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Complexes of a bis-bidentate ligand with d^{10} ions: a mononuclear complex with Ag(I), and a tetrahedral cage complex with Zn(II) which encapsulates a fluoroborate anion

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Abstract

Complexes of the bis-bidentate ligand 2,3-bis[{3-(2-pyridyl)-pyrazol-1-yl}methyl]naphthalene (L^2) with Ag(I) and Zn(II) have been prepared and structurally characterised. In $[Ag(L^2)][ClO_4]$ both bidentate pyrazolyl–pyridine arms of L^2 interact with the same Ag(I) centre, which has two short Ag–N bonds and two much longer, weaker interactions such that the coordination is best described as linear and bidentate. In contrast, in $[Zn_4(L^2)_6(BF_4)][BF_4]_7$ the ligands L^2 act as bis-bidentate bridges; the structure consists of a tetrahedral cage of Zn(II) ions with a bridging ligand L^2 along each of the six edges. The cavity at the centre of this three-dimensional tetrahedral cage accommodates a tetrafluoroborate anion which is completely encapsulated, and inverted with respect to the Zn_4 tetrahedron. The F atoms of this encapsulated anion are involved in close F—HC contacts with parts of the bridging ligands. ^{11}B and ^{19}F NMR spectra show that the encapsulated anion does not exchange with free tetrafluoroborate anions in MeCN solution, even up to 70 °C.

Keywords: Self-assembly; Bridging; Ligand; Tetrahedral cage; Anion binding

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1. Introduction

The self-assembly of polynuclear metal complexes to give elaborate architectures such as helicates, boxes and cages is one of the most intensively studied areas in contemporary inorganic chemistry because of the possibilities it offers for preparing structures which are not accessible by more conventional synthetic routes [1–19]. Our recent work in this area has focussed on the coordination behaviour of bridging ligands such as L^1–L^3 (Scheme 1) in which two bidentate pyrazolyl–pyridine units are connected to an aromatic unit via flexible methylene spacers [20–23]. Reaction of these tetradentate ligands with metal ions having a preference for octahedral coordination is expected to lead to complexes with the stiochiometry M_2L_3, as long as no other species such as counter-ions or solvent molecules are involved in coordination. The simplest expression of this stoichiometry is the well-known triple helicate structure in which all three ligands span both six-coordinate metal centres [24].

In complexes of L^1 and L^2 with first-row transition metal dictations we observed two different types of structure, both having the same metal:ligand ratio [20,22]. With Ni(II) the complexes $[LNi(\mu\text{-}L)NiL]X_4$ ($X^- =$ perchlorate or tetrafluorborate) formed, in which the expected Ni_2L_3 stoichiometry occurs, but with only one bridging ligand; the remaining two ligands act as tetradentate chelates, each to a single metal ion. Thus the nature of these complexes is therefore dictated by the fact that L^1 and L^2 are flexible enough to coordinate in either tetradentate chelating or bis-bidentate bridging coordination modes, as circumstances dictate. In contrast, with Co(II) the tetrahedral cage complexes

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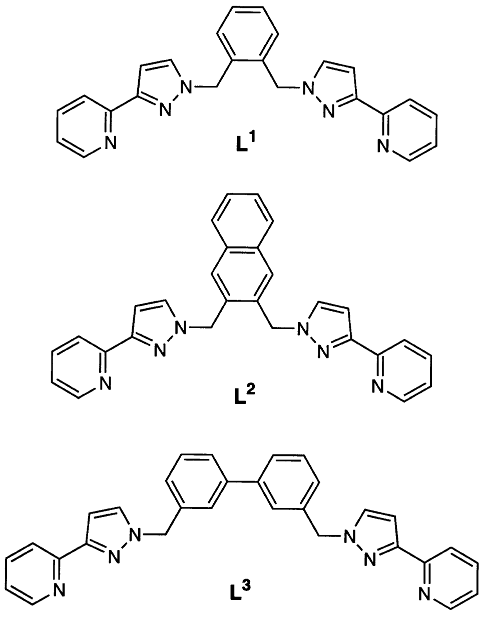

Scheme 1.

