Design of chiral homodinuclear complexes based on the coordinating behaviour of some symmetric ligands†

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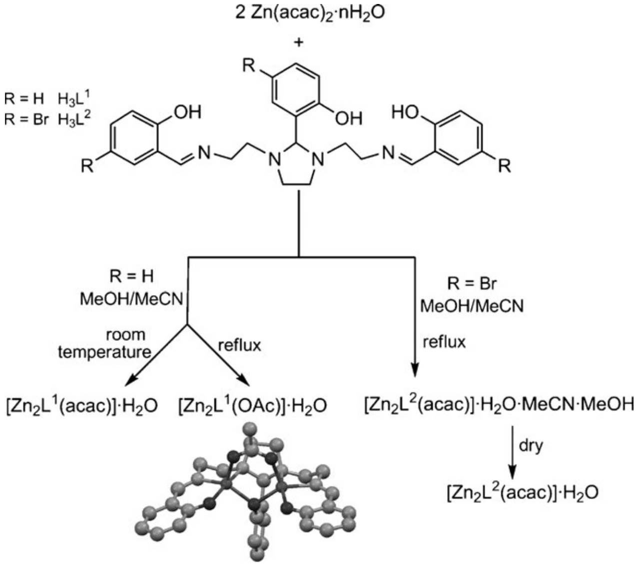
The crystal structures determined for [Zn_2L^1(acac)]·H_2O and [Zn_2L^2(acac)]·H_2O·MeCN·MeOH show that both compounds are chiral, although crystallising as racemates. This was not unexpected, as these complexes had been designed on the basis of the coordinating behaviour of acac in combination with 2-(2-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine (H_3L^1) and 2-(5-bromo-2-hydroxyphenyl)-1,3-bis[4-(5-bromo-2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine (H_3L^2). The reactivity of Zn(acac)$_2$·$n$$H_2O$ with compartmental H_3L^x (x = 1 or 2) has been investigated under different reaction conditions. Thus, depending on the temperature, the reaction with H_3L^1 can yield [Zn_2L^1(acac)]·H_2O or [Zn_2L^1(OAc)]·H_2O, whilst the interaction of Zn(acac)$_2$·$n$$H_2O$ with H_3L^2 only gives rise to crystalline [Zn_2L^2(acac)]·H_2O·MeCN·MeOH. This latter species loses the most volatile solvates on drying to yield [Zn_2L^2(acac)]·H_2O. Both [Zn_2L^x(acac)]·H_2O complexes have been fully characterised by analytical and spectroscopic methods.

Since the origin of the chirality of the building blocks of life is a fundamental issue still unsolved, molecular asymmetry is a central field of research in chemistry. One of the questions to be answered is what practical features might facilitate the design of systems that could spontaneously generate optically active products from achiral starting materials.[1]

This interest is not limited to organic chemists, since coordination chemistry offers multiple opportunities in this field. Thus, the varied coordination requirements of metal ions, combined with untold numbers of different ligands can give rise to chirality. The predetermination of chirality is very difficult, especially when using achiral ligands;[2,3] however, the careful selection of metal ions and ligands can facilitate the formation of chiral complexes. Thus, there are numerous examples of chiral mono- and polynuclear complexes where helical motifs are rather common.[3a,c]

As we are interested in coordination stereochemistry,[4] here we present two chiral homodinuclear Zn(II) complexes that have been designed on the basis of our experience with two types of symmetric achiral ligand: H_3L^x [4g,h,5–7] and acetylacetonate (acac)[5a,i,6] (Scheme 1).



Scheme 1 Routes for the isolation of the metal complexes. This scheme includes a representation of the molecular structure of [Zn_2L^1(OAc)],[5a] in order to illustrate the typical achiral homodinuclear complexes obtained with H_3L^1 and H_3L^2.

