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Co(II), Cu(II) and Zn(II) dinuclear complexes of a polypodal ligand containing phenolate and pyridyl donor groups

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ABSTRACT

Acetate and perchlorate dinuclear metal complexes of Co(II), Cu(II) and Zn(II) with the cresolate polypodal ligand having mixed phenolate and pyridyl pendant functionalities, H_3L , have been synthesized. The complexes were characterized by microanalysis, LSI mass spectrometry, IR, UV–Vis spectroscopy, magnetic studies and conductivity measurements. Crystal structures of H_3L , $[Cu_2(HL)(OAc)(H_2O)_2](OAc)\cdot 1.5H_2O$ and $[Zn_2L(CH_3OH)_3](ClO_4)CH_3OH\cdot 2H_2O$ complexes, have been also determined.

The X-ray studies show the presence of dinuclear complexes with the metal ions joined by the bridging cresolate group and coordinated to the tertiary amine nitrogen and their corresponding attached pyridyl and phenol/phenolate pendant groups. The coordination environment for the metal ions is completed by acetate, water or solvent molecules to generate mixed distorted coordination geometries; square plane/ square pyramidal for Cu(II) and octahedral/trigonal bipyramidal for Zn(II) complexes. Different intramo-lecular interactions through hydrogen bonds are also observed in both complexes.

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1. Introduction

It is well-known that the important functional role of many metalloproteins in the active sites is based in the polynuclear nature of the metal centers [1–3].

One strategy for the synthesis of multimetallic complexes includes the use of polypodal ligands, which allow accommodation of two or more metal ions. They can be used to hold the metal centers at a fixed distance providing interesting properties. In this sense, a considerable number of complexes of several polypodal binucleating ligand systems have been reported as models of different metalloproteins from several decades ago [4–8].

The presence in many of these polypodal ligands of a phenolate group as a bridge to hold two metal ion centers in close proximity, and also providing additional donor sites, have been required to obtain suitable biomimetic complexes [9–14].

In another hand, the synthesis and characterization of new binuclear complexes with relevant N,O-donor ligands is an important area of investigation. In last years the synthesis of dinuclear complexes of different metal ions with the symmetric end-off compartmental ligand 2,6-bis[(2-hydroxybenzyl)(2-pyridylmethyl)amino)methyl]-4methylphenol (H_3L , Scheme 1) having cresol, phenol and pyridyl pendant functionalities, have been reported [15–27]. It have been observed that the presence of coordinating anion usually drives to the formation of an anion-based exogenous bridge, but non-coordinating anion inhibit the formation of that exogenous bridge and instead, encourages the interaction of the dinuclear core with the solvent.

In this way, the reaction of H_3L and Co(II), Cu(II) and Zn(II) with anions of different coordinative capabilities, as acetate and perchlorate, has been investigated in this paper.

The X-ray crystal structure of the polypodal ligand, H_3L , and the dinuclear crystal structures of Cu(II) acetate and Zn(II) perchlorate complexes are also reported.

2. Experimental

2.1. Chemicals and starting materials

The precursors, 2,6-bis(chloromethyl)-4-methylphenol and (2-hydroxybenzyl)-(2-pyridylmethyl)amine were synthesized following a similar method as described in the literature [27,28]. Metal salts were commercial products (from Alfa and Aldrich) and were used without further purifications. Solvents were of reagent grade and were purified by the usual methods.

Caution: Although no problems were encountered during the course of this work, perchlorate salts must be handled with care due to their potentially explosive nature.

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2.2. Synthesis of the ligand H₃L

The ligand, 2,6-bis[(2-hydroxybenzyl)(2-pyridylmethyl)amino)methyl]-4-methylphenol (H_3L), was synthesized by modification of the method of Krebs et al. [27].

A methanol (20 ml) solution of 2,6-bis(chloromethyl)-4-methylphenol (2.76 g, 14.6 mmol) was added slowly over a methanol (100 mL) cooled solution at 0 °C of (2-hydroxybenzyl)-(2-pyridylmethyl)amine (6.17 g, 28.8 mmol) and Et₃N (4.37 g, 43.2 mmol). When the addition was completed, the resulting mixture was warmed to room temperature and stirred for 12 h. The solution was evaporated to dryness. The residue was dissolved in chloroform (60 mL) washed with water (3 × 30 mL). The organic layer was dried over anhydrous MgSO₄, filtered off and evaporated to dryness to obtain a white solid characterized as H₃L. Crystals appropriate to be studied by X-ray diffraction could be obtained by slow recrystallization of the compound from acetonitrile.

