

Modulating the M–M Distance in Dinuclear Complexes. New Ligand with a 2,2'-Biphenol Fragment as Key Unit: Synthesis, Coordination Behavior, and Crystal Structures of Cu(II) and Zn(II) Dinuclear Complexes

Gianluca Ambrosi,[†] Mauro Formica,[†] Vieri Fusi,^{*,†} Luca Giorgi,[†] Annalisa Guerri,[‡] Mauro Micheloni,^{*,†} Paola Paoli,[‡] Roberto Pontellini,[†] and Patrizia Rossi[‡]

Institute of Chemical Sciences, University of Urbino, P.zza Rinascimento 6, I-61029 Urbino, Italy, and 'Sergio Stecco' Department of Energy Engineering, University of Florence, Via S. Marta 3, I-50139 Florence, Italy

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The synthesis and characterization of the new polyamino-phenolic ligand 3,3'-bis[*N,N*-bis(2-aminoethyl)aminomethyl]-2,2'-dihydroxybiphenyl (**L**) are reported. **L** contains two diethylenetriamine units linked by a 1,1'-bis(2-phenol) group (BPH) on the central nitrogen atom which allows two separate binding amino subunits in a noncyclic ligand. The basicity and binding properties of **L** toward Cu(II) and Zn(II) were determined by means of potentiometric measurements in aqueous solution (298.1 ± 0.1 K, $I = 0.15$ mol dm⁻³). **L** behaves as a pentaprotic base and as a monoprotic acid under the experimental conditions used, yielding the H₅L⁵⁺ or H₋₁L⁻ species, respectively. **L** forms both mono- and dinuclear species with both metal ions investigated; the dinuclear species are largely prevalent in aqueous solution with a L/M(II) molar ratio of 1:2 at pH higher than 7. **L** shows different behavior in Cu(II) and Zn(II) binding, affecting the dinuclear species formed and the distance between the two coordinated metal ions, which is greater in the Zn(II) than in the Cu(II) dinuclear species. This difference can be attributed to the different degree of protonation of BPH which influences the angle between the phenyl rings in the two systems. In this way, it is possible to modulate the M(II)–M(II) distance by the choice M(II) and to space the two M(II) farther away than was possible with the previously synthesized ligands. **L** does not saturate the coordination sphere of the coordinated M(II) ions in the dinuclear species, and thus, these latter species are prone to add guests. ¹H and ¹³C NMR experiments carried out in aqueous solution, as well as the crystal structures of the dinuclear Cu(II) and Zn(II) species formed in aqueous solution, aided in elucidating the involvement of **L** and BPH in Zn(II) and Cu(II) stabilization.

Introduction

Dinuclear metal complexes are useful devices for the selective recognition, activation, or assembly of external species. For this reason, research in the synthesis of new ligands able to form dinuclear complexes with various metal ions is of great interest. Within this field, dinuclear species based on transition metals have been attracting increasing interest in the field of synthetic, biological, and supramolecular chemistry due to the key roles they play in many applications.^{1–4} New impulses have been given by the better

understanding we now have of the processes, reactivity, and structures of biological functions. Indeed, many of these are based on transition metal centers which in many cases

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* To whom correspondence should be addressed. E-mail: vieri@uniurb.it.

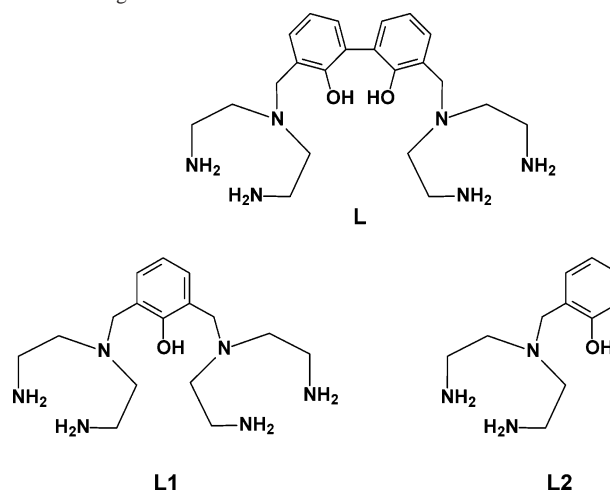
[†] University of Urbino.

[‡] University of Florence.

cooperate with each other, thus inspiring chemists to produce synthetic metal receptors mimicking the active site and/or reproducing the biological activity.^{5,6} Seen in this light, many of the biologically active centers are formed by a dimetallic core and make the design of new ligands able to form stable dinuclear complexes prone to interact with biological substrates interesting.^{7–10} For example, metal-complex-mediated hydrolysis of phosphate esters is providing valuable information for use in modeling and elucidating the reactivity of metal-containing nuclease molecules.¹¹

In polynuclear metal-receptors, the distance between the metals is crucial to allow the cooperation of metal ions in the active center; for example, 3.7 Å is the distance between the two copper ions in hemocyanins necessary to allow binding and transport of dioxygen in the hemolymph of mollusks.¹² In keeping with this concept, we planned the design of a new molecule able to modulate the metal–metal distance to form a dimetallic core suitable to host molecules. The modulation of the distance between the two metal ions permits the metalloceptor to selectively recognize different substrates depending on whether the substrate has the active dimetallic center available or not. In other words, the guidelines in designing the ligand herein reported were the

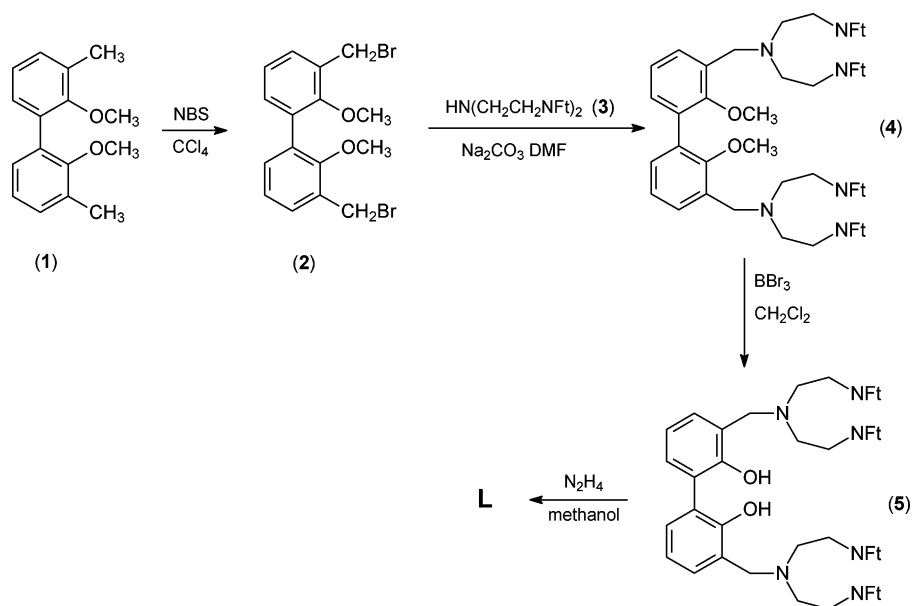
Chart 1. Ligands



following: (i) the donor groups of the ligand must not fulfill the coordination requirement of the two coordinated metal ions, and can therefore interact with secondary species; (ii) the two metal centers should cooperate in forming the host site. The nature of the two metal ions and the distance between them are the key elements in assembling guests and thus were the target of this study. Dinuclear hosts are often obtained by using macrocyclic ligands having a high number of donor atoms, and the transition metal ions usually guide the ligand arrangement fixed by their coordination requirement. We found that the phenol group, with its bridging coordination properties, permits the assembly of two transition metal ions close to each other with a metal–metal distance around 3 Å.^{13–14} In particular, ligand **L1** (Chart 1) is able to form simple and stable unsaturated dinuclear complexes with various metal ions; the dinuclear species hosts small molecules bound in a bridge disposition between the two metal ions.¹⁵ In addition, we noted that using **L2** (see Chart 1), which can be seen as consisting of a half molecular skeleton of **L1** and providing the same set of the donor atoms of **L1** for the coordination of one metal ion, did not complete the coordination requirement of the bound metal ion. In this case, the requirement was satisfied by the formation of dinuclear complexes with 2:2 L/M(II) molar ratio in which the phenolate oxygen atom plays the key role.¹⁶

Following the aim of enlarging the metal–metal distance and also of obtaining a versatility in modulating this distance, we synthesized the new ligand **L** (Chart 1) which has a

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Scheme 1. Synthesis of **L**

binding skeleton resembling that of **L1** but substituting the phenol with the 1,1'-bis(2-phenol) group (BPH) to space the two triamine dien units farther apart. **L** can also be seen as formed by two **L2** units linked together by the aromatic fragments. In other words, we wanted to preserve the coordination environment with one metal ion furnished by the **L2** unit or by half subunits of **L1**, while trying to enlarge the distance between the two coordinated metal ions in a dinuclear species. Indeed, although its binding properties were not studied in depth, the BPH groups should preserve the binding properties of the phenol with the plus of modulating the distance between two coordinated metal ions by rotating the angle between the two phenyl groups.

The preorganization of the dinuclear center should lead to selectivity toward guests that can be bound in a bridged disposition between the two metal ions, affording discrimination between them on the basis of the distance between the metals.

In this first study, in addition to the synthesis of **L**, we report its characterization, acid–base properties, and coordination behavior toward the transition metal ions Cu(II) and Zn(II) in aqueous solution. A structural characterization of mono- and dinuclear Zn(II) complexes in aqueous solution as well as the X-ray crystal structures of dinuclear species obtained with Zn(II) and Cu(II) are also reported.