In the cases of compartmental H_3L^1 and H_3L^2, they markedly favour the formation of dinuclear complexes, when using a 2 : 1 metal : ligand ratio, behaving as either trianionic[4g,h,5,7] or less commonly dianionic.[6] Thus, they usually hold two metal ions in their two *O*,*N*,*N*,*O* compartments, which are bridged by the phenoxo-O atom of their central arm, with rare exceptions.[5c,e] The central imidazolidine ring with the short central arm contributes some rigidity. In contrast, the two side arms are more flexible, appearing as two flapping wings that can be more or less spread. This spatial arrangement allows their donor sets to provide a seesaw-shaped geometry around each metal ion. This type of geometry is not a typical coordinative preference of any common metal ion. This fact, and the practical absence of steric hindrance on one side of the ligand (Fig. 1), facilitates the coordination of other exogenous ligands. Therefore, the chosen metals and ligands will condition the nature of the complex obtained.

Thus, heterodinuclear complexes of H_3L^1 and H_3L^2 would be chiral *per se*, as the C_s symmetry of these ligands disappears (Fig. 1). Likewise, if both metal ions favour different

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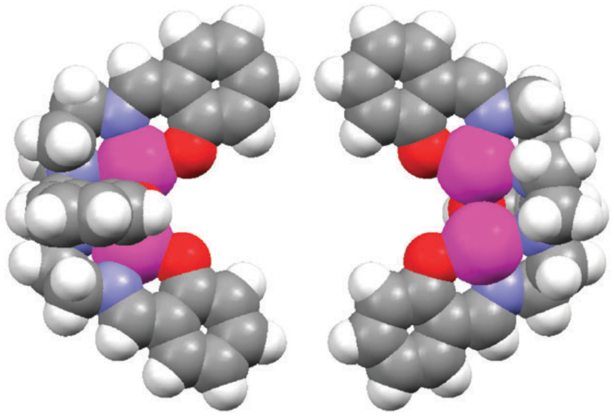

Fig. 1 Opposite views (with a half-turn) of the $[Zn_2(L^1)]^+$ units in $[Zn_2L^1(OAc)]\cdot H_2O$, showing C_s symmetry. The right view shows the unoccupied coordination positions of the two Zn(II) ions (the biggest ones).

geometries, the addition of an exogenous chelating ligand could give rise to two different coordination environments by forming an asymmetric bridge, and so the formation of these chiral complexes can be favoured.[8]

In contrast, for homodinuclear complexes, the only possibility of achieving chirality is by adding asymmetry through exogenous ligands. This could occur with two different exogenous ligands[4h,5c,h,7] or with the formation of an asymmetric bridge. This latter scenario can be related either to dissymmetric ligands or to the coordination mode.

In this way, we have obtained complexes with different exogenous ligands (water, methanol, acetate, . . .) coordinated through symmetric bridges (Scheme 1).[4h,5a–d,f–j] Therefore, we decided to research the coordinating behaviour of acac with $(L^x)^{3-}$ and Zn^{II} ions. The selection of acac was based not only on the recurrence of asymmetric bridges in polynuclear acetylacetonates,[9,10] including Zn(II) acetylacetonates,[10a,d] but also on the fact that we have previously obtained Ni^{II} and Co^{II}/Co^{III} complexes with $(L^x)^{3-}$ that also presented asymmetric acac bridges.[5i,6] These complexes were obtained by employing metal acetylacetonates as starting materials, and other carboxylates were intended to substitute for the acac anion.[5i,j,6] Thus, we have already used Zn(II) acetylacetonate to prepare some carboxylate complexes.[5j]

With these precedents, and in order to combine the acetylacetonate anion with $[Zn(L^1)]^+$ and $[Zn(L^2)]^+$ units, we have used a variation of a previously described method.[11] In this method, reactions take place under reflux, but in our case, the reaction conditions were different, according to the ligand employed (Scheme 1).