H₃L: *Anal.* Calc. for C₃₅H₃₆N₄O₃: C, 75.0; H, 6.5; N, 10.0. Found: C, 74.7; H, 6.6; N, 10.1%. Yield: 75%. IR (KBr, cm⁻¹): 1431, 1489, 1572, 1591 [ν (C=N)_{py} and (C=C)_{ar}], 3070 [ν (-OH)]. LSI-MS (*m*/*z*): 561 [H₃L]⁺. Colour: white.

2.3. Synthesis of metal complexes

To a heated at reflux methanolic solution (10 mL) of H₃L (0.056 g, 0.1 mmol), a solution of the corresponding acetate metal salt (0.2 mmol) in methanol (5 mL) was slowly added. The reaction mixture was refluxed for 30 min and stands to cool. The resulting solution was concentrated until *ca*. 10 mL. The product obtained was filtered off and dried under vacuum. In the case of the perchlorate complexes, a solution of sodium perchlorate (0.2 mmol) in methanol (5 mL) was added to the metallic acetate/ligand mixture, and the resulting solution allowed to cool to room temperature giving rise a precipitate. The precipitate obtained was filtered off and dried under vacuum.

2.3.1. [Co2L](OAc)·6H2O

Anal. Calc.: C, 52.7; H, 5.7; N, 6.7. Found: C, 52.8; H, 5.5; N, 6.5%. Yield: 21%. IR (KBr, cm⁻¹): 1450, 1475, 1595, 1612 [ν (C=N)_{py} and (C=C)_{ar}], 1558 [ν (OAc⁻)]. LSI-MS (m/z): 675 [Co₂L]⁺. Λ_{M}/Ω^{-1} cm² mol⁻¹(in CH₃CN): 192 (1:1). Colour: brown.

2.3.2. [Co₂L](ClO₄)·3CH₃OH·2H₂O

Anal. Calc.: C, 50.3; H, 5.4; N, 6.2. Found: C, 49.8; H, 5.6; N, 6.1%. Yield: 24%. IR (KBr, cm⁻¹): 1450, 1476, 1595, 1612 [ν (C=N)_{py} and

 $(C=C)_{ar}$], 623, 1103 [ν (ClO₄⁻)]. LSI-MS (m/z): 675 [Co₂L]⁺. Λ_M/Ω^{-1} cm² mol⁻¹(in CH₃CN): 205 (1:1). Colour: brown.

2.3.3. [Cu2L](OAc)-3H2O

Anal. Calc.: C, 55.7; H, 5.3; N, 7.0. Found: C, 55.4; H, 5.2; N, 6.8%. Yield: 30%. IR (KBr, cm⁻¹): 1447, 1474, 1576, 1611 [ν (C=N)_{py} and (C=C)_{ar}], 1560 [ν (OAc⁻)]. LSI-MS (m/z): 684 [Cu₂L]⁺. Λ_M/Ω^{-1} cm² mol⁻¹(in CH₃CN): 190 (1:1). Colour: green.

2.3.4. [Cu₂L](ClO₄)·CH₃OH·3H₂O

Anal. Calc.: C, 49.8; H, 5.0; N, 6.4. Found: C, 49.5; H, 5.2; N, 6.2%. Yield: 32% IR (KBr, cm⁻¹): 1450, 1477, 1597, 1610 [ν (C=N)_{py} and (C=C)_{ar}], 626, 1095 [ν (ClO₄⁻)]. LSI-MS (*m*/*z*): 684 [Cu₂L]⁺. Λ_{M} / Ω^{-1} cm² mol⁻¹(in CH₃CN): 200 (1:1). Colour: green.