$[Co_4L_6X]X_7$ ($X^- =$ perchlorate or tetrafluorborate) are formed. In these complexes the metal ions are arranged in an approximately tetrahedral array, with a bridging ligand spanning each edge of this tetrahedron. Each metal ion is therefore in a tris-chelate environment and interacting with three different ligands, and all four metal centres have the same chirality such that the complexes have *T* symmetry in solution, in the absence of crystal packing effects. The central cavity of the cage is occupied by a $[ClO_4]^-$ or $[BF_4]^-$ anion, which (fortuitously) is an ideal guest in that it is exactly complementary to the host in terms of shape, size and charge. In fact in these cases the cages do not form without the tetrahedral anion being present; the anion acts as an effective template around which the metal/ligand cage assembles [22]. The assembly of tetrahedral cages of this general type, and the study of their host/guest chemistry, has been an area of intense recent interest [7–15] since such structures were first reported by Saalfrank et al., [16–19].

It is slightly surprising that such different types of structure should arise with Ni(II) and Co(II), despite the similarity of these ions. Both occur in these complexes in octahedral tris-chelate geometries; the ions have the same charge, and similar ionic radii (≈ 0.8 Å). Yet, reaction of L^1 and L^2 with Ni(II) in the presence of $[BF_4]^-$ or $[ClO_4]^-$ anions gives only a dinuclear complex, with no evidence of formation of a tetrahedral cage despite the fact that the Co(II) complexes are tetrahedral cages under the same conditions. In this paper we describe the coordination behaviour of L^2 with two d^{10} metal ions, viz. Ag(I) and Zn(II), and report the structures of the mononuclear complex with Ag(I) as well as a new example of a cage complex with Zn(II), the first example of such a cage with these ligands that is not based on Co(II).

2. Results and discussion

The ligand L^2 was prepared according to the previously-described method, by reaction of 3-(2-pyridyl)pyrazole with 2,3-bis(bromomethyl)naphthalene in the presence of hydroxide ion under phase-transfer conditions [22]. The crystal structure of the ligand is shown in Fig. 1. The individual bond distances and angles within the molecule are unremarkable. The two pyrazolyl–pyridine units have an approximately trans-coplanar arrangement such that the N lone pairs avoid each other; the angles between the pyrazolyl and pyridyl mean planes in each bidentate unit are 8°, and each pyrazolyl unit is nearly perpendicular to the naphthyl unit (98° between mean planes).

To study the coordination behaviour of L^2 under circumstances where cage formation is not expected, we prepared the Ag(I) complex $[Ag(L^2)][ClO_4]$ whose crystal structure is shown in Fig. 2. This is a mononuclear complex in which L^2 acts as a chelate to a single metal centre, with the Ag(I) ion in a near-planar coordination environment. Two of the bonds [Ag(1)–N(11), 2.229 Å and Ag(1)–N(52), 2.173 Å] are relatively short, with the bond to N(22) being significantly longer (2.543 Å) and the bond to N(61) being even more remote (2.836 Å), such that the coordination geometry about the metal ion is best described as linear two-coordinate with two much weaker interactions making an approximate plane. The weakness of the $Ag(1)\cdots N(61)$ interaction is shown by the fact that the pyridyl ring containing N(61) is twisted out of the plane of the adjacent pyrazolyl ring by 23°, such that N(61) is not pointing directly at the metal centre. The naphthyl unit of L^2 is near-perpendicular to the plane of the coordinated pyrazolyl units (95° between planes), giving an 'L-shaped' structure which in the solid state is involved in aromatic π-stacking interactions with adjacent molecules (which presumably accounts for the presence of a peak in the mass spectrum corresponding to a dimer, viz. $[\{Ag(L^2)\}_2(ClO_4)]^+$). The unusual planar coordination environment for Ag(I) in this case appears to be imposed by the aromatic stacking interactions in the solid state. The important point for our purposes is that it illustrates how L^2 is capable of behaving as a chelating ligand to a single metal ion, i.e. the bridging behaviour which results in cage formation does not always occur, since there is a simpler mononucleating coordination mode also available to the ligand.

