*Inorg. Chem.* **2007**, *46*, 4737–4748

Inorganic Chemistry
Article

# A New Branched Phenanthroline Derivative Ligand: Synthesis, Solution Chemistry, and Crystal Structures of Copper(II) and Zinc(II) Complexes

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Received January 31, 2007

The synthesis and characterization of the new ligand 2,9-bis[*N*,*N*-bis(2-aminoethyl)aminomethyl]-1,10-phenanthroline (**L**) are reported. **L** contains two diethylenetriamine units connected on the central nitrogen atom by a 1,10-phenanthroline group forming a symmetrical branched ligand. The basicity and binding properties of **L** toward Cu(II) and Zn(II) in aqueous solution were determined by means of potentiometric, UV–vis, fluorescence, and $^1$H and $^{13}$C NMR techniques. **L** behaves as pentaprotic base under the experimental conditions used; from $\mathrm{H}\mathbf{L}^+$ to $\mathrm{H_4}\mathbf{L}^{4+}$ species it is the secondary amine functions that are protonated while in the $\mathrm{H_5}\mathbf{L}^{5+}$ species also the phenanthroline is involved in protonation. **L** does not show fluorescence properties in the range of pH (0–14) investigated. It forms both mono- and dinuclear stable species where the phenanthroline is directly involved with both nitrogens in the coordination of the first metal which is coordinated in a pentacoordination environment also by one dien unit. The other dien unit undergoes easy protonation in the mononuclear complex while it binds the second metal in the dinuclear species. For this reason, **L**, in providing two different binding areas for metal coordination, behaves as an unsymmetrical compartmental ligand; one area is formed by one dien unit and by the phenanthroline, and the other by the remaining dien unit. This produces unsymmetrical metal complexes both for the mono- and dinuclear species; however, the role of the binding areas is fast exchanging in aqueous solution, at least on the NMR time scale. Solution studies and the three crystal structures of the $[\mathrm{Zn(H_2}\mathbf{L})]^{4+}$, $[[\mathrm{Cu(H_2}\mathbf{L})](\mathrm{ClO_4})]^{3+}$, and $[[\mathrm{Cu_2}\mathbf{L}\mathrm{Cl_2}](\mathrm{ClO_4})]^+$ species highlight the unsymmetrical compartmental behavior of **L** as well as the host properties of the complexes in adding exogenous ligands such as hydroxide, pherchlorate, and chloride anions.

## Introduction

Due to their countless possible applications, both into theoretical and practical fields, there has been a continuous scientific interest in the use of polynuclear metal complexes as model systems for biological substrates, devices for hosting small molecules or ions, catalysts, sensor devices, and others.[1−4]

The most commonly investigated polynuclear complexes are those formed by two metal ions and, in particular, by

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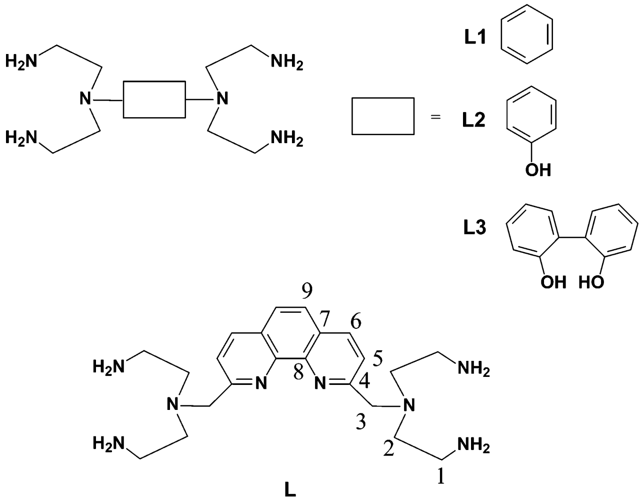
10.1021/ic070184j CCC: $37.00