2.3.5. [Zn₂L](OAc)·2H₂O

Anal. Calc.: C, 56.7; H, 5.1; N, 7.1. Found: C, 56.3; H, 5.2; N, 7.0%. Yield: 26%. IR (KBr, cm⁻¹): 1453, 1492, 1602 [ν (C=N)_{py} and (C=C)_{ar}], 1560 [ν (OAc⁻)]. LSI-MS (m/z): 689 [Zn₂L]⁺. Λ_M/Ω^{-1} cm² mol⁻¹(in CH₃CN): 200 (1:1). Colour: colourless.

2.3.6. [Zn₂L](ClO₄)·3CH₃OH

Anal. Calc.: C, 51.8; H, 5.1; N, 6.3. Found: C, 51.5; H, 5.3; N, 6.4%. Yield: 28%. IR (KBr, cm⁻¹): 1437, 1460, 1577, 1610 [ν (C=N)_{py} and (C=C)_{ar}], 625, 1092 [ν (ClO₄⁻)]. LSI-MS (*m/z*): 689 [Zn₂L]⁺. $\Lambda_{\rm M}/\Omega^{-1}$ cm² mol⁻¹(in CH₃CN): 196 (1:1). Colour: colourless.

2.4. Physical measurements

Elemental analyses were performed in a Carlo-Erba EA microanalyser. Infra-red spectra were recorded as KBr discs on a Bruker IFS-66V spectrophotometer. LSI-MS were recorded using a Micromass Autospec spectrometer with 3-nitrobenzyl alcohol as the matrix. Conductivity measurements were carried out in 10^{-3} mol dm⁻³ acetonitrile solutions at 20 °C using a WTW LF3 conductivimeter. Solid state electronic spectra were recorded on a Hitachi 4-3200 spectrophotometer using MgCO₃ as reference. Magnetic studies were determined at room temperature on a vibration sample magnetometer (VSM) Digital Measurement System 1660 with a magnetic field of 5000 G.

2.5. X-ray data collection, structure determination, and refinement

The details of the X-ray crystal data, and the structure solution and refinement are given in Table 1. Measurements were made on a Bruker Smart CCD area detector. All data were corrected for Lorentz and polarization effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections. Complex scattering factors were taken from the program package SHELXTL [29]. The structures were solved by direct methods which revealed the position of all non-hydrogen atoms. All the structures were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were located in their calculated positions and refined using a riding model. For [Cu₂(HL)(OAc)(H₂O)₂](OAc)-1.5H₂O data set was truncate to 50° in 2 θ .

3. Results and discussion

The polypodal ligand H_3L was readily obtained in a one-pot synthesis from the precursors reagents in satisfactory yield and purity. Crystals suitable for X-ray diffraction of H_3L were obtained from an acetonitrile solution. Crystal data and structure refinement are given in Table 1. Molecular structure and selected bond lengths and angles for H_3L are given in Fig. 1a. The structure belongs to mono-

Table 1

Crystal data and structure refinement for H₃L, [Cu₂(HL)(OAc)(H₂O)₂](OAc)·1.5H₂O and [Zn₂L(CH₃OH)₃](ClO₄)·CH₃OH·2H₂O.