In this way, the reaction of H_3L^1 with $Zn(acac)_2\cdot nH_2O$ under reflux lead to the isolation of $[Zn_2L^1(OAc)]\cdot H_2O$, which has been previously reported.[5a] This was obtained in high purity and in a practically quantitative yield, being unequivocally identified by single X-ray diffraction studies and NMR spectroscopy.[12] Nevertheless, when the same reaction was performed at room temperature, $[Zn_2L^1(acac)]\cdot H_2O$ was suitably obtained.

These results show that, at least in this case, a raising of the temperature favours the oxidation of the acetylacetonate ligand to acetate. This reaction is not without precedent,[12–14] but, as far as we know, it has never been described for zinc compounds. Therefore, to the best of our knowledge, $[Zn_2L^1(acac)]\cdot H_2O$ constitutes the first example of an acetylacetonate zinc complex that suffers this kind of degradation. In fact, the first microbial degradation pathway of acetylacetone was described for a novel enzyme, where Fe(II) is bound to the active protein and is essential for its catalytic activity. This enzyme cleaves acetylacetone to equimolar amounts of methylglyoxal and acetate, consuming one equivalent of molecular oxygen.[15]

In the case of H_3L^2, its reaction with $Zn(acac)_2\cdot nH_2O$ under reflux allowed the isolation of single crystals of $[Zn_2L^2(acac)]\cdot H_2O\cdot MeCN\cdot MeOH$. These crystals lost the most volatile solvates on drying to give $[Zn_2L^2(acac)]\cdot H_2O$, which has been conveniently characterised (*vide infra*). However, in this case, no evidence of acetate complex formation was detected. Thus, the presence of an electronic acceptor (Br) in the aromatic rings of the Schiff base appears to prevent the oxidation of the acetylacetonate ligand.

The crystal structures of $[Zn_2L^1(acac)]\cdot H_2O$ and $[Zn_2L^2(acac)]\cdot H_2O\cdot MeCN\cdot MeOH$ were determined, with ORTEP views of $[Zn_2L^1(acac)]$ and $[Zn_2L^2(acac)]$ being shown in Fig. 2 and Fig. 3, respectively. The main distances and angles are listed in Table 1, while experimental details and crystal data are given in Table 2.

The complexes are very similar, meaning that they can be discussed together. Their crystal structures show that they consist of neutral $[Zn_2L^x(acac)]$ units joined with different solvates. The heptadentate $(L^x)^{3-}$ Schiff base (x = 1, 2) accommodates two zinc ions into its two *O*,*N*,*N*,*O* donor compartments. The imidazolidinic *NCN* group (N103, C120, N104) and central phenol oxygen atom (O103) are bridging both zinc ions. As expected, the coordination spheres of the metal centres are completed by a bidentate acetylacetonate anion, which shows a μ_2-η^2:η^1-*O*,*O′* coordinating mode. Accordingly, both zinc ions are triply-bridged, with Zn· · ·Zn distances close to 3.1 Å.

This asymmetric coordination mode, combined with the absence of other exogenous donors gives rise to two different

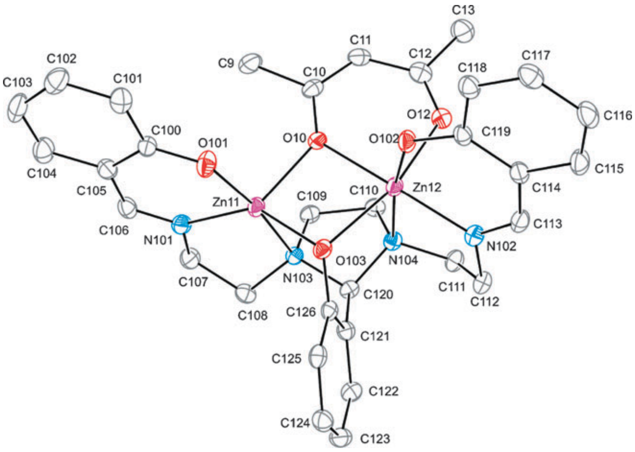

Fig. 2 An ORTEP view of the ($\Delta\Lambda_3$,*trans*)-(λ,δ) enantiomer of $[Zn_2L^1(acac)]\cdot H_2O$. Ellipsoids are represented at 50% of probability.