Experimental Section

General Methods. IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer. Melting points were determined on a Büchi B 540 melting point apparatus and are uncorrected. EI-MS spectra (70 eV) were recorded on a Fisons Trio 1000 spectrometer;

ESI mass spectra were recorded on a ThermoQuest LCQ Duo LC/MS/MS spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 200 instrument, operating at 200.13 and 50.33 MHz, respectively, and equipped with a variable temperature controller. The temperature of the NMR probe was calibrated using 1,2-ethanediol as calibration sample. For the spectra recorded in D_2O , the peak positions are reported with respect to HOD (4.75 ppm) for ^1H NMR spectra, while dioxane was used as reference standard in ^{13}C NMR spectra ($\delta = 67.4$ ppm). For the spectra recorded in CDCl_3 and CD_3OD the peak positions are reported with respect to TMS.

Synthesis. Ligand **L** was obtained following the synthetic procedure reported in Scheme 1. 2,2'-Dimethoxy-3,3'-dimethylbiphenyl (**1**) and *N,N*-bis(2-phthalimidoethyl)amine (**3**) were prepared as previously described.^{17,18} All other chemicals were purchased, using the highest quality commercially available. The solvents were RP grade, unless otherwise indicated.

3,3'-Bis(bromomethyl)-2,2'-dimethoxybiphenyl (2). Compound **1** (6 g, 0.025 mmol), *N*-bromosuccinimide (9.8 g 0.055 mol), and 2,2'-azobis(2-methylpropionitrile) (0.15 g, 0.91 mmol) were dissolved in 300 cm^3 of CCl_4 under nitrogen. The reaction was stirred under reflux for 24 h and then cooled and filtered and the solvent removed under reduced pressure. The crude product was washed with methanol ($5 \times 50 \text{ cm}^3$) and dried, giving a yellow solid (4.8 g, 48%). ^1H NMR: (CDCl_3 , 25 °C) δ 3.50 (6H, s, OCH_3), 4.66 (4H, s, CH_2Br), 7.17 (2H, t, $J = 7.3$ Hz, *ArH*), 7.36 (2H, dd, $J = 7.3$, 1.8 Hz, *ArH*), 7.43 (2H, dd, $J = 7.3$, 1.8 Hz *ArH*). Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{Br}_2\text{O}_2$: C, 48.03; H, 4.03; N, 0.00. Found: C, 48.0; H, 4.1; N, 0.0.

3,3'-Bis[*N,N*-bis(2-phthalimidoethyl)aminomethyl]-2,2'-dimethoxybiphenyl (4). A solution of 180 cm^3 of DMF containing **2** (4.5 g, 11.25 mmol) was added dropwise to a suspension of *N,N*-bis(2-phthalimidoethyl)amine (**3**) (8.2 g, 22.5 mmol) and Na_2CO_3 (9.54 g, 90.0 mmol) in 300 cm^3 of DMF at 110 °C under nitrogen. The reaction mixture was stirred for a further 3 h. Subsequently,

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the solution was concentrated to 100 cm³ under reduced pressure and poured into cold water (500 cm³), obtaining a white solid. The product was crystallized from ethanol, obtaining the desired compound **4** (10.5 g, 97%). ¹H NMR: (CDCl₃, 25 °C) δ 2.84 (8H, t, *J* = 5.8 Hz, CH₂), 3.28 (6H, s, OCH₃), 3.77 (4H, s, Ar-CH₂), 3.80 (8H, t, *J* = 5.9 Hz, CH₂), 6.47 (2H, t, *J* = 7.5 Hz, ArH), 7.02 (4H, d, *J* = 7.5 Hz, ArH), 7.65–7.80 (16H, m, phthalimide). ¹³C NMR: (CDCl₃, 25 °C) δ 35.8, 51.5, 51.9, 60.7, 123.0, 129.8, 130.4, 131.5, 131.8, 132.4, 133.6, 156.0, 168.2, 198.9. Anal. Calcd for C₅₆H₄₈N₆O₁₀: C, 69.70; H, 5.01; N, 8.71. Found: C, 69.7; H, 5.1; N, 8.6.

3,3'-Bis[*N,N*-bis(2-phthalimidoethyl)aminomethyl]-2,2'-dihydroxybiphenyl (5). A 40 cm³ portion of BBr₃ (0.424 mol) was added dropwise to a solution of **4** (10.0 g, 10.6 mmol) in 1 dm³ of dry CH₂Cl₂ at 0 °C under nitrogen. The reaction was kept under stirring at room temperature for a further 18 h. The excess of BBr₃ was eliminated by adding 100 cm³ of methanol to the suspension kept at 0 °C. The solution was evaporated under reduced pressure, and the residue was washed with methanol (10 × 50 cm³). The product was obtained as dihydrobromide salt (**5**·2HBr, 11.0 g, 94%). ¹H NMR: (CD₃OD, 25 °C) δ 3.72 (8H, t, *J* = 5.6 Hz, CH₂), 4.22 (8H, t, *J* = 5.6 Hz, CH₂), 4.77 (4H, s, Ar-CH₂), 7.04 (2H, t, *J* = 7.6 Hz, ArH), 7.28 (2H, d, *J* = 7.6 Hz, ArH), 7.53 (2H, d, *J* = 7.6 Hz, ArH), 7.72–7.85 (16H, m, phthalimide). ¹³C NMR: (CD₃OD, 25 °C) δ 27.9, 47.4, 49.3, 112.5, 116.2, 118.3, 120.6, 127.7, 129.1, 129.5, 148.7, 163.5, 198.0. Anal. Calcd for C₅₄H₄₆Br₂N₆O₁₀ (**5**·2HBr): C, 59.03; H, 4.22; N, 7.65. Found: C, 59.0; H, 4.2; N, 7.7.

3,3'-Bis[*N,N*-bis(2-aminoethyl)aminomethyl]-2,2'-dihydroxybiphenyl (L). Compound **5**·6HBr (11.0 g, 10.2 mmol) was suspended in a mixture of 200 cm³ of methanol and 200 cm³ of hydrazine (80% solution in water). The reaction was left under vigorous stirring for 3 days at room temperature. The solvent was removed at reduced pressure, and the hydrazine in excess was eliminated by coevaporating with ethanol (10 × 50 cm³). The ethanol solution was filtered to remove the phthalhydrazide, evaporated, and left at 50 °C and 10⁻² Torr for 48 h. The residue was dissolved in ethanol, filtered, and treated with a solution of ethanol (95%)/48% hydrobromic acid 1:1, yielding a yellowish solid. The product was then crystallized from methanol/ethanol affording 2.8 g (30%) of **L**·6HBr·H₂O. ¹H NMR: (D₂O, pH = 3, 25 °C) δ 2.96 (8H, t, *J* = 6.7 Hz, CH₂), 3.20 (8H, t, *J* = 6.6 Hz, CH₂), 4.31 (4H, s), 7.06 (2H, t, *J* = 7.5 Hz, ArH), 7.25 (2H, d, *J* = 7.5 Hz, ArH), 7.32 (2H, d, *J* = 7.5 Hz, ArH). ¹³C NMR: (D₂O, pH = 3, 25 °C) δ 36.2, 50.1, 53.9, 121.2, 122.9, 125.4, 131.5, 131.8, 152.4. Anal. Calcd for C₂₂H₄₄Br₆N₆O₃ (**L**·6HBr·H₂O): C 28.72; H 4.82; N 9.13. Found: C, 28.7; H, 4.7; N, 9.0.

[Cu₂(H₋₁L)(OH)](ClO₄)₂(H₂O) (6). A sample of Cu(ClO₄)₂·6H₂O (37 mg, 0.1 mmol) in water (30 cm³) was added to an aqueous solution (30 cm³) containing **L**·6HBr·H₂O (46 mg, 0.05 mmol). The pH of the resulting solution was adjusted to 8 with 0.1 M NaOH and saturated with solid NaClO₄. After a few minutes, **6** precipitated as a microcrystalline blue-green solid (35 mg, 91%). Anal. Calcd for C₂₂H₃₈Cl₂Cu₂N₆O₁₂: C 34.03; H 4.93; N 10.82. Found: C 33.9; H 5.0; N 10.7. Crystals suitable for X-ray analysis were obtained by slow evaporation of an aqueous solution containing **6**.

[Zn₂(H₋₂L)(H₂O)₂](ClO₄)₂ (7). This compound was synthesized from **L**·6HBr·H₂O (46 mg, 0.05 mmol) and Zn(ClO₄)₂·6H₂O (37 mg, 0.1 mmol) following the same procedure reported for **6**, obtaining **7** as colorless microcrystals (32 mg, 83%). Crystals suitable for X-ray analysis were obtained by slow evaporation of an aqueous solution containing **7**. ¹H NMR: (D₂O, pH = 8, 25 °C) δ 2.75 (8H, m, H²), 2.87 (8H, m, H¹), 3.84 (4H, s, H³), 6.80 (2H,

t, *J* = 7.5 Hz, H⁶), 7.18 (2H, d, *J* = 7.5 Hz, H⁵ and H⁷). ¹³C NMR: (D₂O, pH = 8, 25 °C) δ 37.1 (C1), 52.0 (C2), 56.4 (C3), 116.5 (C6), 125.8 (C8), 131.3 (C7), 131.7 (C4), 132.0 (C5), 161.5 (C9). Anal. Calcd (%) for C₂₂H₃₈Cl₂N₆O₁₂Zn₂: C 33.87; H 4.91; N 10.77. Found: C 33.7; H 4.8; N 10.7.

Caution! Perchlorate salts of organic compounds are potentially explosive; these compounds must be prepared and handled with great care!