Reaction of L^2 with zinc(II) acetate hydrate in MeOH afforded a clear solution from which a precipitate was isolated after addition of aqueous $NaBF_4$. The elemental analysis indicated an empirical formula

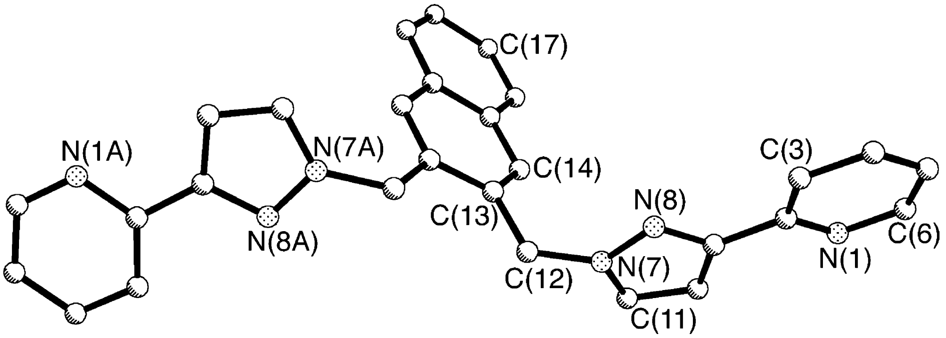

Fig. 1. Molecular structure of L^2.

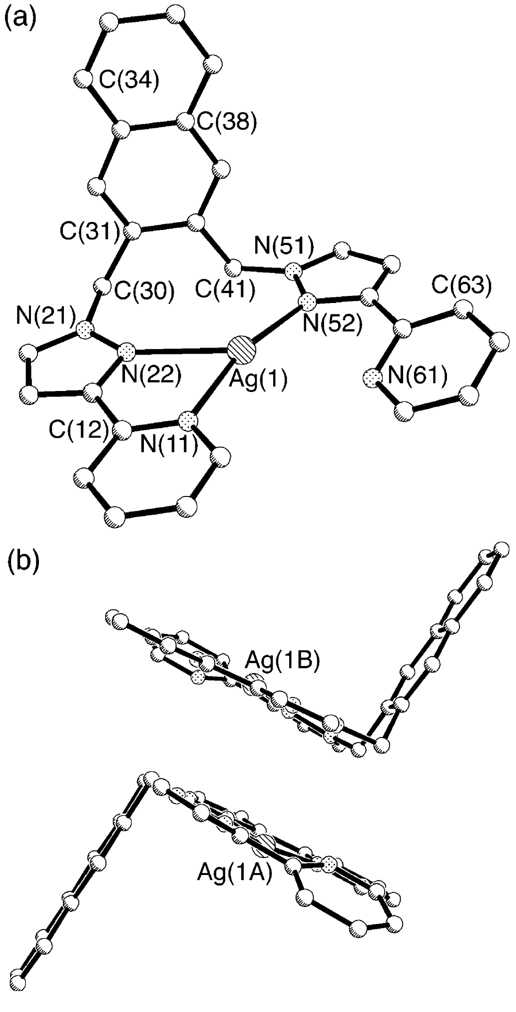

Fig. 2. Molecular structure of $[Ag(L^2)][ClO_4]$: (a) a mononuclear complex cation, (b) the face-to-face stacking between adjacent complex cations. Selected bond distances (Å) and angles (°): Ag(1)–N(52), 2.173(7); Ag(1)–N(11), 2.229(7); Ag(1)–N(22), 2.543(7); N(52)–Ag(1)–N(11), 166.2(3); N(52)–Ag(1)–N(22), 120.2(2); N(11)–Ag(1)–N(22), 71.3(2).