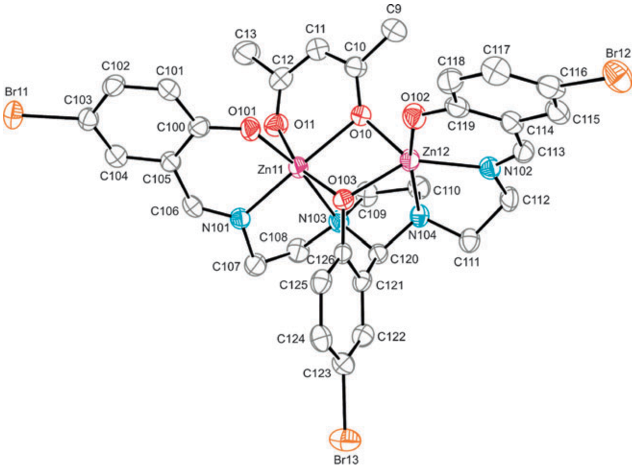

Fig. 3 An ORTEP view of the ($\Delta_3\Lambda$,*trans*)-(δ,δ) enantiomer of $[Zn_2L^2(acac)]\cdot H_2O\cdot MeCN\cdot MeOH$. Ellipsoids are represented at 50% of probability.

Table 1 The main distances (Å) and angles (°) for $[Zn_2L^1(acac)]\cdot H_2O$ and $[Zn_2L^2(acac)]\cdot H_2O\cdot MeCN\cdot MeOH$

	$[Zn_2L^1(acac)]\cdot H_2O$	$[Zn_2L^2(acac)]\cdot H_2O\cdot MeCN\cdot MeOH$
Zn11–O101	1.9812(17)	2.018(3)
Zn11–N101	2.024(2)	2.061(3)
Zn11–N103	2.335(2)	2.291(3)
Zn11–O103	1.9775(16)	2.089(3)
Zn11–O10	2.0271(16)	2.113(3)
Zn11–O11	—	2.086(3)
Zn12–O102	1.9951(17)	1.978(3)
Zn12–N102	2.0388(19)	2.040(3)
Zn12–N104	2.290(2)	2.293(3)
Zn12–O103	2.1764(17)	2.005(3)
Zn12–O10	2.0762(16)	2.022(3)
Zn12–O12	2.1832(18)	—
Zn11···Zn12	3.0622(5)	3.0804(7)
O103–Zn11–N101	141.54(7)	—
O101–Zn11–N103	169.95(7)	168.49(12)
N101–Zn11–O10	—	171.38(13)
O11–Zn11–O103	—	162.60(11)
O103–Zn12–O12	162.98(6)	—
N102–Zn12–O10	170.26(7)	—
O102–Zn12–N104	172.20(7)	167.88(12)
O103–Zn12–N102	—	141.65(13)
Zn12–O103–Zn11	94.87(7)	97.57(12)
Zn12–O10–Zn11	96.53(6)	96.28(12)

Table 2 The main crystal and refinement data for $[Zn_2L^1(acac)]\cdot H_2O$ and $[Zn_2L^2(acac)]\cdot H_2O\cdot MeCN\cdot MeOH$

	$[Zn_2L^2(acac)]\cdot H_2O$	$[Zn_2L^2(acac)]\cdot H_2O\cdot MeCN\cdot MeOH$
Empirical formula	$C_{32}H_{36}N_4O_6Zn_2$	$C_{35}H_{40}Br_3N_5O_7Zn_2$
Formula weight	703.39	1013.19
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$	$P2_1/c$
T/K	120(2)	120(2)
a/Å	10.1551(12)	12.0335(17)
b/Å	19.124(2)	11.6409(16)
c/Å	15.2374(18)	27.861(4)
α (°)	90	90
β (°)	90	94.400(2)
γ (°)	90	90
Volume/Å^3	2959.2(6)	3891.3(9)
Z	4	4
μ/mm^{-1}	1.674	4.366
Reflections collected	27784	36166
Independent reflections	7141 (R_{int} = 0.0401)	9387 (R_{int} = 0.0015)
Data/restraints/parameters	7141/1/407	9387/0/482
Flack parameter	−0.005(7)	
Final R index [$I > 2\sigma(I)$]	R_1 = 0.0269 wR_2 = 0.0561	R_1 = 0.0445 wR_2 = 0.0859
R index [all data]	R_1 = 0.0368 wR_2 = 0.0604	R_1 = 0.0736 wR_2 = 0.0965