	H ₃ L	$[Cu_2(HL)(OAc)(H_2O)_2](OAc) \cdot 1.5H_2O$	$[Zn_2L(CH_3OH)_3](ClO_4)\cdot CH_3OH\cdot 2H_2O$
Empirical formula	$C_{35}H_{36}N_4O_3$	C ₃₉ H ₄₇ N ₄ O _{10.5} Cu ₂	C ₃₉ H ₅₃ ClN ₄ O ₁₃ Zn ₂
Formula weight	560.68	866.89	952.08
Temperature (K)	150(2)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	Pna21	$P2_1/c$
Unit cell dimensions			
a (Å)	9.116(2)	13.0301(2)	12.2162(10)
b (Å)	12.227(3)	29.667(3)	21.5446(17)
<i>c</i> (Å)	26.787(7)	11.0106(7)	15.5498(2)
β(°)	97.725(5)		90.772(2)
Volume (Å ³)	2958.3(12)	4256.6(7)	4092.2(6)
Ζ	4	4	4
D_{calc} (mg/m ³)	1.259	1.395	1.516
Absorption coefficient (mm ⁻¹)	0.081	1.058	1.305
Crystal size (mm ³)	$0.40 \times 0.17 \times 0.06$	$0.30\times0.13\times0.10$	$0.30 \times 0.15 \times 0.10$
θ Range for data collection (°)	1.53–27.56	1.37–25	1.62–27.50
Index ranges	$-11 \leqslant h \leqslant 11$	$-15 \leqslant h \leqslant 15$	$-15 \leqslant h \leqslant 14$
	$-15 \leqslant k \leqslant 15$	$-35 \leqslant k \leqslant 35$	$-27 \leqslant k \leqslant 23$
	$-34 \leqslant l \leqslant 34$	$-13 \leqslant l \leqslant 13$	$-20 \leqslant l \leqslant 20$
Reflections collected	24921	39768	22974
Independent reflections	$6725 [R_{int} = 0.1188]$	7499 $[R_{int} = 0.1560]$	9165 $[R_{int} = 0.0519]$
Completeness to θ (°)	99.9% (26.42)	100% (25)	97.4% (27.5)
Absorption correction	Semi-empirical	Semi-empirical	Semi-empirical
Maximum and minimum transmission	0.9762 and 0.9503	0.9016 and 0.7420	0.8806 and 0.6956
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F ²	Full-matrix least-squares on F^2
Data/restraints/parameters	6725/0/379	7499/1/491	9165/4/526
Goodness-of-fit on F^2	0.987	1.027	1.016
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0655, wR_2 = 0.1398$	$R_1 = 0.0777, wR_2 = 0.1896$	$R_1 = 0.0525, wR_2 = 0.1183$
R indices (all data)	$R_1 = 0.1750, wR_2 = 0.1897$	$R_1 = 0.1404, wR_2 = 0.2434$	$R_1 = 0.0997, wR_2 = 0.1410$
Largest difference in peak and hole (e $Å^{-3}$)	0.251 and -0.356	0.903 and -0.448	1.145 and -0.796

clinic space group $P2_1/c$. All bond distances and angles are all within the normal ranges.

Different intramolecular hydrogen bonding interactions between cresol, phenol, pyridine and amine groups are present in the crystal lattice: (a) phenol groups and their corresponding tertiary amine $[O2-H2A\cdots N1 = 157.46^{\circ}, 1.752 \text{ Å}]$ and $[O3-H3A\cdots N3 = 1578.11^{\circ}, 1.756 \text{ Å}]$; (b) cresol group and one pyridyl ring $[O1-H1A\cdots N2 = 157.39^{\circ}, 1.914 \text{ Å}]$. The dihedral angles between the cresol ring [C2-C7-O1] and the pyridyl rings, [C10-C14-N2 (rms 0.0103)] and [C24-C28-N4 (0.0072)], are 19.59° and 19.54°, respectively, whilst the phenol groups, [C16-C21-O2 (rms 0.0063)] and [C30-C35-O3 (rms 0.0097)], form with the cresol ring dihedral angles of 81.4° and 78.3°, respectively.

Also, intermolecular *offset* (slipped) π -stacking interactions between cresol groups of adjacent molecules, and *face-to-face* π -



Fig. 1a. Crystal structure of H_3L and selected bond lengths (Å) and angles (°). O(1)-C(5) 1.367(3), O(2)-C(21) 1.363(3), O(3)-C(35) 1.367(3), N(1)-C(9) 1.465(3), N(1)-C(15) 1.472(3), N(1)-C(8) 1.477(3), N(2)-C(10) 1.345(3), N(2)-C(14) 1.347(4), N(3)-C(23) 1.468(3), N(3)-C(29) 1.474(3), N(3)-C(22) 1.482(3), N(4)-C(24) 1.338(4), N(4)-C(28) 1.349(4), C(9)-N(1)-C(15) 110.9(2), C(9)-N(1)-C(8) 110.5(2), C(15)-N(1)-C(8) 111.5(2), C(10)-N(2)-C(14) 117.1(3), C(23)-N(3)-C(29) 109.0(2).

stacking between phenol rings of different ligand molecules [30] are observed (Fig. 1b). The distances between the centroids d_{c-c} have a value of 3.452 Å with a slipping angle (β) (defined by the centroid–centroid vector and the normal to the planes containing the rings) of 41°, in the first case, and 4.221 Å with β = 10.5° in the second case.