two transition or post-transition metals placed in close proximity.[5,6] What is more, these metal systems have attracted ever more due to the key roles they can play in the selective recognition, activation, or assembly of external species.[7−11] New horizons in the use of the dinuclear metal complexes have opened up thanks to the better understanding we now have of the processes, reactivities, and structures of biological functions. Indeed, many of these are based on transition metal centers which in many cases cooperate with each other, thus inspiring chemists to produce synthetic metal receptors mimicking an active site and/or reproducing a biological activity.[12,13] In polynuclear metalloreceptors, the distance between the metals is crucial to allow the cooperation of the metal ions in forming the active center, but the coordination sphere of each metal as well as its nature is also important in determining a specific function or activity. For example, it has been demonstrated that the two Ni(II) metal ions forming the catalytic center of urease show a different coordination environment and this is the key for the activity of the enzyme.[14]

**Chart 1.** Schematic Drawing of Ligands with **L** Labeling for the NMR Resonances



In our group, we find the use of polyamine ligands attractive because, depending on their protonation state, i.e., the solution pH, they can turn their binding ability from anions to metal cations, in some cases modulating also the number of both anion or metal cations coordinated.[15] Recently, we synthesized a series of branched ligands showing two triamine dien units separated by an aromatic spacer having (or not having) binding properties (Chart 1); these ligands are able to form dinuclear metal complexes in which both metals show a similar coordination environment.[16] In this case, we planned the design of a new molecule able to form dinuclear metal complexes with transition metal ions in which the two metals show a different coordination environment, i.e., stable unsymmetrical dinuclear metal complexes. To do this, we inserted a new aromatic spacer, the 1,10-phenanthroline unit, to separate the two dien subunits obtaining the new ligand 2,9-bis[*N*,*N*-bis(2-aminoethyl)aminomethyl]-1,10-phenanthroline (**L**) reported in Chart 1. The 1,10-phenanthroline group is frequently used as binding unit because, in addition to the photochemical properties typical of this heterocycle, it provides further and different binding sites; for this reason, several examples of ligands joining polyamine groups to 1,10-phenanthroline have been prepared and studied.[17,18] The spatial position of the aromatic donor nitrogen atoms should prevent the simultaneous involvement of the phenanthroline unit in binding two metal ions and the subsequent obtaining of symmetrical dinuclear complexes.

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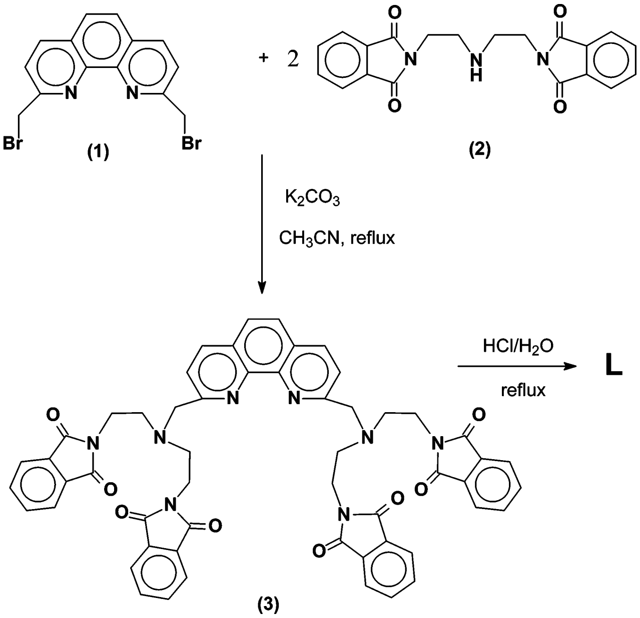
**Scheme 1.** Synthetic Route to the Preparation of Ligand **L**



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 mono- and dinuclear species obtained with Zn(II) and Cu(II) is 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.