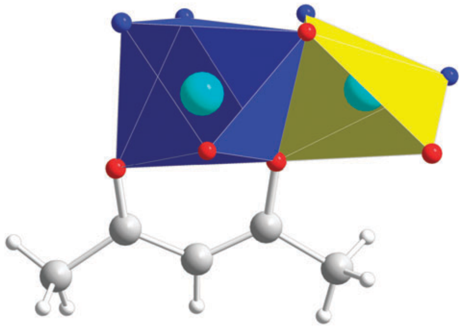

Fig. 4 A ball and stick diagram of the metal chromophores, denoted as polyhedra, found in $[Zn_2L^1(acac)]$. The whole acac anion is shown for a better understanding.

coordination environments around the metal atoms (Fig. 4). One of the zinc ions (Zn11 for $[Zn_2L^1(acac)]$ and Zn12 for $[Zn_2L^2(acac)]$) displays N_2O_3 chromophores, with a highly distorted square pyramid geometry according to their τ parameters (τ = 0.473 for x = 1 and 0.437 for x = 2).[16] In these pyramids, O10, the bridging atom of the acac anion, occupies the apical site, whilst the four donor atoms of the Schiff base form their bases. This can be considered as a *trans* or achiral disposition.[2a,3b]

The second metal atom (Zn12 for $[Zn_2L^1(acac)]$ and Zn11 for $[Zn_2L^2(acac)]$) is N_2O_4-hexacoordinated, with distances and angles that indicate a clear distortion of a perfect octahedral geometry. The four donor atoms of $(L^x)^{3-}$ for $[Zn_2L^1(acac)]$ and $[Zn_2L^2(acac)]$ are folded with Δ-*cis*β and Λ-*cis*β configurations for their edges, respectively.[2a,3b] Both polyhedrons share the edge formed by the two bridging O-atoms (Fig. 4).

These circumstances lead to a molecular asymmetry that induces chirality. As the precursors are not chiral, they are unable to induce a predetermined enantiomeric excess,[2] so the crystals are racemic mixtures where both enantiomers co-exist at 50%. However, $[Zn_2L^1(acac)]$ crystallises in the non-centrosymmetric $Pna2_1$ space group, which belongs to the *mm*2 crystal class. Although this class is not qualified as chiral or enantiomorphic, it does present a polar axis direction (z).[17] This means that the unit cell origin may be arbitrarily placed along this axis. Therefore, the value found for the Flack parameter[18] determines the correctness of the absolute structure, as well as a closely coincident orientation of the structure with respect to the polar axis, more than the enantiopurity or racemic twinning evaluation related to homochiral crystals. This polarity also means that both enantiomers form alternate layers of each enantiomer that are perpendicular to c (Fig. 5). Therefore, the crystal shows optical properties in this direction that are lacking in the other directions.