$[Zn_2(L^2)_3][BF_4]_2$, indicating that the complex would be either dinuclear [like the Ni(II) complex] or a tetrahedral cage [like the Co(II) complex]. Electrospray mass spectrometry in MeCN indicated formation of a tetranuclear cage complex. Under 'normal' conditions (a cone voltage of 40 V) the spectrum was uninformative, showing only low molecular weight fragments such as $\{HL^2\}^+$ and $\{Zn(L^2)\}^{2+}$. However by reducing the cone voltage to 5 V, matters improved considerably. The peak at highest m/z value (1717, relative intensity 100%) is assignable to $\{Zn_4(L^2)_6(BF_4)_6\}^{2+}$ (the half-integral isotopic spacing confirms this), and a peak at 1116 (relative intensity 30%) with one third integral isotopic spacing corresponds to $\{Zn_4(L^2)_6(BF_4)_5\}^{3+}$. These two peaks provide strong evidence that the complex is $[Zn_4(L^2)_6][BF_4]_8$. Numerous smaller fragment ions could also be identified, such as $\{Zn_3(L^2)_5(BF_4)_4\}^{2+}$ (m/z 1376.5, 70%), $\{Zn(L^2)(BF_4)\}^+$ (m/z 1035, 100%), $\{Zn(L^2)(BF_4)\}^+$ (m/z 593, 20%), $\{HL^2\}^+$ (m/z 443, 70%) and $\{Zn(L^2)\}^{2+}$ (m/z 253, 20%).

The crystal structure of the complex (Figs. 3 and 4) confirmed that the complex is $[Zn_4(L^2)_6(BF_4)][BF_4]_7$, a tetrahedral cage incorporating a $[BF_4]^-$ anion. There are two crystallographically independent cage units in the crystal, each lying on a threefold axis which passes through one metal ion and the centre of the opposite face. The Zn···Zn separations along the edges of the metal tetrahedra lie in the range 9.35–10.08 Å; Zn–N distances lie between 2.11 and 2.21 Å. As in the Co(II) complexes with L^1 and L^2, the encapsulated $[BF_4]^-$ anion is inverted with respect to the Zn_4 tetrahedron such that an F atom is directed towards the centre of a triangular face of the tetrahedron and is not involved in any close contacts with the Zn(II) ions. This minimises steric interactions, and is in interesting contrast to an example of an M_4L_6 cage described by Hüttner and co-workers in which the encapsulated $[BF_4]^-$ anion is oriented such that M···F interactions are optimised [25]. Instead, in $[Zn_4(L^2)_6(BF_4)][BF_4]_7$ the F atoms of the anion are involved in close contacts with protons associated with the CH_2 spacers of each ligands (non-bonded H···F separations, 2.3–2.4 Å), possibly indicative of weak CH···F hydrogen-bonding interactions [26,27] which will help to keep the anion bound in the cavity. That the anion is located approximately centrally in the cavity in each case is shown by the fact that the non-bonded Zn···B separations are all similar (5.79–6.23 Å); as in the analogous Co(II) complexes [20,22],

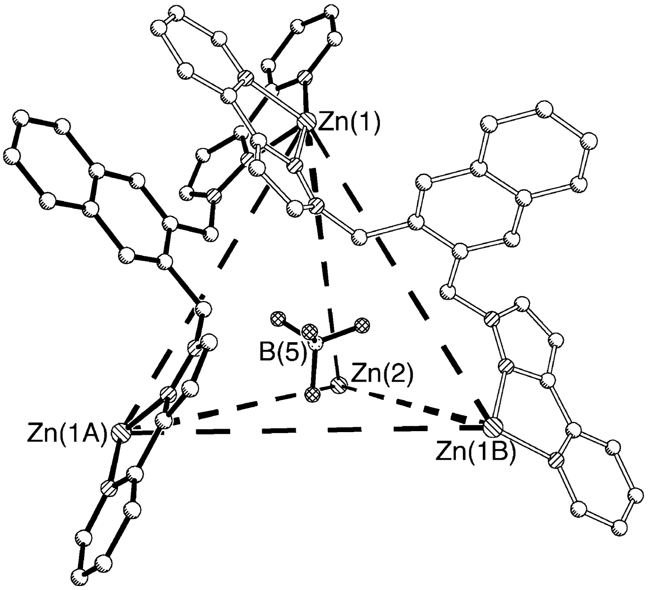

Fig. 3. Structure of part of the complex cation of $[Zn_4(L^2)_6][BF_4]_8\cdot(MeCN)_{6.75}(H_2O)_2$, emphasising (i) the approximately tetrahedral array of Zn(II) ions, (ii) the edge-bridging arrangement of the ligands (only two, shaded differently from each other, are shown for clarity); and (iii) the position and orientation of the encapsulated $[BF_4]^-$ anion. Zn–N distances lie in the range 2.11–2.21 Å. There are two crystallographically independent cages in the crystal; the other (not shown) is very similar.