**Synthesis.** Compound **L** was obtained according to the synthetic pathway reported in Scheme 1. 2,9-Bis(bromomethyl)-1,10-phenanthroline (**1**) and *N*,*N*-bis(2-phthalimidoethyl)amine (**2**) were prepared as previously described.[19,20] All other chemicals were purchased, using the highest quality commercially available. All solvents were RP grade unless otherwise indicated.

**2,9-Bis[(*N*,*N*-bis(2-phthalimidoethyl)amino)methyl]-1,10-phenanthroline (3).** A solution of 250 cm$^3$ of $CH_3CN$ containing **1** (2.2 g, 6 mmol) was added dropwise to a suspension of *N*,*N*-bis(2-phthalimidoethyl)amine (**2**) (4.4 g, 12 mmol) and $K_2CO_3$ (16.6 g, 0.12 mol) in 800 cm$^3$ of $CH_3CN$ at reflux under nitrogen. The reaction mixture was stirred for a further 4 h. The solvent was removed under reduced pressure and the solid residue treated with $CHCl_3$. The suspension obtained was filtered to remove the inorganic solid, and the organic phase was evaporated under reduced pressure. The solid residue was purified by chromatography on activated alumina (10% water) by eluting with a $CH_2Cl_2$/$CHCl_3$ (3:1) mixture, obtaining **3** as a yellow solid (2 g, 36%). $^1$H NMR ($CDCl_3$; 25 °C) [$\delta$ (ppm)]: 2.96 (t, 8H); 3.83 (t, 8H); 4.27 (s, 4H); 7.47 (d, 2H); 7.52 (s, 2H); 7.62 (d, 2H); 7.68 (m, 16H). $^{13}$C NMR ($CDCl_3$; 25 °C) [$\delta$ (ppm)]: 35.8; 52.3; 60.8; 122.0; 123.0; 125.8; 127.6; 132.3; 133.7; 136.1; 144.9; 160.2; 168.1. Anal. Calcd for $C_{54}H_{42}N_8O_8$: C, 69.67; H, 4.55; N, 12.04. Found: C, 69.7; H, 4.7; N, 11.9.

**2,9-Bis[(*N*,*N*-bis(2-aminoethyl)amino)methyl]-1,10-phenanthroline (L)·6HCl.** **3** (0.93 g, 1 mmol) was suspended in a mixture of 20 cm$^3$ of HCl (37%) and 7 cm$^3$ of water. The reaction was refluxed under vigorous stirring for 16 h and then cooled and filtered. The solid residue was washed with a mixture of 20 cm$^3$ of water and 2 cm$^3$ of HCl (37%), and the aqueous solutions were collected and concentrated under reduced pressure up to 10 cm$^3$. By addition of a few drops of ethanol, a white solid precipitated, which was filtered off, washed with ethanol, and dried under vacuum. The product was recrystallized from an ethanol/water/HCl mixture obtaining it as hexahydrocloride salt **L**·6HCl (0.54 g, 86%). $^1$H NMR ($D_2O$; pH = 3; 25 °C) [$\delta$ (ppm)]: 3.19 (t, 8H); 3.34 (t, 8H); 4.54 (s, 4H); 8.28 (d, 4H); 8.96 (d, 2H). $^{13}$C NMR ($D_2O$; pH = 3; 25 °C) [$\delta$ (ppm)]: 36.1; 50.8; 57.3; 124.8; 127.4; 129.5; 137.5; 142.7; 156.4. Anal. Calcd for $C_{22}H_{40}Cl_6N_8$ (**L**·6HCl): C, 41.99; H, 6.41; N, 17.81. Found: C, 42.1; H, 6.5; N, 17.7.