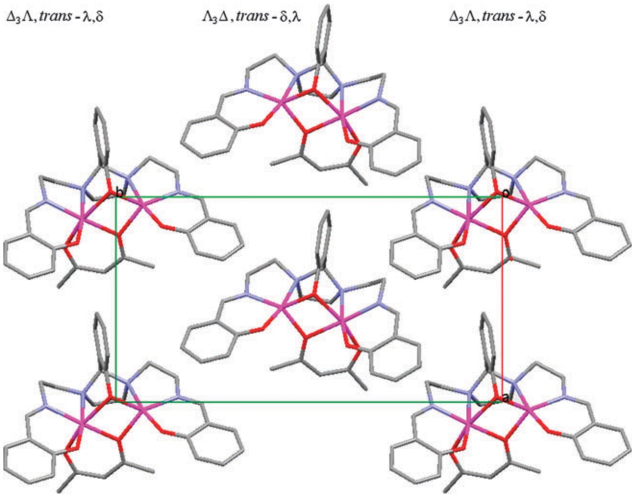

Fig. 5 The crystal packing of $[Zn_2L^1(acac)]\cdot H_2O$ showing the disposition that allows the formation of alternate layers of each enantiomer. Hydrogen atoms and water molecules have been omitted for clarity.

According to the Λ and Δ descriptors for chiral configurations,[19] Fig. 2 shows the enantiomer of $[Zn_2L^1(acac)]$ that can be considered as $\Delta_3\Lambda$ with respect to its pseudo-octahedral chromophore, whilst Fig. 3 shows the corresponding mirror image ($\Delta\Lambda_3$), although in that case referred to as $[Zn_2L^2(acac)]$.

With regard to chirality, the most significant difference between the two complexes is related to the conformation of the ethylene spacers of the Schiff base ligands. For a better perception, their Newman projections are represented in Fig. 6. They show that the $\Delta_3\Lambda$, *trans* enantiomer of $[Zn_2L^1(acac)]$ displays different dispositions of its *gauche*-conformed ethylene chains, while in the $\Delta\Lambda_3$, *trans* enantiomer of $[Zn_2L^2(acac)]$, both spacers show the same disposition. Therefore, the racemate solved for $[Zn_2L^1(acac)]$ could be described as being formed by their ($\Delta\Lambda_3$, *trans*)-(λ,δ) and ($\Delta_3\Lambda$, *trans*)-(λ,δ) enantiomers, whereas for $[Zn_2L^2(acac)]$, the other one should be considered as being formed by a ($\Delta\Lambda_3$, *trans*)-(δ,δ) and ($\Delta_3\Lambda$, *trans*)-(λ,λ) couple. These two latter stereoisomers are illustrated in Fig. 7.

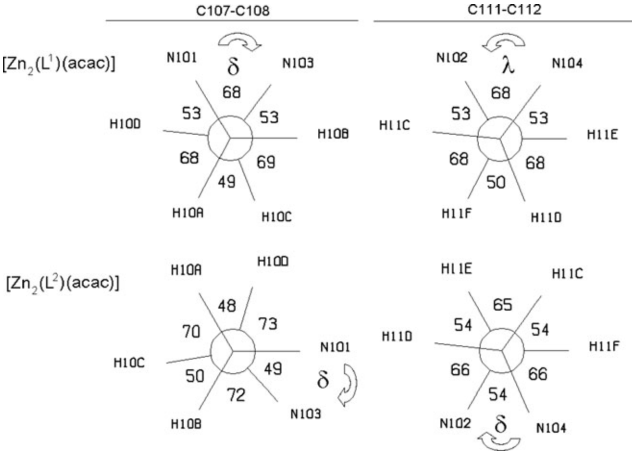

Fig. 6 Newman projections of the *gauche* conformations of the ethylene backbones of the enantiomers of $[Zn_2L^1(acac)]\cdot H_2O$ and $[Zn_2L^2(acac)]\cdot H_2O\cdot MeCN\cdot MeOH$, as shown in Fig. 2 and Fig. 3, respectively.

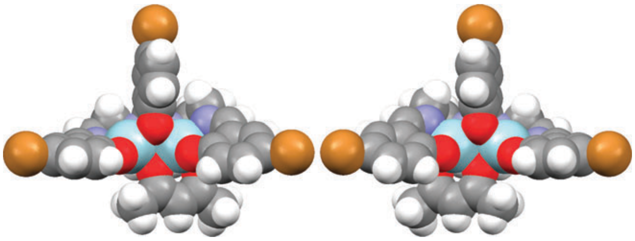

Fig. 7 Space filling representations of the two enantiomers found in the unit cell of $[Zn_2L^2(acac)]\cdot H_2O\cdot MeCN\cdot MeOH$. They can be described as ($\Delta_3\Lambda$, *trans*)-(δ,δ) (left) and ($\Delta\Lambda_3$, *trans*)-(λ,λ) (right).