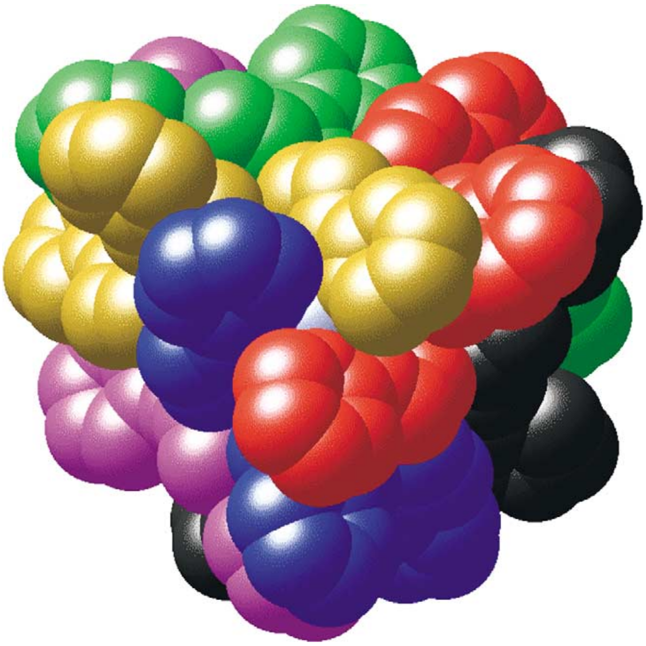

Fig. 4. Space-filling view of the complex cation of $[Zn_4(L^2)_6][BF_4]_8$, with each ligand coloured different for clarity; this view looks down a C_3 axis.

it is apparent that the fluoroborate anion is a good match in terms of size, shape and charge for the tetrahedral cavity in which it is located. The space-filling view in Fig. 4 emphasises the chirality of each complex cation and the way in which the ligands are intertwined around each other, with aromatic π-stacking interactions between adjacent naphthyl segments.

That the assembly $[Zn_4(L^2)_6(BF_4)]^{7+}$ remains intact in solution—and also that the complex is pure—are both clearly shown by NMR spectroscopy. The ^1H NMR spectrum is rather broad and not very informative, with the signals all occurring in a small chemical shift range [unlike the Co complexes, where the paramagnetism of Co(II) acted as a shift reagent to spread the signals out over a wide range (22)]. However the ^{19}F and ^{11}B NMR spectra are definitive, showing two signals in a 7:1 ratio for the free and encapsulated anions. In the ^{19}F spectrum in MeCN the signals are at −167 and −177 ppm for encapsulated and free $[BF_4]^-$, respectively (Fig. 5); the ^{11}B spectrum is exactly comparable, with the two signals at −1.3 (minor) and −2.2 (major) ppm for encapsulated and free $[BF_4]^-$, respectively. The presence of two different ^{11}B and ^{19}F environments in a 7:1 ratio is only consistent with retention of the cage structure with its trapped anion. If other (open-chain) $Zn/L^2/BF_4$ complexes were present, the 7:1 integral ratio would not occur; there would be an apparent deficit of the encapsulated anion.

These spectra do not change significantly at temperatures up to 70 °C, indicating slow exchange of free and encapsulated anions. From the space-filling view of the crystal structure it is apparent that it is not possible for the anion to escape through the centre of one of the tetrahedral faces, such that exchange would have to involve cleavage of several Zn–N bonds at the same time. Although Zn(II) is a highly labile metal ion, it is likely that the mutual intertwining of several ligands which characterises these structures results in a highly stable, kinetically inert structure. Williams and co-workers have shown how intertwining three ligands around two Co(II) centres in a triple helical array results in an increase of five orders of magnitude for the time taken for dissociatively-activated rearrangements to

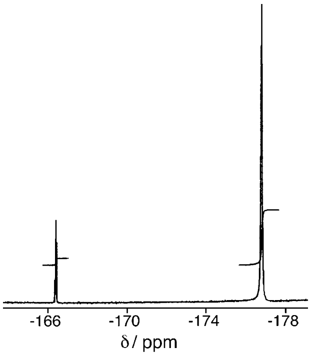

Fig. 5. ^{19}F NMR spectrum of $[Zn_4(L^2)_6][BF_4]_8$ in MeCN at room temperature.

take place [28], and we suspect that a similar effect operates in these M_4L_6 cages; such studies are in progress.