**$[Zn(H_2L)](ClO_4)_4 \cdot 1.5H_2O$ (4).** A sample of $Zn(ClO_4)_2 \cdot 6H_2O$ (18.6 mg, 0.05 mmol) in water (15 cm$^3$) was added to an aqueous solution (15 cm$^3$) containing **L**·6HCl (31 mg, 0.05 mmol). The pH of the resulting solution was adjusted to 6 with 0.1 M NaOH and saturated with solid $NaClO_4$. After a few minutes, **4** precipitated as a microcrystalline colorless solid (40 mg, 89%). NMR $^1$H NMR ($D_2O$, pH = 6.2, 25 °C): $\delta$ 3.12 (16H, b, H$^1$ and H$^2$), 4.46 (4H, b, H$^3$), 8.13 (2H, b, H$^6$), 8.22 (2H, s, H$^9$), 8.84 (2H, d, $J$ = 4.2 Hz, H$^5$). $^{13}$C NMR ($D_2O$, pH = 6.2, 25 °C): $\delta$ 37.8 (C1), 52.6 (C2), 59.1 (C3), 124.0 (C6), 126.8 (C5), 128.5 (C7), 139.6 (C8), 141.5 (C9), 158.8 (C4). Anal. Calcd for $C_{22}H_{39}Cl_4N_8O_{17.5}Zn$: C, 29.27; H, 4.35; N, 12.41. Found: C, 29.4; H, 4.4; N, 12.5. Crystals suitable for X-ray analysis were obtained by slow evaporation of an aqueous solution containing **4**.

**$[Cu(H_2L)](ClO_4)_4 \cdot 3H_2O$ (5).** This compound was synthesized from L·6HCl (31 mg, 0.05 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (18.5 mg, 0.05 mmol) by following the same procedure reported for **4**, obtaining **5** as blue microcrystals (43 mg, 93%). Anal. Calcd for $C_{22}H_{42}Cl_4CuN_8O_{19}$: C, 28.48; H, 4.56; N, 12.08. Found: C, 28.3; H, 4.5; N, 11.9. Crystals suitable for X-ray analysis were obtained by slow evaporation of an aqueous solution containing **5**.

**$[Cu_2(L)Cl](ClO_4)_3$ (6).** This compound was synthesized from **L**·6HCl (31 mg, 0.05 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (37 mg, 0.1 mmol) by following the same procedure reported for **4**, obtaining **6** as blue microcrystals (32 mg, 73%). Anal. Calcd for $C_{22}H_{34}Cl_4Cu_2N_8O_{12}$: C, 30.32; H, 3.93; N, 12.86. Found: C, 30.3; H, 4.1; N, 12.7.

Crystals suitable for X-ray analysis were obtained by slow evaporation of an aqueous solution containing **6**.

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**Table 1.** Crystal and Structure Refinement Data for **4**−**6**

| param | **4** | **5** | **6** |
|---|---|---|---|
| chem formula | $[Zn(H_2\mathbf{L})](ClO_4)_4{\cdot}1.5H_2O$ | $[Cu(H_2\mathbf{L})](ClO_4)_4{\cdot}3H_2O$ | $[Cu_2(\mathbf{L})Cl](ClO_4)_3$ |
| $M_r$ | 902.78 | 927.98 | 871.45 |
| cryst system, space group | triclinic, $P\bar{1}$ | triclinic, $P\bar{1}$ | monoclinic, $P2_1/a$ |
| cell params (Å, deg) | $a = 10.225(6)$, $\alpha = 102.033(7)$ | $a = 9.4067(7)$, $\alpha = 77.837(5)$ | $a = 17.493(6)$ |
|  | $b = 15.880(1)$, $\beta = 100.026(6)$ | $b = 9.6940(6)$, $\beta = 80.571(6)$ | $b = 10.969(4)$, $\beta = 114.08(3)$ |
|  | $c = 24.179(2)$, $\gamma = 105.365(7)$ | $c = 20.412(1)$, $\gamma = 85.084(5)$ | $c = 18.647(5)$ |
| $V$ (Å$^3$) | 3591(2) | 1792.5(2) | 3266.6(19) |
| $Z$ | 4 | 2 | 4 |
| $D_x$ (g cm$^{-3}$) | 1.670 | 1.719 | 1.772 |
| $\lambda$ (Å) | 0.710 69 | 0.710 69 | 0.710 69 |
| $\mu$ (mm$^{-1}$) | 1.066 | 0.998 | 1.701 |
| temp (K) | 298 | 120 | 298 |
| reflcns collcd/unique | 28 196/11 513 [R(int) = 0.0685] | 29 194/11 315 [R(int) = 0.0351] | 4496/1945 [R(int) = 0.0947] |
| refinement method | full-matrix least squares on $F^2$ | full-matrix least squares on $F^2$ | full-matrix least squares on $F^2$ |
| data/params | 11 513/935 | 11 315/655 | 1945/263 |
| final R indices [$I > 2\sigma(I)$] | R1 = 0.0800, wR2 = 0.1840 | R1 = 0.0434, wR2 = 0.0966 | R1 = 0.0971, wR2 = 0.2161 |
| R indices (all data) | R1 = 0.2131, wR2 = 0.2263 | R1 = 0.0730, wR2 = 0.1062 | R1 = 0.1397, wR2 = 0.2483 |