Furthermore, the hydrate complexes $[Zn_2L^1(acac)]\cdot H_2O$ and $[Zn_2L^2(acac)]\cdot H_2O$ were spectroscopically characterised (*vide infra*). The ^1H NMR spectra of these compounds were recorded in DMSO-d_6, and their spectra showed the usual set of peaks for the aromatic protons,[5a,c,j] indicating that the species are unique in solution. They also showed signals corresponding to typical imine (8.22 ppm) and imidazolidine (*ca.* 4.07 ppm) protons.[5a,c,j] The absence of signals above 8.5 ppm is consistent with the trianionic character of the Schiff base in the complex. Moreover, two new singlets at *ca.* 1.80 ppm (6H) and *ca.* 5.35 ppm (1H) agree with the presence and coordination of the $acac^-$ ligand in solution.[20–22]

It is worth mentioning that only one peak is observed for both methyl groups of the acetylacetonate ligand, appearing to be equivalent in solution at room temperature, despite not being equivalent in the solid state. This fact could indicate that a fast interconversion of both enantiomers occurs in the solid state.[23] Accordingly, no evidence of the existence of stereoisomers was detected in solution.

The electrospray mass spectra of methanol solutions of $[Zn_2L^1(acac)]\cdot H_2O$ and $[Zn_2L^2(acac)]\cdot H_2O$ are dominated by peaks of 100% intensity at m/z = 585 or 823, assigned to $[Zn_2L^x]^+$ (x = 1 or 2) fragments. Moreover, the spectra show peaks of high intensity related to the whole molecules at m/z = 687 ($[Zn_2L^1(acac)H]^+$) or 945 ($[Zn_2L^2(acac)Na]^+$).

As a result of these studies, it can be inferred that the complexes retain their dinuclear nature, with the external ligand coordinated to the metal ions in solution.

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Experimental

Chemicals

Chemicals of the highest commercial grade available (Aldrich) were used without further purification. H_3L^1 and H_3L^2 were synthesized as previously described and were satisfactorily characterised.[5a,c]

Physical measurements

Elemental analyses of C, H and N were performed on a Carlo Erba analyser. Infrared spectra were recorded as KBr pellets on a FT-IR Bruker IFS-66v spectrophotometer in the range 400–4000 cm^{-1}. Electrospray mass spectra were obtained on a

Hewlett-Packard LC/MS spectrometer, with methanol as the solvent. NMR spectra of the metal complexes were recorded on a Bruker AMX500 spectrometer using DMSO-d_6 as the solvent.

Syntheses of the metal complexes

[Zn_2L^1(acac)]·H_2O. This complex was obtained when H_3L^1 (0.334 g, 0.73 mmol) was added to a $Zn(acac)_2 \cdot nH_2O$ (0.384 g, 1.46 mmol) methanol/acetonitrile (20/20 mL) solution. The mixture was stirred in air at room temperature for 4 h. The resultant solution was left to slowly evaporate until pale yellow crystals suitable for single X-ray diffraction studies had precipitated. The crystals were filtered off and dried in air.