X-ray Crystallography. For compounds [Cu₂(H₋₁L)(OH)](ClO₄)₂·(H₂O) (**6**) and [Zn₂(H₋₂L)(H₂O)₂](ClO₄)₂ (**7**), intensity data collections were performed by using a Siemens SMART diffractometer equipped with CCD area detector and rotating anode. The software used was the SMART¹⁹ software, and the radiation Cu Kα (λ = 1.5418 Å) was used. Five settings of ω were employed, and narrow data “frames” were collected for 0.3° increments in ω. A total of 3000 frames of data were collected providing a sphere of data. Data reduction was performed with the SAINT 4.0²⁰ program. Absorption corrections were performed with the SADABS program.²¹ Structures were then solved using the SIR97 program²² and refined by full-matrix least-squares against F² using all data (SHELX97).²³

In **6** the carbon atom C(17) is affected by disorder, and two different positions (a and b) were assigned to it with population factors 0.7 and 0.3, respectively. As a consequence, atoms N(3), C(16), and C(17) were refined isotropically, and the hydrogen atoms bound to them were not included in the refinement. Moreover, in both the crystal structures the oxygen atoms of the perchlorate counter ions are affected by disorder, and for several of them, two different positions were taken into account. In both structures, all the non-hydrogen atoms, with the exception of atoms N(3), C(16), and C(17) in **6**, and all of the oxygen atoms of the perchlorate anions in **6** and **7**, were refined anisotropically. The hydrogen atoms of **L**, except those bound to the oxygen atoms, were set in calculated positions with their coordinates and temperature factors refined accordingly to the riding atoms. Concerning this latter point, the quality of the X-ray data did not allow us to discern if the BPH grouping of **L** has both its acidic protons, only one or none, or to identify the species additionally bound by the metals (i.e., to distinguish between OH⁻ and H₂O). As a consequence, the assignment of the ligand (i.e., H₋₁L⁻ in **6** and H₋₂L⁻² in **7**) and of the guest species (i.e., OH⁻ in **6** and H₂O in **7**) was based both on geometric issues and on the solution outcomes (see Results and Discussion section), since both the metal complexes must have an overall +2 charge.

Geometrical calculations were performed by PARST97²⁴ and molecular plots were produced by the ORTEP3 program.²⁵

Crystallographic data and refinement parameters are reported in Table 1.

Cambridge Structural Database (CSD) Search. A search in the Cambridge Structural Database (v 5.27)²⁶ was carried out to retrieve molecular fragments featuring the BPH moiety in order to gain some insight into the relationship between the conformation

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Table 1. Crystallographic Data and Refinement Parameters for Compounds **6** and **7**

	6	7
empirical formula	C ₂₂ H ₃₈ Cl ₂ Cu ₂ N ₆ O ₁₂	C ₂₂ H ₃₈ Cl ₂ N ₆ O ₁₂ Zn ₂
fw	776.56	780.22
T (K)	293	293
wavelength (Å)	1.5418	1.5418
cryst syst, space group	monoclinic, <i>Pc</i>	orthorhombic, <i>Pbca</i>
unit cell dimensions (Å, deg)	<i>a</i> = 7.5752(8) <i>b</i> = 12.3110(4), β = 93.465(6) <i>c</i> = 16.698(2)	<i>a</i> = 10.955(1) <i>b</i> = 14.075(1) <i>c</i> = 40.522(4)
<i>V</i> (Å ³)	1554.4(3)	6248(1)
<i>Z</i> , <i>D_c</i> (mg/cm ³)	2, 1.659	8, 1.659
μ (mm ⁻¹)	3.874	4.065
<i>F</i> (000)	800	3216
cryst size (mm ³)	0.4 × 0.3 × 0.2	0.3 × 0.3 × 0.2
θ range (deg)	3.59–56.19	4.36–55.94
reflns collected/unique	4932/2867	15860/3895
data/params	2867/365	3895/366
GOF on <i>F</i> ²	0.897	0.895
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0565, <i>wR</i> 2 = 0.1377	<i>R</i> 1 = 0.0777, <i>wR</i> 2 = 0.1974
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1215, <i>wR</i> 2 = 0.1653	<i>R</i> 1 = 0.1591, <i>wR</i> 2 = 0.2545

of the interannular C–C bond and (i) its protonation degree; (ii) coordination modes toward metal ions. In all cases, 2D constraints were turned on in order to avoid unwanted additional steric effects. The absolute value of the dihedral angle of the C–C interannular bond (τ) and the distance between the two oxygen atoms were monitored (*d*).

EMF Measurements. Equilibrium constants for protonation and complexation reactions with **L** were determined by pH-metric measurements (pH = $-\log [\text{H}^+]$) in 0.15 M NaCl at 298.1 ± 0.1 K, using fully automatic equipment that has already been described;^{15a} the EMF data were acquired using the PASAT computer program.²⁷ The combined glass electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO₂-free NaOH solutions and determining the equivalent point by Gran's method,²⁸ which gives the standard potential *E*^o and the ionic product of water ($\text{p}K_w = 13.83(1)$) at 298.1 K in 0.15 M NaCl, $K_w = [\text{H}^+][\text{OH}^-]$). At least three potentiometric titrations were performed for each system in the pH range 2–11, using different molar ratios of M/L (M = Cu(II) and Zn(II)) ranging from 1:1 to 3:1. All titrations were treated either as single sets or as separate entities, for each system; no significant variations were found in the values of the determined constants. The HYPERQUAD computer program was used to process the potentiometric data.²⁹

Results and Discussion

Synthesis. The synthetic pathway used to obtain ligand **L** is depicted in Scheme 1. Dibromo derivative **2** was synthesized following a classical bromuration of methyl-substituted anisoles.³⁰ The first step consisted in attaching two *N,N*-bis(2-phthalimidoethyl)amine (**3**) groups to the methyl-protected 2,2'-biphenol (**2**). The reaction gave the fully protected intermediate **4**. Deprotection of the phenol groups was carried out by using a large excess of BBr₃. The unreacted BBr₃ was treated with methanol; the methyl borate ester formed was removed by vacuum evaporation to leave

5·2HBr. The final ligand **L** was obtained by removing the phthaloyl groups using hydrazine in methanol. After the workup, **L** was further purified as hexahydrobromide salt. Deprotection of **5** using an acidic medium as well as the change of the deprotection sequence did not afford the desired compound.

X-ray Solid-State Structures. The asymmetric unit of **6** contains a di-copper μ_2 -hydroxo complex (Figure 1), a crystallization water molecule, and two perchlorate anions while one di-zinc di-aqua complex cation (Figure 2) and two perchlorate anions are placed in the asymmetric unit of **7**. In both complexes, the ligand provides four donor atoms to each metal ion (i.e., the nitrogen atoms and the oxygen atom of each ligand subunit). Bond distances and angles of the coordination spheres are reported in Table 2. Moreover, in **6** a bridging oxygen atom O(3), belonging to a hydroxide ion, completes the coordination sphere of the copper ions, keeping them 3.546(3) Å apart. The Cu(1)–O(3) and Cu(2)–O(3) bond distances are 1.90(1) and 1.95(1) Å, respectively, and 134.1(6)° is the Cu(1)–O(3)–Cu(2) bond angle. In **7** two independent coordination domains originate with the metal cations 4.969(2) Å apart and the two Zn-coordinated water molecules pointing inside the complex cavity at 4.08(1) Å from each other (Figure 2).

In **6** the two metal ions have slightly different coordination environments, i.e., square pyramidal (sp) and trigonal bi-

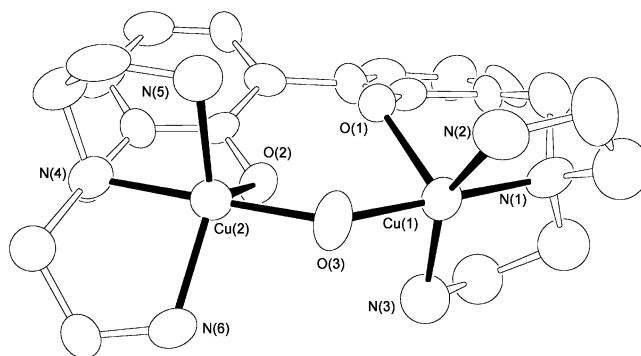


Figure 1. ORTEP3 view of the complex cation [Cu₂(H-**1L**)(OH)]²⁺ with the essential labeling scheme. Ellipsoids are drawn at 30% probability.