Finally, we note that the formation of an M_4L_6 cage with this ligand using Co(II) and Zn(II)—but not with Ni(II) for which an open-chain M_2L_3 complex forms [22]—points to small changes in ionic radius being the determining factor. For $[Co_4(L^2)_6(BF_4)][BF_4]_7$ the average Co–N separation is 2.143 Å [22]; for $[Ni_2(L^2)_3][BF_4]_4$ it is 2.096 Å [22]; and for $[Zn_4(L^2)_6(BF_4)][BF_4]_7$ it is 2.168 Å. This is in accord with the Irving–Williams series, which results from the fact that octahedral Ni(II) has a slightly smaller ionic radius than either octahedral Co(II) or Zn(II). From the figures above it can be seen that the average Co–N and Zn–N separations are similar to one another, but the average Ni–N separation is 2–3% shorter. Evidently the compression in the coordination sphere that this causes prevents formation of a $Ni_4(L^2)_6$ cage due to the unfavourable inter-ligand contacts that would result.

3. Experimental

3.1. General details

The ligand L^2 was prepared according to the recently described method [22]. Other reagents were obtained from the usual commercial sources (Avocado, Aldrich) and used as received. Fast atom bombardment (FAB) mass spectra were recorded on a VG-Autospec instrument, and electrospray mass spectra on a VG Quattro II triple quadrupole instrument. ^1H, ^{19}F and ^{11}B NMR spectra were recorded on a Jeol Eclipse 400 MHz spectrometer.

3.2. Synthesis of $[Ag(L^2)][ClO_4]$

Solid $AgClO_4$ (0.025 g, 0.12 mmol)was added to a solution of L^2 (0.050 g, 0.11 mmol) in THF (10 cm^3). An off-white precipitate resulted immediately and the reaction mixture was stirred at room temperature for a further 1 h, after which time the product was filtered off and dried in vacuo. Yield: 0.040 g, 52%. FAB MS: *m/z* 549 $\{Ag(L^2)\}^+$; 1197 $\{Ag_2(L^2)_2(ClO_4)\}^+$ (both based on ^{107}Ag; the correct isotopic patterns were seen in each case). Found: C, 51.2; H, 3.2; N, 12.6%. Required for $[Ag(L^2)](ClO_4)$: C, 51.7; H, 3.4; N, 12.9%.

3.3. Synthesis of $[Zn_4(L^2)_6][BF_4]_8$

This was prepared in the same way as the previously-described Co(II) analogues [18]. A solution of L^2 (0.049 g, 0.11 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise to a solution of $Zn(O_2CMe)_2{\cdot}2H_2O$ (0.015 g, 0.07 mmol) in MeOH (10 cm^3), and the resulting clear solution was stirred for 1 h at room temperature. Addition of a methanolic solution of $NaBF_4$ followed by concentration of the mixture under reduced pressure resulted in precipitation of a cream solid which was filtered off and dried in vacuo; the yield was typically 40%. Further material could be isolated by concentrating and cooling the mother liquor. X-ray quality crystals were grown by diffusion of diethyl ether into solutions