Acetate and perchlorate metal complexes of Co(II), Cu(II) and Zn(II) with H_3L were synthesized in refluxing methanol. The complexes were synthesized as described in Section 2 and, in general, the reactions gave analytically pure products. The complexes were characterized by elemental analysis, LSI mass spectrometry, IR and UV–Vis spectroscopy, magnetic studies and conductivity measurements.

3.1. Crystal structures of complexes

By slow recrystallization of the acetate dinuclear Cu(II) compound in methanol, crystals of $[Cu_2(HL)(OAc)(H_2O)_2](OAc)\cdot 1.5H_2O$ were obtained. The crystal structure was studied by X-ray diffraction and the molecular structure of the complex is shown in Fig. 2, together with the atomic numbering scheme adopted and selected bond distances (Å) and angles (°). Crystal data and structure refinement are given in Table 1.

The crystal structure is consistent with the dinuclear cation complex $[Cu_2(HL)(OAc)(H_2O)_2]^+$ and one non-coordinated acetate group involved in intramolecular hydrogen bonding with the dinuclear complex. Three half free water molecules of crystallization complete the structure, which have been refined isotropically, except for O2W.

The structural analysis of $[Cu_2(HL)(OAc)(H_2O)_2]^*$ cation shows the presence of two Cu(II) ion with different coordination environment. Thus, Cu(1) presents a {N₂O₂} core, being the metal ion coordinated to the cresolate oxygen atom, O1, which is acting as asymmetric μ^2 -bridge between the copper ions, the tertiary amine nitrogen, N1, and their corresponding attached pyridyl ring, N2, and a water molecule, O2W. Bond lengths vary from 1.915 to 2.040 Å. The non-deprotonated phenol group [Cu(1)–O(2), 2.513(6) Å], and another water molecule [Cu(1)–O(1W), 2.529(10) Å] are slightly interacting with the metal center, commonly expected



Fig. 1b. Partial view of the ligand packing showing the different π -stacking interactions between cresolate and phenol rings of different molecules.



Fig. 2. Crystal structure of $[Cu_2(HL)(OAc)(H_2O)_2](OAc) \cdot 1.5H_2O$ and selected bond lengths (Å) and angles (°): Cu(1)–O(1) 1.920(7), Cu(1)–O(2W1.976(7), Cu(1)–N(2) 2.010(9), Cu(1)–N(1) 2.037(9), Cu(1)–Cu(23.7284(17), Cu(2)–O(3) 1.918(7), Cu(2)–O(4) 1.936(7), Cu(2)–N(4) 1.984(9), Cu(2)–N(3) 2.021(8), Cu(2)–O(1) 2.319(7), O(1)–Cu(1)–O(2W) 90.1(3), O(1)–Cu(1)–N(2) 173.3(3), O(2W)–Cu(1)–N(2) 92.8(3), O(1)–Cu(1)–N(1) 94.6(3), O(2W)–Cu(1)–N(1) 175.1(3), N(2)–Cu(1)–N(2) 92.8(3), O(1)–Cu(1)–Cu(2) 31.5(2), O(2W)–Cu(1)–Cu(2) 66.19(17), N(2)–Cu(1)–Cu(2) 146.4(2), N(1)–Cu(1)–Cu(2) 118.7(2), O(3)–Cu(2)–O(4) 90.3(3), O(3)–Cu(2)–N(4) 175.4(4), O(4)–Cu(2)–N(4) 90.7(4), O(3)–Cu(2)–N(3) 94.0(3), O(4)–Cu(2)–N(3) 168.2(3), N(4)–Cu(2)–N(3) 84.1(4), O(3)–Cu(2)–O(1) 96.8(3), O(4)–Cu(2)–Cu(1) 99.1(3), N(4)–Cu(2)–Cu(1) 87.5(3), N(3)–Cu(2)–O(1) 91.3(3), O(3)–Cu(2)–Cu(1) 103.4(2), O(1)–Cu(2)–Cu(1) 125.61(16).