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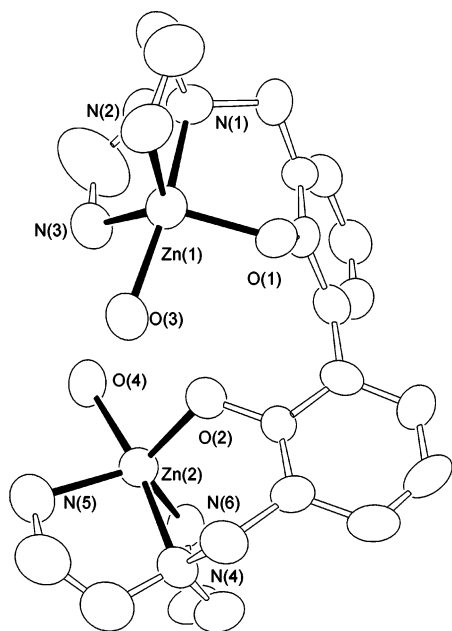


Figure 2. ORTEP3 side view of the complex cation $[Zn_2(H-2L)(H_2O)_2]^{2+}$ with the essential labeling scheme. Ellipsoids are drawn at 30% probability.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds **6** and **7**

	6		7
Cu(1)—O(1)	2.208(9)	Zn(1)—O(1)	1.952(7)
Cu(1)—N(1)	1.99(1)	Zn(1)—N(1)	2.21(1)
Cu(1)—N(2)	2.05(2)	Zn(1)—N(2)	1.99(1)
Cu(1)—N(3)	2.03(2)	Zn(1)—N(3)	2.04(1)
Cu(1)—O(3)	1.90(1)	Zn(1)—O(3)	2.080(8)
Cu(2)—O(2)	2.232(8)	Zn(2)—O(2)	1.961(7)
Cu(2)—N(4)	2.00(1)	Zn(2)—O(4)	2.123(8)
Cu(2)—N(5)	2.02(1)	Zn(2)—N(4)	2.19(1)
Cu(2)—N(6)	2.02(1)	Zn(2)—N(5)	2.071(9)
Cu(2)—O(3)	1.95(1)	Zn(2)—N(6)	2.016(8)
N(1)—Cu(1)—O(1)	91.3(4)	N(1)—Zn(1)—O(1)	90.9(3)
N(2)—Cu(1)—O(1)	107.6(5)	N(2)—Zn(1)—O(1)	111.3(4)
N(3)—Cu(1)—O(1)	99.7(5)	N(3)—Zn(1)—O(1)	122.8(3)
O(3)—Cu(1)—O(1)	89.1(4)	O(3)—Zn(1)—O(1)	95.0(3)
O(3)—Cu(1)—N(1)	179.4(6)	O(3)—Zn(1)—N(1)	165.8(3)
N(1)—Cu(1)—N(2)	85.5(6)	N(1)—Zn(1)—N(2)	85.0(4)
N(3)—Cu(1)—N(2)	151.9(6)	N(3)—Zn(1)—N(2)	123.8(4)
O(3)—Cu(1)—N(2)	93.9(6)	O(3)—Zn(1)—N(2)	104.8(4)
N(1)—Cu(1)—N(3)	87.1(6)	N(1)—Zn(1)—N(3)	80.4(4)
O(3)—Cu(1)—N(3)	93.3(6)	O(3)—Zn(1)—N(3)	85.6(4)
N(4)—Cu(2)—O(2)	90.0(4)	N(4)—Zn(2)—O(2)	91.9(3)
N(5)—Cu(2)—O(2)	110.8(5)	N(5)—Zn(2)—O(2)	121.5(4)
N(6)—Cu(2)—O(2)	107.5(4)	N(6)—Zn(2)—O(2)	116.2(3)
O(3)—Cu(2)—O(2)	89.8(4)	O(4)—Zn(2)—O(2)	95.2(3)
O(3)—Cu(2)—N(4)	178.7(6)	O(4)—Zn(2)—N(4)	171.4(3)
N(4)—Cu(2)—N(5)	83.6(6)	N(4)—Zn(2)—N(5)	83.0(4)
N(6)—Cu(2)—N(5)	140.1(5)	N(6)—Zn(2)—N(5)	120.0(4)
O(3)—Cu(2)—N(5)	95.3(6)	O(4)—Zn(2)—N(5)	89.1(4)
N(4)—Cu(2)—N(6)	85.7(6)	N(4)—Zn(2)—N(6)	80.1(4)
O(3)—Cu(2)—N(6)	95.6(6)	O(4)—Zn(2)—N(6)	101.0(3)

pyramid (tbp), as provided by the corresponding τ^{31} indexes: 0.46 for Cu(1) and 0.64 for Cu(2). On the contrary, the zinc ions in **7** are shaped with the same tbp coordination environment (τ indexes 0.70 for Zn(1) and 0.83 for Zn(2)). In **6** the bridging hydroxide ion O(3) and the nitrogen atoms (N(1)—N(3)) provided by the ligand describe the base of the distorted square pyramid around Cu(1), with the latter slightly

displaced (0.195(2) Å) toward the apical atom O(1). The quite long Cu(1)—O(1) distance, 2.208(9) Å, testifies to the usual axial elongation observed in square-pyramidal copper(II) complexes.³² The tertiary nitrogen atom N(4) of the tripod arm and the oxygen atom O(3) occupy the axial positions of the tbp around Cu(2), slightly distorted toward the sp geometry (N(5)—Cu(2)—N(6) 140.1(6)°). Considering the sp case, the oxygen O(2) is at the apex at a significantly longer distance (2.232(8) Å). In **7** the oxygen water molecules O(3) and O(4) together with the tripod nitrogen atoms N(1) and N(4) occupy the axial positions of the tbp about Zn(1) and Zn(2), respectively. In all the cases of tbp coordination the metal ion is slightly displaced toward the axial water oxygen atom.

Indeed, in both complexes the ligand provides the metal ions with an almost identical coordination environment which is saturated thanks to external guests. However, the conformation of the interannular C—C bond of the BPH is definitely different in the two metal complexes: the dihedral angle τ is $-38(2)^\circ$ and $67(2)^\circ$ in **6** and **7**, respectively, and the O(1)⋯O(2) interatomic distance d is 2.38(1) and 3.14(1) Å in **6** and **7**, respectively. The different arrangement of the BPH coordination site suggests a different protonation degree for it in **6** and **7**.

In **7** the zinc bond distances involving the guests species O(3) and O(4) are significantly longer than those involving the oxygen atoms O(1) and O(2) provided by BPH and definitely comparable with the average Zn(II)—H₂O bond distance (2.04 Å) retrieved in the CSD for pentacoordinated Zn complexes. (The mean Zn—OH bond distance as obtained from the data deposited in the CSD is 1.99 Å.) As a consequence, assuming two water molecules as guests species and given the charge balance, the complex should feature a fully deprotonated biphenol, as also suggested by the quite large torsion angle τ between the phenyl rings³³ and by the NMR data (vide infra).

Concerning the dicopper complex, verification of the metal—oxygen distances did not help us to discern the guest species because both the oxygen atoms provided by BPH are at the apex of a distorted sp, and thus their bonds are necessarily elongated with respect to the Cu—O(3) bond. However, a comparison between the structural parameters defining the biphenol coordination site (i.e., τ and d) in **6** with the average values retrieved in the CSD for monoprotonated BPH fragments³³ could suggest the stoichiometry for this complex. It is possible that in **6** an intramolecular OH⋯O interaction is at work, keeping the oxygen atoms of the biphenol quite close each other ($d = 2.38(1)$ Å) and forcing τ to a quite small value ($-38(2)^\circ$). If a monodepro-

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(33) The \pm gauche conformation is by far the preferred one for the biphenol (CSD data). The fully protonated BPH shows the largest range of torsion values (mean τ and d values: 68.5° , 3.1 Å; 39 hits retrieved), while the mononegative BPH species appears to be more rigid and definitely more planar, essentially thanks to the intramolecular OH⋯O hydrogen bond (mean τ and d values: 41.7° , 2.5 Å; 5 hits retrieved). Uncoordinated dinuclear BPH moieties were not found, and only two hits feature dinuclear metal complexes involving this species in a coordination pattern similar to **6** and **7** ($\tau > 55^\circ$, $d > 2.8$ Å).

Table 3. Basicity Constants of **L** (log *K*) Determined by Potentiometry in 0.15 mol dm⁻³ NaCl Aqueous Solution at 298.1 ± 0.1 K

reaction	log <i>K</i>
H ₋₁ L ⁻ + H ⁺ = L	10.58(4) ^a
L + H ⁺ = HL ⁺	10.52(1)
HL ⁺ + H ⁺ = H ₂ L ²⁺	9.56(1)
H ₂ L ²⁺ + H ⁺ = H ₃ L ³⁺	9.34(1)
H ₃ L ³⁺ + H ⁺ = H ₄ L ⁴⁺	6.09(2)
H ₄ L ⁴⁺ + H ⁺ = H ₅ L ⁵⁺	3.78(3)

^a Values in parentheses are the standard deviation to the last significant figure.

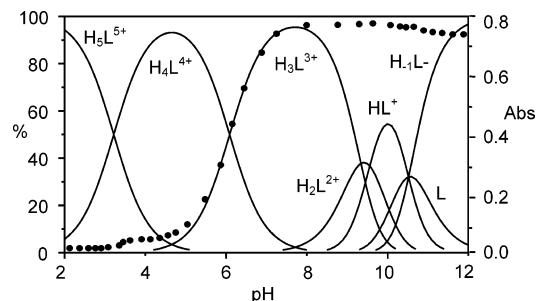
tonated species is assumed for the biphenol in **6**, the bridging oxygen atom O(3) must belong to a hydroxide ion for the overall charge balance.

Thus, the BPH spacer accomplishes both our initial goals: that is, to increase the M–M distance with respect to analogous metal complexes featuring the phenol as spacer unit (ca. 3 Å is the usual value),^{14–16} and to modulate it (from 3.55 Å in **6** to 4.97 Å in **7**). This attractive feature is the result of the torsional degree of freedom about the interannular C–C bond of BPH, which in turn depends on its protonation state.

As a final point in **6**, the crystallization water molecule is kept in place by the interactions with the oxygen atom O(1) ((O(4)···O(1), 2.84(2) Å) and the nitrogen atom N(5) ((O(4)···N(5), 3.05(2) Å). Additional H-bond contacts involve the oxygen atoms of the perchlorate ions and the NH₂ groups provided by the ligand. These latter interactions are also present in the crystal lattice of **7**, together with some contacts involving the coordinated water molecules.

Solution Studies. Basicity. Table 3 reports the log *K* values of the protonation constants of **L** which are determined potentiometrically in 0.15 M NaCl aqueous solution at 298.1 K. The neutral species **L** behaves as a pentaprotic base and as a monoprotic acid under the experimental conditions used. As shown in Table 3, it can be present in solution as anionic species H₋₁L⁻, indicating the permanence of one acidic hydrogen atom on the ligand in the pH range of the potentiometric measurements. In fact, taking into account that the BPH shows two acidic protons, we could not detect, in this case, the H₋₂L²⁻ species which could theoretically be achieved in strong alkaline solution.