Table 1
Crystallographic data for the three structures

Compound	L^2	$[Ag(L^2)][ClO_4]$	$[Zn_4(L^2)_6][BF_4]_8{\cdot}(MeCN)_{6.75}(H_2O)_2$
Empirical formula	$C_{28}H_{22}N_6$	$C_{28}H_{22}AgClN_6O_4$	$C_{181.5}H_{156.25}B_8F_{32}N_{42.75}O_2Zn_4$
Formula weight	442.52	649.84	3924.20
Crystal dimensions (mm)	0.6 × 0.4 × 0.2	0.2 × 0.1 × 0.1	0.4 × 0.3 × 0.3
Crystal system,	monoclinic,	trigonal,	trigonal,
Space group	*C*2/c	$R\bar{3}$	$R\bar{3}$
a (Å)	20.110(2)	27.128(4)	18.536(2)
b (Å)	13.8852(15)	27.128(4)	18.536(2)
c (Å)	7.7784(9)	17.767(4)	181.64(3)
β (°)	98.902(2)	90	90
V (Å^3)	2145.8(4)	11323(3)	54049(12)
Z	4	18	12
ρ_{calc} (g cm^{-3})	1.370	1.715	1.447
Absorption coefficient (mm^{-1})	0.085	0.957	0.627
Reflections collected: total/independent/R_{int}	10981, 2456, 0.0532	19885, 4437, 0.2453	79236, 21170, 0.1828
Data/restraints/parameters	2456, 0, 154	4437, 0, 361	21170, 3, 1620
Final R_1, wR_2[a,b]	0.0374, 0.1057	0.0524, 0.1086	0.1053, 0.2939

Data in common: $T = 173$ K; $\lambda = 0.71073$ Å; instrument, a Bruker SMART-CCD diffractometer.

[a] 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 $F \geqslant 4\sigma(F)$.

[b] $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

of the complexes in MeCN at 0 °C. Found: C, 53.2; H, 3.8; N, 13.3%. Required for $[Zn_4(L^2)_6][BF_4]_8 \cdot 8H_2O$: C, 53.7; H, 3.9; N, 13.4%.

3.4. X-ray crystallography

Details of the crystal, data collection and refinement parameters for the new structures are summarised in Table 1. All data were collected in a Siemens SMART diffractometer with a CCD area detector using graphite-monochromatised Mo Kα radiation ($\lambda = 0.71073$ Å). In each case structure solution and refinement used the SHELX package (version 5.03) comprising SHELXS-97 [29] and SHELXL-97 [30]; absorption corrections were applied to the data using SADABS [31]. H atoms were included in calculated positions (except for on lattice solvent molecules, where they were omitted from the refinement) with isotropic thermal parameters and refined as riding atoms. All structural determinations were carried out at 173 K. The structural determinations of L^2 and $[Ag(L^2)][ClO_4]$ were straightforward.

For $[Zn_4(L^2)_6][BF_4]_8 \cdot (MeCN)_{6.75}(H_2O)_2$ the structural determination was complicated by the very long *c*-axis which results in overlapping diffraction spots, and poor crystallinity (and hence weak diffraction) associated with rapid loss of solvent from the crystal lattice. The asymmetric unit contains one third of each of two independent cage complexes on C_3 axes. There are also several MeCN molecules of which four (in general positions) were well-behaved, one lies on a C_3 axis (i.e. one third occupancy on the asymmetric unit), and another lies on a C_3 axis but with only 50% site occupance for each atom, i.e. one sixth occupancy in the asymmetric unit. The asymmetric unit also contains two isolated electron-density peaks which were assigned as the oxygen atoms of water molecules; one in a general position, and one on a C_3 axis. The unit cell contents therefore constitute two thirds of a $[Zn_4(L^2)_6][BF_4]_8$ cage complex, 4.5 MeCN and 1.333 H_2O, i.e. the overall formula is $[Zn_4(L^2)_6][BF_4]_8 \cdot (MeCN)_{6.75}(H_2O)_2$. Most of the non-hydrogen atoms could be refined successfully with anisotropic thermal parameters, with the exception of some of the MeCN solvent molecules and some of the $[BF_4]^-$ anions; attempts to make these anisotropic resulted in the refinement becoming unstable. Considering these problems the final R_1 value of 10.5% is reasonable.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers 184 778 for L^2, 184 779 for $[Ag(L^2)][ClO_4]$ and 184 780 for $[Zn_4(L^2)_6][BF_4]_8 \cdot (MeCN)_{6.75}(H_2O)_2$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.ac.uk; or www: http://www.ccdc.cam.ac.uk).

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