due to the Jahn–Teller effect for d^9 ions. The geometry around Cu(1) can be described as square plane, N(1)-N(2)-O(1)-O(2W)(rms 0.065), and the distance between the Cu(1) and the plane of 0.0361 Å. Instead, the Cu(2) ion presents a $\{N_2O_3\}$ core, being coordinated to the bridging cresolate oxygen atom, O1, the tertiary amine nitrogen, N3, and their corresponding attached pyridyl ring, N4, and phenolate group, O3. The fifth coordination position is occupied by an oxygen atom from a monodentated coordinated acetate anion, O4. The geometry around Cu(2) can be described as slightly distorted square pyramidal [$\tau = 0.11$] [31] with Cu(2) 0.137 Å away from the best plane defined by N(3)-N(4)-O(3)-O(4) (rms 0.052). Bond lengths vary from 1.917 to 2.019 Å for these atoms. The apical position is occupied by the μ^2 -cresolate group, O1, at 2.322 Å from the metal. Banerjee et al. recently reported a dinuclear Cu(II) crystal structure for L, [Cu₂(HL)(O₂CPh)(H₂O)]Ph-CO₂·3H₂O [26]. The structure shows a benzoate bridging group and both Cu(II) ions in a pentacoordinated environment.

The distance between the copper ions $Cu(1) \cdots Cu(2)$ is 3.730 Å, longer to consider the presence of intermetallic interactions.

In both cases, the main distortion from a regular geometries can be attributed to the small bite of the five-membered chelate rings formed by the tertiary amine and their corresponding pyridyl donor group $[N(2)-Cu(1)-N(1), 83.0(3)^{\circ}]$ and $[N(3)-Cu(2)-N(4), 84.0(4)^{\circ}]$.

Inter and intramolecular hydrogen bonds interactions between the free and coordinated acetate anions and water molecules and the phenol group were found in the crystal structure (Table 2).

The complex $[Zn_2L(CH_3OH)_3](CIO_4)\cdot CH_3OH\cdot 2H_2O$ was obtained by recrystallization of the perchlorate Zn(II) complex from metha-

2655

nol. The molecular structure together with selected bond lengths (Å) and angles (°) are given in Fig. 3. The crystal data and structure refinement are given in Table 1. The X-ray crystal structure shows also a dinuclear cation complex of type $[Zn_2L(CH_3OH)_3]^+$, similar to that described by Fenton et al. for $[Zn_2L(H_2O)_3](CIO_4)$ [21]. A methanol and a water solvent molecule are disordered in two positions with occupancies of 67/33% and 52/48%, respectively. They were refined isotropically. A free perchlorate counterion is also present in the crystal lattice. The metal centers present different coordination environment, six-coordinate {N₂O₄} core in a distorted octahedral geometry for Zn(2) and five-coordinate {N₂O₃} core in a distorted trigonal bipyramidal geometry [$\tau = 0.81$] for Zn(1).

The Zn(2) ion is bonded to the cresolato oxygen atom, O1, which is acting as μ^2 -bridge between the metal ions, a tertiary amine nitrogen, N3 and their corresponding attached pyridyl, N4, and terminal phenolate group, O3. The coordination environment is completed by two methanol molecules, O5 and O6. The equatorial plane of the octahedral geometry can be described by the amine nitrogen, their corresponding attached pyridyl and terminal phenolate groups, and one of the methanol molecules [N(3)–N(4)– O(3)–O(5), rms 0.0257], with Zn(2) 0.0454 Å away from that plane. The axial positions are determined by the oxygen atoms from the central phenolate and the other methanol molecule, O1–Zn2–O6, 173.3°.

The equatorial plane of the distorted trigonal bipyramidal geometry around Zn(1) can be defined by the bridging cresolate oxygen atom and the pyridyl and phenolate group attached to the other tertiary amine of the ligand, O(1)-N(2)-O(2). The axial positions are occupied by the tertiary amine nitrogen and one methanol molecule, N1–Zn1–O4, 170.13(11)°. In both cases, the main distortion from a regular geometries can be also attributed to the small bite of the five-membered chelate rings formed by the amine and their corresponding pyridyl donor group [N(2)–Zn(1)–N(1), 79.18(12)°] and [N(3)–Zn(2)–N(4), 81.47(13)°].