Analysis of the protonation constant values starting from the anionic H₋₁L⁻ species revealed that it behaves as a rather strong base in the addition of the first four protons, with protonation constant values ranging from 10.58 to 9.34 logarithmic units; a decrease in the fifth protonation step (log *K* = 6.09) and a further decrease in the last proton addition (log *K* = 3.78) were observed. This trend suggests that the first four protonation steps involve sites located far from each other in order to minimize the electrostatic repulsion, helped by the open structure of **L**. In particular, the first four proton additions are in the range of protonation of the amine functions of dien subunits linked to a phenolate function as shown in the acid–base behavior of **L1**, **L2**, and similar ligands, while the fifth addition is similar to the protonation of a phenolate group in similar topology.^{14b,15a,b,16a} This analysis suggests the presence of a phenolate moiety not only

**Figure 3.** Absorption titration at $\lambda = 309$ nm (●) ($[L] = 8.5 \times 10^{-5}$ M), and distribution curves of the species (—) in aqueous solution at 298.1 K in 0.15 M NaCl.

in the H₋₁L⁻ species but in the **L**, HL⁺, H₂L²⁺, and H₃L³⁺ species, too. Taking into account that the values of p*K*_a of the free BPH in aqueous solution are p*K*_{a1} = 7.5 and p*K*_{a2} > 14,³⁴ we can suppose that under our experimental conditions the remaining acidic proton in the H₋₁L⁻ species is located in the 2,2'-biphenol group. In other words, the BPH is mononegatively charged in the H₋₁L⁻, **L**, HL⁺, H₂L²⁺, and H₃L³⁺ species (i.e., those with one phenolic and one phenolate group) while it is in its neutral form in the other more charged species.

UV–vis absorption electronic spectra of **L** in aqueous solutions performed at different pH values gave further information about the role of the 2,2'-biphenolic function in the acid–base behavior of **L**, supporting the previous hypothesis. The spectra show that below pH = 5, where the H₄L⁴⁺ and H₅L⁵⁺ species are present in solution, the BPH function is in its neutral form (band with λ_{\max} at 281 nm and $\epsilon = 6700$ cm⁻¹ mol⁻¹ dm³, characteristic for the neutral form of BPH).^{34a} On the contrary, above pH = 7, where the H₃L³⁺, H₂L²⁺, HL⁺, **L**, and H₋₁L⁻ species are present, the spectra are characteristic for the presence of the anionic phenolate form (two bands with λ_{\max} at 255 and 309 nm and $\epsilon = 8100$ and 9100 cm⁻¹ mol⁻¹ dm³, respectively).^{34a} In other words, the deprotonation of one of the hydroxyl functions of BPH occurs in the pH range which involves the H₄L⁴⁺ and the H₃L³⁺ species, and this latter species, as well as those with lower protonation degree, is present in solution in zwitterionic form, furnishing a separation of the positive and negative charges. The trend of the λ_{\max} at 309 nm (that of the phenolate moiety) has been reported as a function of pH together with the distribution diagram of the **L** species in Figure 3; the figure highlights which species are undergoing the deprotonation of BPH and which are those where BPH is mononegatively charged. The fact that the spectra recorded at higher alkaline pH values, such as 14, did not show any change from the spectral features recorded at pH = 12, suggests that the complete deprotonation of BPH is not reachable for this system in aqueous solution.

Coordination of Metal Ions. The coordination behavior of **L** toward the metal cations Cu(II), and Zn(II) was studied

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Table 4. Logarithms of the Equilibrium Constants Determined in 0.15 mol dm⁻³ NaCl at 298.1 K for the Complexation Reactions of **L** with Cu(II) and Zn(II) Ions

reaction	log <i>K</i> , M = Cu(II)	log <i>K</i> , M = Zn(II)
M ²⁺ + H ₋₁ L ⁻ = MH ₋₁ L ⁺	20.52(3) ^a	14.79(3)
M ²⁺ + L = ML ²⁺	19.61(2)	13.85(3)
MH ₋₁ L ⁺ + H ⁺ = ML ²⁺	9.67(2)	9.64(3)
ML ²⁺ + H ⁺ = MHL ³⁺	7.83(2)	8.87(2)
MHL ³⁺ + H ⁺ = MH ₂ L ⁴⁺	4.81(1)	5.05(2)
MH ₋₁ L ⁺ + OH ⁻ = MH ₋₁ LOH	2.58(3)	
M ₂ H ₋₁ L ³⁺ + H ⁺ = M ₂ L ⁴⁺	4.07(3)	
M ²⁺ + MH ₋₁ L ⁺ = M ₂ H ₋₁ L ³⁺	13.77(2)	8.84(2)
M ₂ H ₋₁ L ³⁺ + OH ⁻ = M ₂ H ₋₁ LOH ²⁺	8.44(3)	
M ₂ H ₋₁ LOH ²⁺ + OH ⁻ = M ₂ H ₋₁ L(OH) ₂ ⁺	2.31(4)	
M ₂ H ₋₁ L ³⁺ = M ₂ H ₋₂ L ²⁺ + H ⁺		-6.72(2)
M ₂ H ₋₂ L ²⁺ + OH ⁻ = M ₂ H ₋₂ LOH ⁺		3.98(3)
M ₂ H ₋₂ LOH ⁺ + OH ⁻ = M ₂ H ₋₂ L(OH) ₂		3.06(3)

^a Values in parentheses are the standard deviations on the last significant figure.

in 0.15 mol dm⁻³ NaCl aqueous solution at 298.1 K. The stability constants for the equilibrium reactions were potentiometrically determined and are reported in Table 4.

L forms mono- and dinuclear species with both the Cu(II) and Zn(II) ions examined. The dinuclear species are largely prevalent in aqueous solution when the ligand–metal ratio is 1:2; when the **L**/M(II) molar ratio is 1:1, the mono- and dinuclear species coexist in solution. The distribution diagrams of these species for the system **L**/M(II) in 1:1 and 1:2 molar ratios as a function of pH are reported in Figure 4.

Mononuclear Complexes. **L** forms stable mononuclear complexes with both metal ions examined. Comparing the species having the same stoichiometry, the Cu(II) species show higher stability than do the Zn(II) species.

The values for the addition constants (log *K*) of M(II) to the H₋₁L⁻ species are similar to those of M(II) to the **L** species. This means that both H₋₁L⁻ and **L** species provide a similar coordination environment for the metal (see Table 4), and it also indicates that the addition of a proton to the H₋₁L⁻ species does not involve groups coordinated to the metal. These values are also similar to the constants for the addition of both M(II) to the neutral species of **L1** and **L2** as well as to the H₋₁**L2**⁻ species (the addition of M(II) to the H₋₁**L1**⁻ species cannot be calculable);^{15b,16a} in these cases, the involvement of one tri-amine dien unit and of the phenolic oxygen atom in its deprotonated form was suggested.

In other words, in the mononuclear [MH₋₁L]⁺ and [ML]²⁺ species the metal ion is stabilized by only one dien unit and by only one phenolate oxygen atom of BPH while the other part of the molecule, i.e., the other dien unit and phenolic group of BPH, remains unbound undergoing protonation; in this way, it would appear that the involvement of both BPH oxygen atoms in binding M(II) can be excluded. A coordination mode for M(II) in the mononuclear species is schematically depicted in Figure 5 for the [MHL]³⁺ species. This hypothesis is supported by the easy addition of two protons to the [MH₋₁L]⁺ species with values rather similar to the third and fourth protonation steps for the free ligand, leading

us to suppose that the protonation involves two primary amine functions not engaged in coordination, belonging to the other dien unit.

Dinuclear Complexes. The presence of a second equivalent of M(II) in solution gives rise to the formation of dinuclear species that are the only species existing in solution at pH higher than 5 or 6.5 for Cu(II) and Zn(II), respectively (see Figure 4d,b). The addition of the second M(II) ion to the [MH₋₁L]⁺ species gives the [M₂H₋₁L]³⁺ species for both systems; however, the addition of the second M(II) to the H₋₁L⁻ species is lower than the first one. This aspect is mainly attributable to the fact that the second addition occurs to a positively charged [MH₋₁L]⁺ species.

The main dinuclear species for both metal systems is the formally written M₂H₋₂L²⁺ species; it is the same charged species found in both crystal structures reported herein and shown in Figures 1 and 2, and it is prevalent in solution at pH values around neutrality in both systems. As in the case of both crystal structures (see above), it is difficult to discern the degree of protonation of the BPH unit in the species. This aspect did not allow us to establish the exact stoichiometry of the complexed species formed, depending on the protonation degree of the two phenol functions. In fact, when BPH is in its neutral form, with both phenol groups, the species formed is the [M₂L(OH)₂]²⁺ one; when it is mononegative, with one phenol and one phenolate groups, the species is [M₂H₋₁LOH]²⁺; when it is binegative, with both phenolate groups, the species is [M₂H₋₂L]²⁺. UV–vis absorption electronic spectra carried out on both M(II)/**L** dinuclear systems always showed bands characteristic of the deprotonation of the BPH group, thus excluding the presence of the neutral form of BPH in the dinuclear species (data not reported). The analysis of the two crystal structures as well as the NMR experiments carried out on the Zn(II)/**L** system (see below) lead us to suppose that Cu(II) and Zn(II) dinuclear species produce a different behavior of BPH, and precisely, Cu(II) forms [Cu₂H₋₁LOH]²⁺ while Zn(II) forms the [Zn₂H₋₂L]²⁺ species.