[Zn_2L^1(acac)]·H_2O. Pale yellow crystals (0.20 g, 38.9%). mp 285–287 °C. Anal. found: C, 54.25; H, 5.40; N, 7.89. Calc. for $C_{32}H_{36}N_4O_6Zn_2$: C, 54.63; H, 5.12; N, 7.96%. MS (ESI): m/z = 585.0 [Zn_2L^1]$^+$, 687.0 [Zn_2L^1(acacH)]$^+$. IR (KBr, cm^{-1}): $\nu(OH)_w$ 3433 (b, m), ν(C=N) 1615 (vs). ^{1}H NMR (500 MHz, DMSO-d_6, ppm): 1.78 (s, 6H, $CH_{3\ acac}$), 2.68–3.51 (m, 12H, 4H1 + 4H2 + 4H3), 4.07 (s, 1H, H17), 5.36 (s, 1H, –CH_{acac}–), 6.39–6.47 (m, 3H, 2H7 + H14), 6.56–6.68 (m, 3H, 2H8 + H12), 7.05–7.18 (m, 6H, 2H6 + 2H9 + H11 + H13), 8.22 (s, 2H, 2H4).

If the same reaction was carried out by refluxing the mixture, the complex [Zn_2L^1(OAc)]·H_2O was isolated as a pure product, as proved by NMR spectroscopy and X-ray diffraction studies.[5a]

[Zn_2L^2(acac)]·H_2O. This complex was obtained by a similar method to that reported for [Zn_2L^1(acac)]·H_2O. Thus, to a methanol–acetonitrile (20/20 ml) solution of $Zn(acac)_2 \cdot nH_2O$ (0.24 g, 0.88 mmol) was added H_3L^3 (0.30 g, 0.44 mmol). The mixture was refluxed for 4 h and a yellow solution obtained. This solution was left to slowly evaporate until single crystals of [Zn_2L^2(acac)]·H_2O·MeCN·MeOH suitable for X-ray diffraction studies had formed. The crystals were filtered off and dried in air. All the characterisation data agreed with the formulation of [Zn_2L^2(acac)]·H_2O, indicating that the crystals lost most of their volatile solvates upon drying.

[Zn_2L^2(acac)]·H_2O. Pale yellow crystals (0.28 g, 68.0%). mp > 300 °C. Anal. found: C, 41.18; H, 3.99; N, 6.21. Calc. for $C_{32}H_{33}Br_3N_4O_6Zn_2$: C, 40.87; H, 3.51; N, 5.96%. MS (ESI): m/z = 823.0 [Zn_2L^2]$^+$, 945.0 [Zn_2L^3(acac)Na]$^+$. IR (KBr, cm^{-1}): $\nu(OH)_w$ 3398 (b, m), ν(C=N) 1632 (vs). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): 1.80 (s, 6H, $CH_{3\ acac}$), 2.62–2.69 (m, 2H), 2.73–2.86 (m, 4H), 2.99–3.11 (m, 2H), 3.22–3.28 (m, 2H), 3.42–3.53 (m, 2H) (4H1 + 4H2 + 4H3), 4.06 (s, 1H, H17), 5.34 (s, 1H, –CH_{acac}–), 6.40 (d, 1H, H14), 6.58 (d, 2H, 2H9), 7.15–7.23 (m, 5H, 2H6 + 2H8 + H13), 7.37 (s, 1H, H11), 8.22 (s, 2H, 2H4).

X-Ray diffraction studies

Single crystals of [Zn_2L^1(acac)]·H_2O and [Zn_2L^2(acac)]·H_2O·MeCN·MeOH were obtained, as detailed above. Diffraction data were collected at 120 K using a Bruker SMART CCD-1000 diffractometer employing graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). No significant decays were observed, and data were corrected for Lorentz and polarization effects. Multi-scan absorption corrections were applied using SADABS.[24] The structures were solved by standard direct methods employing SIR-2004[25] and refined by Fourier techniques based on F^2 using SHELXL-97.[26]

Non-hydrogen atoms were anisotropically refined. The hydrogen atoms of organic groups were included at geometrically calculated positions, with thermal parameters derived from the parent atoms. Hydrogen atoms attached to water molecules or to groups suitable to form hydrogen bonds could be located on the Fourier maps, fixed and given isotropic displacement parameters of 0.08 Å^2, or depending on the parent atoms.

The figures within were drawn with the help of Mercury, PLATON and ORTEP for Windows.[27]

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