 6H_2O$ (0.008 g, 0.02 mmol) was added and the suspension stirred until dissolution was complete. Filtration followed by slow vapour diffusion of ethyl acetate into the solution gave $[Zn_2(\mathbf{L}^1)_2](ClO_4)_4$ as large colourless crystals, which were isolated by filtration and dried under vacuum. Yield: 0.021 g, 68%. ESMS: *m*/*z* 1381 $\{Zn_2(\mathbf{L}^1)_2(ClO_4)_3\}^+$. Found: C, 41.9; H, 1.9; N, 11.8. $C_{52}H_{32}N_{12}S_4Zn_2Cl_4O_{16}$ requires C, 42.1; H, 2.2; N, 11.3%.

**$[Ni_2(L^1)_2](ClO_4)_4$.** To a suspension of $\mathbf{L}^1$ (0.010 g, 0.03 mmol) in nitromethane (2 cm$^3$), $Zn(ClO_4)_2\cdot 6H_2O$ (0.008 g, 0.02 mmol) was added and the solution stirred until dissolution was complete. Filtration followed by slow vapour diffusion of ethyl acetate into the solution gave $[Ni_2(\mathbf{L}^1)_2](ClO_4)_4$ as large green crystals, which were isolated by filtration and dried under vacuum. Yield: 0.007 g, 50%. ESMS: *m*/*z* 1368 $\{Ni_2(\mathbf{L}^1)_2(ClO_4)_3\}^+$. Found: C, 42.0; H, 1.8; N, 11.8. $C_{52}H_{32}N_{12}S_4Ni_2Cl_4O_{16}$ requires C, 42.5; H, 2.2; N, 11.4%.

### Crystallography

Suitable crystals of $[Zn_2(\mathbf{L}^1)_2][ClO_4]_4\cdot 2MeNO_2$ and $[Ni_2(\mathbf{L}^1)_2][ClO_4]_4\cdot 2MeNO_2\cdot H_2O$ were mounted on a Siemens SMART-CCD diffractometer under a stream of cold $N_2$ at −100 °C and all subsequent crystallographic studies were carried out at this temperature. The software used were SHELXS-97 for structure solution;[17] SHELXL-97 for structure refinement;[17] and SADABS for the absorption correction.[18] Details of the crystal parameters, data collection and refinement are collected in Table 1, and selected metric parameters are in Tables 2 and 3. Neither structural determination presented any significant problems and both gave satisfactory refinements.

CCDC reference numbers 163221 and 163222.

See http://www.rsc.org/suppdata/dt/b1/b104977c/ for crystallographic data in CIF or other electronic format.

## Acknowledgements

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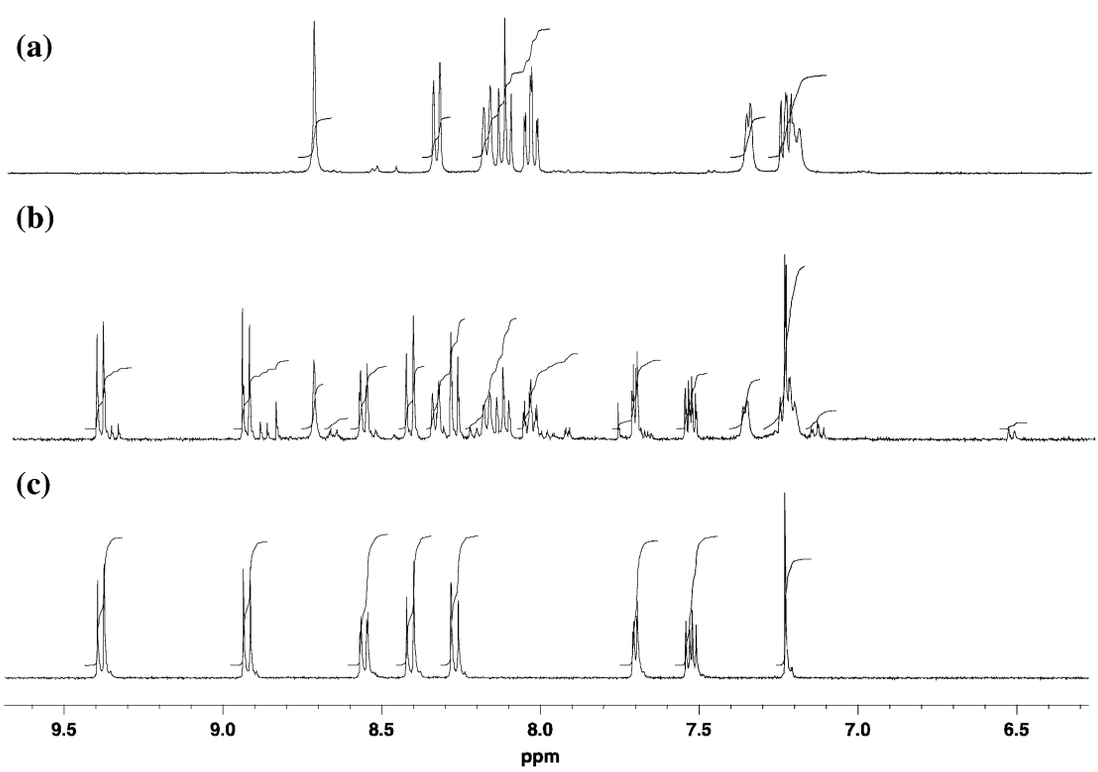