In particular, in support of the hypothesis, we observed that the suggested [Cu₂H₋₁LOH]²⁺ species is present in a very wide range of pH, denoting that the coordination of both metal ions is very stable; this can be obtained by saturation of the binding requirement of both metal ions that can be achieved by the presence of a hydroxide anion displaced in a bridge disposition between the two Cu(II) ions in a stable pentacoordination environment similar to that depicted in Figure 1 and schematically depicted in Figure 5c. The favorable addition of the hydroxide to the [Cu₂H₋₁L]³⁺ species is underlined by the value of 8.44 logarithmic units retrieved for the formation constant of the reaction [Cu₂H₋₁L]³⁺ + OH⁻ = [Cu₂H₋₁LOH]²⁺ (Table 4); this value is in the range of a hydroxide anion bridging two Cu(II) cations.^{16a,b,35} The presence of only further deprotonation occurring to the previous species at high alkaline pH values supports this hypothesis.

(35) Jurek, P.; Martell, A.; Motekaitis, R.; Hancock, R. *Inorg. Chem.* **1995**, *34*, 1823.

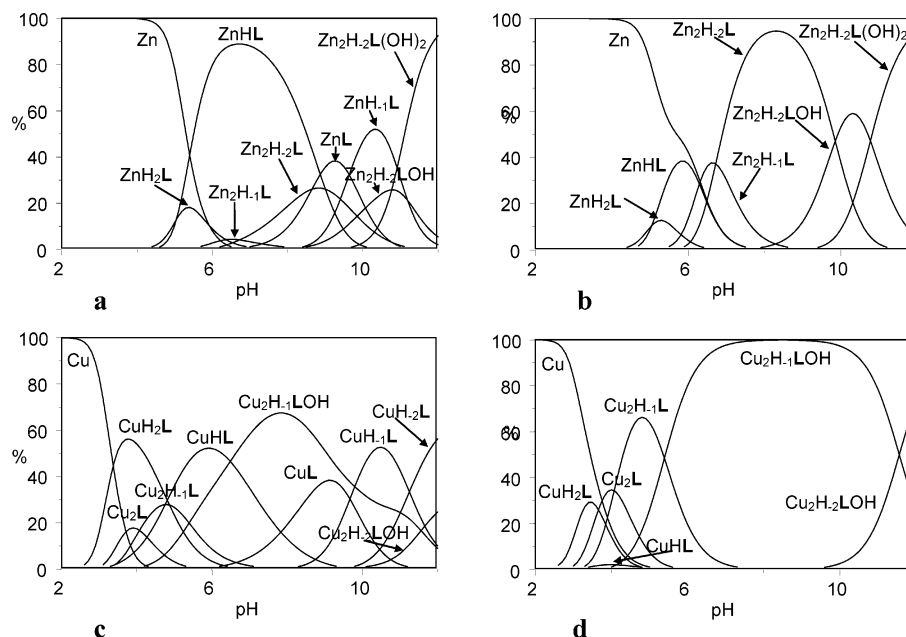


Figure 4. Distribution diagrams of the species for the L/M(II) systems as a function of pH in aqueous solution: $I = 0.15$ M NaCl, at 298.1 K, $[L] = 1 \times 10^{-3}$ M: $[Zn(II)] = 1 \times 10^{-3}$ M (a); $[Zn(II)] = 2 \times 10^{-3}$ M (b); $[Cu(II)] = 1 \times 10^{-3}$ M (c); $[Cu(II)] = 2 \times 10^{-3}$ M (d).

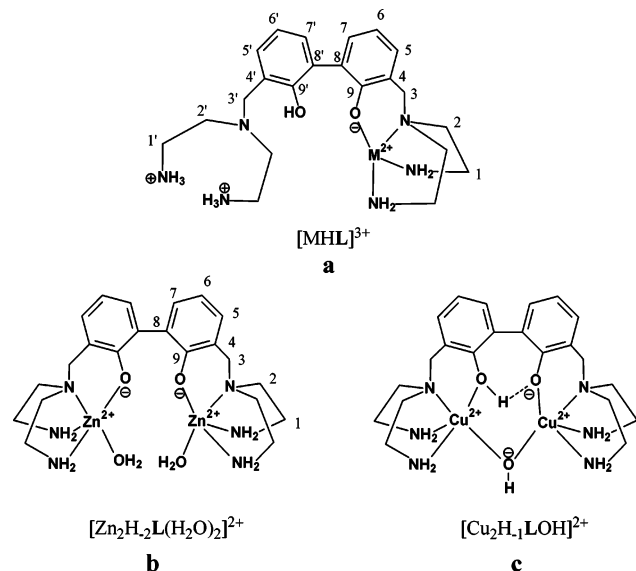


Figure 5. Proposed models for: $[MHL]^{3+}$ species ($M = Zn, Cu$) (a), $[Zn_2H_{-2}L(H_2O)_2]^{2+}$ (b), and $[Cu_2H_{-1}LOH]^{2+}$ species (c), together with labels for the NMR resonances.

Following the same reasoning, it is possible to note that the formally written $Zn_2H_{-2}L^{2+}$ species exists in solution in a more narrow range of pH with respect to Cu(II) (Figures 4b,d); this is mainly due to the fact that it undergoes further deprotonation processes occurring at pH lower than that of the Cu(II) dinuclear species. This aspect indicates a lesser stability of both Zn(II) coordination environments with respect to the Cu(II) species and could be explained with the presence of two coordinated water molecules, one for each Zn(II) ion, as hypothesized in the crystal structures of the $[Zn_2H_{-2}L(H_2O)_2]^{2+}$ cation and schematically drawn in Figure 5b. The deprotonation of these water molecules, which can also be written as the addition of the OH^- ion to the $[Zn_2H_{-2}L]^{2+}$ or $[Zn_2H_{-2}LOH]^+$ species, shows similar constant values, 3.98 and 3.06 logarithmic units, respectively

(Table 4), supporting the hypothesis that the species prevalent from pH 7.0 to 9.5 is the $[Zn_2H_{-2}L]^{2+}$ one with the BPH fully deprotonated.

In conclusion, **L** consists of two independent binding subunits, each equal to **L2**. Each **L2** subunit does not saturate the coordination requirement of the coordinated M(II) ion which is thus prone to add external guests that in these cases are hydroxide or water molecules. Moreover, the coordination of different metal ions such as Cu(II) and Zn(II) seems to affect the degree of protonation of the coordinated BPH unit in different ways.

NMR Studies. 1H and ^{13}C NMR experiments were performed for the Zn(II)/L system in D_2O solution at different molar ratios and pH values to obtain further information about the coordination environment in the mono- and dinuclear Zn(II) complexed species; some of the spectra obtained are reported in Figures 6 and 7. The 1H and ^{13}C NMR spectra of the Zn(II)/L system in a 1:1 molar ratio recorded at pH = 6.5, where the $[ZnHL]^{3+}$ species is prevalent in solution, are reported in Figures 6b and 7b, respectively. In both 1H and ^{13}C NMR spectra, small signals are detectable close to the baseline and are attributable to the other complexed species present in solution at this pH (see Figure 4a), exchanging slowly on the NMR time scale with the $[ZnHL]^{3+}$ species. These signals are difficult to analyze, and thus, they were not considered in the analysis of the spectra. However, this aspect highlights that the complexed species are slowly exchanged, on the NMR time scale; in addition, the spectra of this system recorded at higher temperatures, up to 363.1 K, did not afford a collapse of any signal, once again supporting the idea that the main 1H and ^{13}C spectra are due to only one species (i.e., $[ZnHL]^{3+}$) present in solution and not to two of its conformers. This aspect was also verified by increasing the equivalent of Zn(II) at pH = 6.5 which leads to the coexistence of new

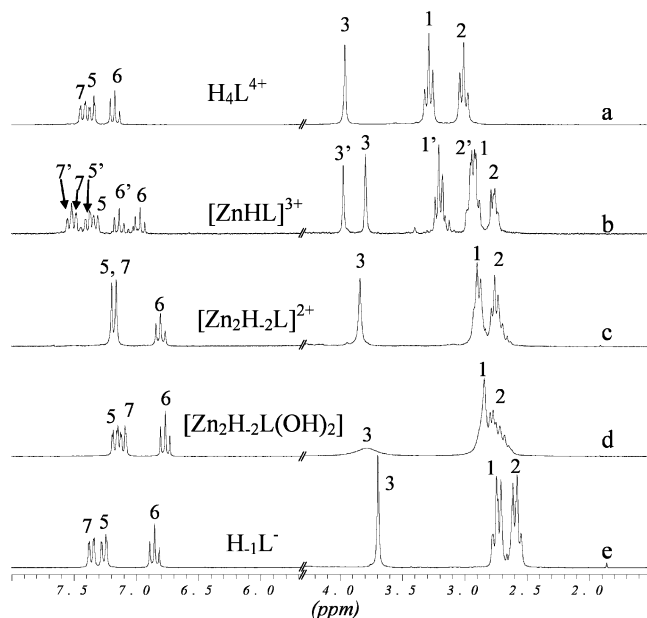


Figure 6. ^1H NMR spectra in aqueous solution of: **L** at pH = 4.5 (H_4L^{4+} species) (a), Zn/**L** system of 1:1 molar ratio at pH = 6.5 ($[\text{ZnHL}]^{3+}$ species) (b), Zn/**L** system of 2:1 molar ratio at pH = 8.2 ($[\text{Zn}_2\text{H}_2\text{L}]^{2+}$ species) (c), Zn/**L** system of 2:1 molar ratio at pH = 12 ($[\text{Zn}_2\text{H}_2\text{L}(\text{OH})_2]$ species) (d), and **L** at pH = 12 (H_-1L^- species) (e).