The Zn(1)···Zn(2) separation is 3.551 Å, not showing interaction between the metal ions. This distance is also longer than others found in similar dinuclear complexes bearing also (μ -phenolate) [19] or (μ -phenolate) and additional exogenous bridge [22,32– 34], but shorter than that for [Zn₂L(H₂O)₃](ClO₄), 3.62 Å [21]. The μ^2 -phenolate bridge is asymmetric, with Zn–O distances of 1.981(2) and 2.168(2) Å, but they are no so different as the case

Table 2

Hydrogen bond interactions (Å and $^\circ)$ for $[Cu_2(HL)(OAc)(H_2O)_2](OAc)\cdot 1.5H_2O$ and $[Zn_2L(CH_3OH)_3](CIO_4)\cdot CH_3OH\cdot 2H_2O.$

	D···A	D−H···A
[Cu ₂ (HL)(OAc)(H ₂ O) ₂](OAc)·1.5H ₂ O		
02-H2···07	2.565	179.9
O1W−H1WB···O4	2.603	151.3
02W-H2WA03	2.730	172.4
02W-H2WB···08	2.662	179.9
01W-H1WA04W_\$1	2.676	179.0
03W-H3WA05_\$2	2.730	179.4
O3W−H3WB···O3_\$2	3.049	179.8
04W-H4WA08_\$3	2.783	179.2
05W-H5WA08_\$4	2.845	179.2
05W-H5WB···01W_\$5	2.915	179.1
$[Zn_2L(CH_3OH)_3](ClO_4)\cdot CH_3OH\cdot 2H_2O$		
04–H4···03	2.541	169.1
05–H5···02	2.628	171.3
01S-H1S···01W	2.669	173.2
01S-H1S···01W'	3.625	151.8
06-H6···01S'_\$6	2.798	167.7
O6-H6···O1S_\$6	2.645	151.5

1: x + 1/2, -y - 1/2, +z - 1;2: x - 1/2, -y - 1/2, +z;3: -x + 1/2, +y + 1/2, +z + 1/2;4: x - 1/2, -y - 1/2, +z - 1;5: -x + 1/2, +y + 1/2, +z - 1/2;6: -x + 1, -y + 2, -z + 1.



Fig. 3. Crystal structure of $[Zn_2L(CH_3OH)_3](ClO_4)\cdot CH_3OH\cdot 2H_2O$ and selected bond lengths (Å) and angles (°): Zn(1)-O(2) 1.970(3), Zn(1)-O(1) 1.981(2), Zn(1)-N(2) 2.091(3), Zn(1)-O(4) 2.097(3), Zn(1)-N(1) 2.148(3), Zn(1)-Zn(2) 3.5513(7), Zn(2)-O(3) 1.985(3), Zn(2)-N(4) 2.095(3), Zn(2)-O(5) 2.109(3), Zn(2)-N(3) 2.138(3), Zn(2)-O(1) 2.168(2), Zn(2)-O(6) 2.250(3), O(2)-Zn(1)-O(1) 110.25(11), O(2)-Zn(1)-N(2) 125.95(12), O(1)-Zn(1)-N(2) 123.54(12), O(2)-Zn(1)-O(4) 93.08(11), O(2)-Zn(1)-N(1) 93.43(12), O(1)-Zn(1)-Zn(2) 141.90(10), O(4)-Zn(1)-Zn(2) 87.96(8), O(1)-Zn(1)-Zn(2) 119.70(8), O(3)-Zn(2)-N(4) 172.57(13), O(3)-Zn(2)-O(5) 93.12(12), N(4)-Zn(2)-O(5) 93.10(12), O(3)-Zn(2)-N(3) 92.24(12), O(5)-Zn(2)-O(1) 90.29(10), N(3)-Zn(2)-O(1) 90.34(11), O(3)-Zn(2)-O(6) 90.13(11), N(4)-Zn(2)-O(6) 85.97(12), O(5)-Zn(2)-O(6) 88.54(11), O(1)-Zn(2)-Zn(1)-Zn(2)-Zn(1) 28.20(8), N(3)-Zn(2)-Zn(1) 116.70(8), O(1)-Zn(2)-Zn(1) 29.62(6).