**Fig. 4** Aromatic region of the $^1$H NMR spectrum of an equilibrium mixture of $[Zn_2(\mathbf{L}^1)_2](ClO_4)_4$ (**a**), $[Zn_2(\mathbf{L}^1)(\mathbf{L}^2)](ClO_4)_4$ (**b**) and $[Zn_2(\mathbf{L}^2)_2](ClO_4)_4$ (**c**), showing the peaks which can be assigned to each component by comparison with the spectra of the two homoleptic complexes.

**Table 1** Crystallographic data for the two structures[a]

| Compound | $[Zn_2(\mathbf{L}^1)_2][ClO_4]_4\cdot 2MeNO_2$ | $[Ni_2(\mathbf{L}^1)_2][ClO_4]_4\cdot 2MeNO_2\cdot H_2O$ |
|---|---|---|
| Empirical formula | $C_{54}H_{38}Cl_4N_{14}O_{20}S_4Zn_2$ | $C_{54}H_{40}Cl_4N_{14}Ni_2O_{21}S_4$ |
| $M$ | 1603.76 | 1608.46 |
| Crystal dimensions/mm | 0.6 × 0.25 × 0.2 | 0.25 × 0.2 × 0.15 |
| Crystal system, Space group | Triclinic, $P\bar{1}$ | Triclinic, $P\bar{1}$ |
| $a$/Å | 12.2805(18) | 13.8523(9) |
| $b$/Å | 12.5562(18) | 15.0576(10) |
| $c$/Å | 21.182(3) | 16.8639(11) |
| $\alpha$/° | 90.258(2) | 74.4310(10) |
| $\beta$/° | 103.166(2) | 68.2440(10) |
| $\gamma$/° | 100.171(2) | 84.9940(10) |
| $V$/Å$^3$ | 3127.0(8) | 3146.8(4) |
| $Z$ | 2 | 2 |
| $\rho_{calc.}$/g cm$^{-3}$ | 1.703 | 1.698 |
| Abs. coeff./mm$^{-1}$ | 1.160 | 0.990 |
| Reflections collected: total/independent/$R_{int}$ | 32976, 14215, 0.0371 | 33084, 14308, 0.0225 |
| Data/restraints/parameters | 14215, 0, 928 | 14308, 89, 1000 |
| Final $R_1$, $wR_2$[b,c] | 0.0432, 0.1203 | 0.0497, 0.1554 |

[a] Data in common: $T$ = 173 K; $\lambda$ = 0.71073 Å; Bruker SMART-CCD diffractometer. [b] Structure was refined on $F_o^2$ using all data; the value of $R_1$ is given for comparison with older refinements based on $F_o$ with a typical threshold of $F \geq 4\sigma(F)$. [c] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