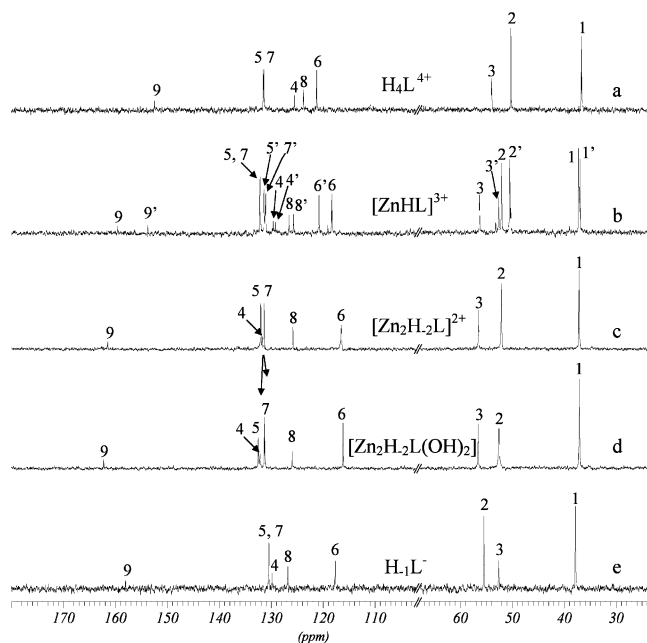


Figure 7. ^{13}C NMR spectra in aqueous solution of: **L** at pH = 4.5 (H_4L^{4+} species) (a), Zn/**L** system of 1:1 molar ratio at pH = 6.5 ($[\text{ZnHL}]^{3+}$ species) (b), Zn/**L** system of 2:1 molar ratio at pH = 8.2 ($[\text{Zn}_2\text{H}_2\text{L}]^{2+}$ species) (c), Zn/**L** system of 2:1 molar ratio at pH = 12 ($[\text{Zn}_2\text{H}_2\text{L}(\text{OH})_2]$ species) (d), and **L** at pH = 12 (H_-1L^- species) (e).

resonances, due to the dinuclear species, with those of the $[\text{ZnHL}]^{3+}$ species, which never affected the ratio of the $[\text{ZnHL}]^{3+}$ signals of spectra 7b and 8b. All resonances due to the $[\text{ZnHL}]^{3+}$ species were assigned on the basis of ^1H – ^1H and ^1H – ^{13}C two-dimensional correlation experiments and were attributed following the labeling reported in Figure 5a. Analysis of the number of signals attributed to the $[\text{ZnHL}]^{3+}$ species in both ^1H and ^{13}C NMR spectra and their coupling system in the ^1H NMR spectrum reveals that a **L** has a

reduced symmetry in the $[\text{ZnHL}]^{3+}$ species with respect to the expected C_{2v} symmetry shown by the free ligand throughout the pH range on the NMR time scale (see for example the spectra of Figures 6a,e and 7a,e). The ^{13}C NMR spectrum of the $[\text{ZnHL}]^{3+}$ species shows a total of 18 peaks, six of which are due to the aliphatic carbon atoms, at δ 36.9 ppm (ascribed to the carbon atom of the ethylene chain (C1)), and at 37.1 (C1'), 50.4 (C2), 52.0 (C2'), 52.6 (C3), 56.2 (C3'), and 12 due to the BPH aromatic group at δ 118.3 (C6), 120.8 (C6'), 125.6 (C8'), 126.5 (C8), 129.1 (C4'), 129.6 (C4), 131.0 and 131.4 (C5 and C7), 132.1 and 132.2 (C5' and C7'), 153.7 (C9'), and 159.6 ppm (C9). Instead, the free ligand shows, throughout the range of pH, a total of nine peaks (see Figure 7a,d) of which three are due to the aliphatic and six to the aromatic carbon atoms. This reduced symmetry in the $[\text{ZnHL}]^{3+}$ species can be attributed to the loss of the symmetry plane passing through the C–C interannular bond of the BPH group and cutting **L** into two **L2** subunits which become inequivalent in the $[\text{ZnHL}]^{3+}$ species with respect to their equivalence in the free **L**, on the NMR time scale. The presence of only two resonances for the two ethylene chains of each dien subunit shows that the other symmetry plane containing the two nitrogen atoms in benzyl position is preserved. In other words, the $[\text{ZnHL}]^{3+}$ species shows a reduced C_s symmetry on the NMR time scale in that the two **L2** subunits of **L** are not equivalent; this can be explained taking into account, as mentioned above, that one subunit is involved in the coordination of Zn(II) while the other one is involved in the stabilization of the acidic protons in a similar arrangement to that schematically reported in Figure 5a. The ^1H NMR spectrum of the $[\text{ZnHL}]^{3+}$ species and its comparison with that of the free ligand (Figure 6a,b) support this hypothesis; in the $[\text{ZnHL}]^{3+}$ species the two phenol groups once again behave independently as underlined by the number of resonances and their coupling systems exhibited by the aromatic protons at δ 7.52 ppm (integrating for one H, dd, $J_1 = 7.6$ Hz, $J_2 = 1.6$ Hz, attributed to $\text{H}^{7'}$), 7.49 (1H, dd, $J_1 = 7.5$ Hz, $J_2 = 1.5$ Hz, $\text{H}^{7'}$), 7.38 (1H, dd, $J_1 = 7.6$ Hz, $J_2 = 1.6$ Hz, $\text{H}^{5'}$), 7.31 (1H, dd, $J_1 = 7.5$ Hz, $J_2 = 1.5$ Hz, $\text{H}^{5'}$), 7.13 (1H, t, $J = 7.6$ Hz, $\text{H}^{6'}$), 6.96 (1H, t, $J = 7.5$ Hz, $\text{H}^{6'}$), by the two singlets at 3.96 (2H, s, $\text{H}^{3'}$), and 3.78 (2H, s, H^2) ascribed to the benzyl hydrogen atoms and by the more complex patterns at 3.19 (2H, t, $J = 6.1$ Hz, $\text{H}^{1'}$), 2.94 (2H, t, $J = 6.1$ Hz, $\text{H}^{2'}$), 2.90 (2H, t, $J = 6.2$ Hz, H^1), 2.74 (2H, t, $J = 6.2$ Hz, H^2) of the ethylene chains of the dien units with respect to only two triplets shown by the free ligand. A more careful analysis permitted us to hypothesize which of the subunits are involved in the coordination of Zn(II), and on this basis the resonances were assigned. The signals due to one subunit are similar in the complex to those of the H_4L^{4+} species (Figure 6a) in which the two aromatic groups of BPH were supposed to be present as phenol and the other four acidic protons located on the four secondary amine groups (see above). The other subunit shows resonances closer to those of the free ligand recorded at pH = 12 in both ^1H and ^{13}C NMR spectra (see Figure 6 and 7); at this pH, the H_-1L^- species is prevalent in solution, and the deprotonation of one of the phenol groups of BPH

was considered. This leads us to suppose that the latter subunit is the one involved in the coordination of Zn(II), stabilizing the metal ion by means of the three amine groups and by a phenolate oxygen atom of BPH, while the first subunit is that bearing protonation showing the other aromatic group as phenol and two secondary ammonium groups as depicted in Figure 5a.

Figures 6c and 7c, respectively, report ^1H and ^{13}C NMR spectra of the system Zn(II)/L in a 2:1 molar ratio recorded at pH = 8.2, where the $[\text{Zn}_2\text{H}_{-2}\text{L}]^{2+}$ species is prevalent in solution. The values and the attribution of the chemical shifts were reported in the experimental section. At first glance, the main difference between Figures 6 and 7 and the previous spectra of the $[\text{ZnHL}]^{3+}$ species is that, in both ^1H and ^{13}C NMR spectra, the $[\text{Zn}_2\text{H}_{-2}\text{L}]^{2+}$ species exhibits a lower number of resonances. This is due to the newly gained higher C_{2v} symmetry mediated on the NMR time scale of the ligand in the complex, the same shown by the free ligand. This can be explained by the higher symmetry of the dinuclear species which can be obtained with a similar coordination environment of both Zn(II) ions in the complex. In the analysis of the shift of the signals with respect to the other species reported in Figures 6 and 7, some aspects should be highlighted. In the ^1H NMR spectrum, the aromatic resonances undergo an upfield shift with respect to those of both the $[\text{ZnHL}]^{3+}$ and H_{-1}L^- species; in particular, the signal of protons H7 and H5 shows a pseudodoublet, H7 exhibits a very high upfield shift, and H6 and H5 shift upfield. All resonances exhibit low values for chemical shift never reached in the free ligand or in the mononuclear complexed species (Figure 6a,e). This can be explained with the complete deprotonation of the BPH unit in the complex affording the diphenolate group; the full deprotonation of BPH produces an increase in the negative charge density in the aromatic rings, shifting the signals of the aromatic protons upfield. It should also be taken into account that the coordination of Zn(II) by the phenolate group causes a decrease in the electronic density which partially compensates this trend.³⁶ The aliphatic resonances show a small downfield shift in the $[\text{Zn}_2\text{H}_{-2}\text{L}]^{2+}$ species produced by the presence of the coordinated Zn(II) ions with respect to the free ligand at alkaline pH, while they show chemical shift values similar to those of the subunit involved in the Zn(II) coordination in the $[\text{ZnHL}]^{3+}$ species. This highlights that the coordination of metal ions such as Zn(II), as usually noted, does not deeply affect the ^1H NMR chemical shifts of the coordinated ligand and in particular of the dien unit.³⁷

The deprotonation of both phenol groups of BPH is supported by the shift in the aromatic carbon atoms observed; in particular the signals of C9, in α -position to the phenolic oxygen atom, as well as C8 and C4 shift downfield while C6 shifts upfield with respect to both the H_{-1}L^- and

$[\text{ZnHL}]^{3+}$ species in which only one phenolate group is present. These shifts are in agreement with a further deprotonation of the phenolic function.^{15b,36a} The presence of the two Zn(II) ions affects the ^{13}C aliphatic resonances of the dien units with respect to the free H_{-1}L^- species (Figure 7c,e). The shift shown is similar to that reported for the dien units involved in the stabilization of Zn(II), and it is mainly highlighted by the upfield shift exhibited by C2 in the $[\text{Zn}_2\text{H}_{-2}\text{L}]^{2+}$ species;^{37,38} the carbon signal of C3 instead shifts downfield with respect to the H_{-1}L^- species due to its benzyl position to the phenol group which once again experiences the deprotonation of the phenol functions.^{16b} However, as in the ^1H NMR spectrum, the aliphatic resonances of the aliphatic carbon atoms preserve a similar chemical shift of the subunit involved in Zn(II) coordination in the $[\text{ZnHL}]^{3+}$ species.