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

**X-ray Crystallography.** For compounds **4**−**6** intensity data were collected on an Oxford Diffraction Xcalibur diffractometer equipped with a CCD area detector, using Mo Kα radiation (0.7107 Å), monochromated with a graphite prism. Data were collected through the CrysAlis CCD program,[21] and the reduction was carried out with the CrysAlis RED program.[22] Absorption correction was performed with the ABSPACK program in CrysAlis RED for compounds **4** and **5** and through the SADABS program[23] for compound **6**. Structures were solved with the direct methods of the SIR97[24] package and refined by full-matrix least squares against $F^2$ with the SHELX97 program.[25]

Geometrical calculations were performed by PARST97,[26] and molecular plots were produced by the ORTEP3 program.[27]

In **4**, whose asymmetric unit contains two independent molecules (a and b), atom N(7b) occupies two different positions both with population parameters 0.5; thus, N(7b), C(19b), and C(20b) were refined isotropically while all the other non-hydrogen atoms were refined anisotropically. All the ligand hydrogen atoms, with the exception of those linked to N(7b), C(19b), and C(20b), were introduced in calculated position and their coordinates as well as their temperature factors were refined accordingly to the linked atoms. Water molecules hydrogen atoms were not introduced.

In compound **5** all the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were found in the Fourier difference map and refined isotropically.

Concerning compound **6**, notwithstanding the many efforts to grow crystals of good quality for X-ray analysis, the latter did not diffract much, and as a consequence, only copper, nitrogen, and chlorine atoms were refined anisotropically because of the otherwise poor ratio collected reflection/refined parameters. Hydrogen atoms were set in calculated position with their coordinates and temperature factors refined accordingly to the bound atoms.

Crystallographic data and refinement parameters for compounds **4**−**6** are reported in Table 1. Table 2 lists selected bonds lengths and angles concerning the coordination sphere of the metal complexes of **4**−**6**.

**EMF Measurements.** Equilibrium constants for protonation and complexation reactions with **L** were determined by pH-metric measurements (pH = −log [H$^+$]) in 0.15 M $NMe_4Cl$ at 298.1 ± 0.1 K, using fully automatic equipment that has already been described;[16a] the EMF data were acquired using the PASAT computer program.[28] The combined glass electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with $CO_2$-free $NMe_4OH$ solutions and determining the equivalent point by Gran's method,[29] which gives the standard potential $E°$ and the ionic product of water (p$K_w$ = 13.83(1) at 298.1 K in 0.15 M $NMe_4Cl$, $K_w = [H^+][OH^-]$). 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.[30]