of the cooper complex described above. In both coordination geometries, the longer bond lengths correspond to the atoms in axial positions, Zn1–N1 2.148(3) and Zn1–O4 2.097(3) Å; Zn2–O1 2.168(2) Å and Zn2–O6, 2.250(3) Å. The shortest bond length corresponds, in both cases, for the terminal phenolate groups, Zn1–O2, 1.970(3) Å and Zn2–O3, 1.985(3) Å. For both metal ions, the Zn–N_{amine} bond lengths is quite longer [Zn1–N1, 2.148(3) and Zn2–N3, 2.138(3) Å] than Zn–N_{py} [Zn1–N2, 2.091(3) and Zn2–N4, 2.095(3) Å], but similar in both cases.

Inter- and intramolecular hydrogen bonds interactions between phenolate groups, water and methanol molecules are present in the crystal lattice (Table 2).

3.2. Spectroscopic and magnetic studies

Elemental analysis are consistent with the presence of dinuclear compounds of the type $[M_2L](X)_2 \cdot xCH_3OH \cdot yH_2O$ (M = Co(II), Cu(II) or Zn(II); X = AcO⁻ or ClO₄⁻).

The IR spectra of the complexes show v(C=N) vibration band of the pyridine groups shifted to higher wavenumber than in the free ligand suggesting coordination to the metal atom [35]. The IR spectra of the perchlorate complexes feature absorptions attributable to ionic perchlorate at 625 and 1100 cm⁻¹. The lack of splitting of this band indicates that there is no coordination of these groups to the metal centers [36,37].

Molar conductivity data, measured at room temperature using acetonitrile as solvent showed the presence of ionic counterions, since they are in the range reported in that solvent for 1:1 [38].

The results of LSI-MS of the complexes provide important evidence of the formation of the dinuclear complexes as they feature peaks attributable in all cases to the species $[M_2L]^+$ (M = Co, Cu or Zn).

The reflectance spectra of the Co(II) complexes show four d-d transition bands at *ca*. 5200, 12 100, 14 500 and 21 000 cm⁻¹ which are indicative of high spin distorted trigonal bipyramidal geometry around the metal ions [39]. The reflectance spectra of the Cu(II) complexes show one broad band, probably a multicomponent band, between 17 000 and 12 000 cm⁻¹, that can be consistent with mixed coordination environments (square plane and square pyramidal) for the dinuclear Cu(II) complexes [40].

The value of the room temperature magnetic moments of the cobalt and copper compounds (4.6–5.2 and 2.5–3.1 BM, respectively) lies in the range usually observed for high-spin Co(II) and Cu(II) dinuclear complexes, respectively [41].

The ¹H and ¹³C NMR spectra of the Zn(II) complexes were recorded in CD₃CN and they are quite complicated due the low solubility of the complexes in the common solvents, but it show the signals in general shifted downfield compared with the free ligand due to the complexation to the Zn(II) ion.

4. Conclusion

The acetate Co(II), Cu(II) and Zn(II) complexes of the potential trianionic, septadentate, N₄O₃, donor polypodal ligand, H₃L, have been synthesized in methanol. The *in situ* metathesis reaction with sodium perchlorate let obtain the corresponding perchlorate complexes. The crystal structure of H₃L as well as of [Cu₂(HL)(OA-c)(H₂O)₂](OAc)·1.5H₂O and [Zn₂L(CH₃OH)₃](CIO₄)·CH₃OH·2H₂O complexes, have been determined. All the complexes are dinuclear acting the cresolate group as bridge between the metal ions. The X-ray structures show the two metal ions in different coordination environment. In the case of the Cu(II) complex, the metal ions present square planar and square pyramidal geometries. For the Zn(II) complex, the metal ions present a distorted octahedral and trigonal bipyramidal geometries.

5. Supplementary data

CCDC 780194, 780195 and 780196 contains the supplementary crystallographic data for H_3L , $[Cu_2(HL)(OAc)(H_2O)_2](OAc)\cdot 1.5H_2O$ and $[Zn_2L(CH_3OH)_3](ClO_4)\cdot CH_3OH\cdot 2H_2O$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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