Figures 6d and 7d report the ^1H and ^{13}C NMR spectra of the Zn(II)/L system in a 2:1 molar ratio recorded at pH = 12, where the $[\text{Zn}_2\text{H}_{-2}\text{L}(\text{OH})_2]$ species is prevalent in solution, respectively. As is possible to note, the C_{2v} symmetry is preserved, at least in the ^{13}C NMR spectrum which shows a total of nine resonances for the carbon atoms of L. The ^{13}C NMR spectrum substantially preserves the same chemical shift of the signals shown in the $[\text{Zn}_2\text{H}_{-2}\text{L}]^{2+}$ species in both the aromatic and aliphatic parts; this suggests a similar involvement of L in the coordination of Zn(II) ions for both species. The ^1H NMR spectrum shows a small upfield shift of all resonances, with respect to those of the $[\text{Zn}_2\text{H}_{-2}\text{L}]^{2+}$ species, a broadening of the signal of the protons in the benzyl position and a resolution of the casual equivalence of the H7 and H5 signals which once again exhibit a doublet of doublets. As expected, ^1H NMR is more sensitive than ^{13}C NMR to the reduced positive charge in the $[\text{Zn}_2\text{H}_{-2}\text{L}(\text{OH})_2]$ species with respect to $[\text{Zn}_2\text{H}_{-2}\text{L}]^{2+}$; this affects all parts of the ligand rather than one part of it, leading us to suppose that, as previously suggested, this species is produced by the insertion of two hydroxide anions each of which is coordinated to one Zn(II) center and not by a deprotonation process occurring to the BPH unit. The ^1H and ^{13}C NMR spectra recorded at pH = 10.3, at which the $[\text{Zn}_2\text{H}_{-2}\text{LOH}]^+$ species is prevalent in solution but in coexistence with the $[\text{Zn}_2\text{H}_{-2}\text{L}]^{2+}$ and $[\text{Zn}_2\text{H}_{-2}\text{L}(\text{OH})_2]$ species (Figure 4a), show similar spectral behavior, both in chemical shifts and related symmetry (C_{2v}), to that of the previous dinuclear species discussed. This highlights that all dinuclear species exchange quickly on the NMR time scale and once again that the $[\text{Zn}_2\text{H}_{-2}\text{LOH}]^+$ species does not show a modified molecular skeleton with respect to that previously discussed.

In conclusion, the NMR experiments performed support that in the Zn/L dinuclear species the BPH unit is fully deprotonated, as also suggested by the potentiometric and solid-state studies, and thus it can be safely hypothesized that the dinuclear species present in solution are $[\text{Zn}_2\text{H}_{-2}\text{L}]^{2+}$, $[\text{Zn}_2\text{H}_{-2}\text{L}(\text{OH})]^+$, and $[\text{Zn}_2\text{H}_{-2}\text{L}(\text{OH})_2]$ in which the BPH shows two phenolate groups. In this way, each Zn(II) ion is coordinated by the three amine functions of the dien unit

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and by an oxygen atom of the phenolate moiety closest to the dien unit; to complete its coordination requirement, each Zn(II) adds a water molecule in the $[\text{Zn}_2\text{H}_{-2}\text{L}]^{2+}$ species by forming the $[\text{Zn}_2\text{H}_{-2}\text{L}(\text{H}_2\text{O})_2]^{2+}$ species in a similar environment to that depicted in Figure 5b. The bound water molecules undergo deprotonation to form the $[\text{Zn}_2\text{H}_{-2}\text{L}(\text{OH})(\text{H}_2\text{O})]^+$ and $[\text{Zn}_2\text{H}_{-2}\text{L}(\text{OH})_2]$ species at highly alkaline pH.

Concluding Remarks. The new ligand **L** shows two dien units separated by a BPH binding aromatic spacer, and can also be described as deriving from two assembled **L2** subunits as well as from **L1** by separating the two dien units with a larger aromatic spacer. Analysis of the acid–base properties of **L** in aqueous solution showed the addition up to five acidic protons to the neutral ligand and the permanence of an acidic proton on the BPH unit also at highly alkaline pH. The species present at highly alkaline pH is the H_{-1}L^- anionic species in which the BPH moiety shows one phenol and one phenolate function, while the $\text{H}_{-2}\text{L}^{2-}$ dianionic species, with the fully deprotonated BPH, was not detected under our experimental conditions.

The ligand is able to form mono- and dinuclear complexed species with Cu(II) and Zn(II) metal ions. The BPH moiety is involved in metal coordination and stabilizes metal ions by coordinating them through only one oxygen atom of its phenolic groups. **L** behaves as a compartmental ligand in which two **L2** subunits can be retrieved, each of them behaving independently in metal ion coordination as well as in proton addition. The only contact between the two subunits is established by the two phenolic functions and by hydrogen contacts formed in that area. This compartmental behavior was highlighted by the analysis of the stability constants as well as by the two crystal structures reported here and by the NMR studies carried out on the Zn(II)/**L** system.

In the complexed species, each M(II) ion is coordinated in a similar coordination environment; in particular, each metal is coordinated by a dien unit and by an oxygen atom of the BPH function. The different binding properties of Cu(II) and Zn(II) affect the dinuclear species formed; Zn(II) much more promotes the deprotonation of both phenol groups of BPH compared with Cu(II). This influences the angle between the phenyl rings which can increase or decrease depending on the protonation state of the phenolic oxygen atoms and thus on the M(II) chosen. It is obvious that the complete deprotonation of the BPH moiety, i.e., two phenolate groups, gives rise to a larger angle between the two aromatic rings due to the electrostatic repulsion between the two negatively charged oxygen atoms while a partial deprotonation of BPH, one phenol and one phenolate group, reduces the angle between the phenyl rings by the formation of a strong H-bond interaction involving the phenolic and the phenolate oxygen atoms. The variation of the angle influences the distance between the two metal centers which is longer in the case of the Zn(II) with respect to the Cu(II) dinuclear species. This aspect is highlighted in the solid state by the two reported crystal structures in which the Cu(II) dinuclear species shows a shorter Cu(II)–Cu(II) distance with respect to that between the two Zn(II) ions in the same charged Zn(II) dinuclear species. In other words, the Zn(II),

by more easily promoting the formation of a diphenolate moiety, gives rise to a longer M(II)–M(II) distance with respect to the Cu(II) system in which the deprotonation of only one phenol group of BPH occurs. The reason for this different behavior of BPH is difficult to ascertain, and only some considerations can be made; the first is that Zn(II) usually easily promotes the deprotonation of acidic protons bound to oxygen atoms involved in Zn(II) coordination, as seen in the mechanisms of many biological functions such as carbonic anhydrase or alkaline phosphatase. Another reason could be the stronger tendency of Cu(II) to bridge the oxygen atom of a hydroxyl function that in this case can be favored by the permanence of one hydrogen on the BPH function. However, this different behavior of Cu(II) and Zn(II) in the dinuclear species is an important aspect as are the properties of this ligand permitting modulation of the distance between two metal ions simply by changing the metal. Moreover, the distance was found to be even greater with respect to ligands similar to **L1**, which was one of the aims of this study. In addition, the two **L2** subunits do not saturate the coordination requirement of the coordinated M(II) ion which is thus prone to add exogenous ligands that in this case are hydroxide or water molecules. In the case of $\text{M} = \text{Cu(II)}$, the shorter distance makes it possible to add guests such as OH^- in a bridge disposition between the two Cu(II) ions, while for $\text{M} = \text{Zn(II)}$ the longer distance prevents this. In the latter situation, simple guests showing two lone pairs on the same donor atom, such as water or OH^- , are not able to bridge the two Zn(II) ions, and the dinuclear species must host two of these guests, one for each Zn(II), to satisfy the coordination requirement of both Zn(II) ions. However, the dinuclear species is prone to host one guest in a bridge disposition, but only a guest showing two donor groups at a distance able to fit the higher metal–metal distance.

The present studies on the dinuclear species formed by **L** have highlighted their potential to act as metalloceptors for external species in solution. Therefore, it will be of interest to study the hosting properties of the dinuclear species toward guests, particularly those of biological relevance, such as carboxylate or others containing phosphate groups such as ATP, ADP, or the series of glucose-phosphates, to test not only the capacity of the dinuclear species to bind these guests but also to selectively bind them. Such selectivity should be retrieved in the better fitting between the distance of the metal centers and the donor groups of the guest. Seen from this standpoint, it will also be interesting to compare the hosting properties of the **L** and **L1** dinuclear species toward the same guests.

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Supporting Information Available: Listings of tables of crystallographic data, positional parameters, isotropic and anisotropic thermal factors, and bond distances and angles in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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