**Table 2** Selected bond distances (Å) and angles (°) for $[Zn_2(\mathbf{L}^1)_2][ClO_4]_4\cdot 2MeNO_2$

| | | | |
|---|---|---|---|
| Zn(1)–N(111) | 1.984(2) | Zn(2)–N(201) | 1.981(2) |
| Zn(1)–N(101) | 2.002(2) | Zn(2)–N(211) | 1.998(2) |
| Zn(1)–N(131) | 2.161(3) | Zn(2)–N(231) | 2.153(3) |
| Zn(1)–N(121) | 2.208(2) | Zn(2)–N(221) | 2.175(2) |
| | | | |
| N(111)–Zn(1)–N(101) | 171.54(10) | N(201)–Zn(2)–N(211) | 172.15(10) |
| N(111)–Zn(1)–N(131) | 110.54(10) | N(201)–Zn(2)–N(231) | 109.03(10) |
| N(101)–Zn(1)–N(131) | 77.88(10) | N(211)–Zn(2)–N(231) | 78.32(10) |
| N(111)–Zn(1)–N(121) | 76.62(10) | N(201)–Zn(2)–N(221) | 77.39(10) |
| N(101)–Zn(1)–N(121) | 100.50(10) | N(211)–Zn(2)–N(221) | 102.01(10) |
| N(131)–Zn(1)–N(121) | 117.38(9) | N(231)–Zn(2)–N(221) | 116.91(10) |

**Table 3** Selected bond distances (Å) and angles (°) for $[Ni_2(\mathbf{L}^1)_2][ClO_4]_4\cdot 2MeNO_2\cdot H_2O$

| | | | |
|---|---|---|---|
| Ni(1)–N(111) | 1.958(3) | Ni(2)–N(211) | 1.955(2) |
| Ni(1)–N(101) | 1.958(2) | Ni(2)–N(201) | 1.965(3) |
| Ni(1)–N(121) | 2.136(3) | Ni(2)–N(231) | 2.137(3) |
| Ni(1)–N(131) | 2.139(3) | Ni(2)–N(221) | 2.158(3) |
| Ni(1)–N(151) | 2.321(3) | Ni(2)–N(251) | 2.302(3) |
| Ni(1)–N(141) | 2.330(3) | Ni(2)–N(241) | 2.369(3) |
| | | | |
| N(111)–Ni(1)–N(101) | 169.78(11) | N(211)–Ni(2)–N(201) | 171.15(11) |
| N(111)–Ni(1)–N(121) | 95.63(10) | N(211)–Ni(2)–N(231) | 99.45(11) |
| N(101)–Ni(1)–N(121) | 77.21(11) | N(201)–Ni(2)–N(231) | 77.26(11) |
| N(111)–Ni(1)–N(131) | 77.04(11) | N(211)–Ni(2)–N(221) | 76.56(11) |
| N(101)–Ni(1)–N(131) | 96.05(11) | N(201)–Ni(2)–N(221) | 95.45(10) |
| N(121)–Ni(1)–N(131) | 94.34(12) | N(231)–Ni(2)–N(221) | 95.20(10) |
| N(111)–Ni(1)–N(151) | 113.42(10) | N(211)–Ni(2)–N(251) | 73.76(10) |
| N(101)–Ni(1)–N(151) | 73.54(10) | N(201)–Ni(2)–N(251) | 114.28(10) |
| N(121)–Ni(1)–N(151) | 150.75(10) | N(231)–Ni(2)–N(251) | 91.24(10) |
| N(131)–Ni(1)–N(151) | 89.12(11) | N(221)–Ni(2)–N(251) | 150.27(10) |
| N(111)–Ni(1)–N(141) | 73.37(10) | N(211)–Ni(2)–N(241) | 110.65(10) |
| N(101)–Ni(1)–N(141) | 113.70(10) | N(201)–Ni(2)–N(241) | 72.65(10) |
| N(121)–Ni(1)–N(141) | 91.60(9) | N(231)–Ni(2)–N(241) | 149.83(10) |
| N(131)–Ni(1)–N(141) | 150.24(10) | N(221)–Ni(2)–N(241) | 89.90(9) |
| N(151)–Ni(1)–N(141) | 99.68(9) | N(251)–Ni(2)–N(241) | 98.93(9) |

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