**NMR and UV−Vis Experiments.** $^1$H 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-ethandiol as calibration sample. For the spectra recorded in $D_2O$, the peak positions are reported with respect to HOD (4.75 ppm) for $^1$H NMR spectra, while dioxane was used as reference standard in $^{13}$C NMR spectra ($\delta$ = 67.4 ppm). For the spectra recorded in $CDCl_3$ the peak positions are reported with respect to TMS. Fluorescence spectra were recorded at 298 K with Varian Cary Eclipse spectrofluorometer. UV absorption spectra were recorded at 298 K with a Varian Cary-100 spectrophotometer equipped with a temperature control unit. The binding of **L** and M(II) ions was also studied in aqueous 0.05 M MES (2-[*N*-morpholino]ethanesulfonic acid) buffer, pH = 6.1 solution. Buffered MES solution containing M(II) (M = Zn or Cu) was added to the

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(21) *CrysAlis CCD*, version 1.171.pre23_10 beta; Oxford Diffraction Ltd. (release 21.06.2004 CrysAlis171.NET) (compiled Jun 21 2004,12:00:08).

(22) *CrysAlis RED*, version 1.171.pre23_10 beta; Oxford Diffraction Ltd. (release 21.06.2004 CrysAlis171.NET) (compiled Jun 21 2004,12:00:08).

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**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for the Complex Cations **4**−**6**[a]

Bond Lengths

| **4** | | **5** | | **6** | |
|---|---|---|---|---|---|
| Zn(1a)−N(1a) | 2.034(9) | Cu(1)−N(1) | 2.181(2) | Cu(1)−N(1) | 2.06(2) |
| Zn(1a)−N(2a) | 2.018(7) | Cu(1)−N(2) | 2.025(2) | Cu(1)−N(2) | 2.08(2) |
| Zn(1a)−N(3a) | 2.26(1) | Cu(1)−N(3) | 2.079(2) | Cu(1)−N(3) | 2.08(2) |
| Zn(1a)−N(4a) | 1.992(7) | Cu(1)−N(4) | 1.931(2) | Cu(1)−N(4) | 1.94(2) |
| Zn(1a)−N(5a) | 2.19(1) | Cu(1)−N(5) | 2.099(2) | Cu(1)−N(5) | 2.11(2) |
| Zn(1b)−N(1b) | 2.029(9) | | | Cu(2)−Cl(1) | 2.316(6) |
| Zn(1b)−N(2b) | 2.046(8) | | | Cu(2)−N(6) | 2.13(2) |
| Zn(1b)−N(3b) | 2.286(7) | | | Cu(2)−N(7) | 1.94(2) |
| Zn(1b)−N(4b) | 2.034(1) | | | Cu(2)−N(8) | 1.95(2) |
| Zn(1b)−N(5b) | 2.183(6) | | | Cu(2)−Cl(1)′ | 2.682(7) |

Angles

| **4** | | **5** | | **6** | |
|---|---|---|---|---|---|
| N(1a)−Zn(1a)−N(2a) | 119.4(3) | N(1)−Cu(1)−N(2) | 102.82(9) | N(1)−Cu(1)−N(2) | 117.3(8) |
| N(1a)−Zn(1a)−N(3a) | 83.7(3) | N(2)−Cu(1)−N(3) | 85.86(8) | N(1)−Cu(1)−N(3) | 86.6(8) |
| N(1a)−Zn(1a)−N(4a) | 112.5(4) | N(2)−Cu(1)−N(4) | 141.98(8) | N(1)−Cu(1)−N(4) | 120.8(8) |
| N(1a)−Zn(1a)−N(5a) | 107.8(3) | N(2)−Cu(1)−N(5) | 105.87(8) | N(1)−Cu(1)−N(5) | 105.1(8) |
| N(2a)−Zn(1a)−N(3a) | 82.6(3) | N(1)−Cu(1)−N(3) | 83.58(8) | N(2)−Cu(1)−N(3) | 85.1(7) |
| N(2a)−Zn(1a)−N(4a) | 120.7(3) | N(1)−Cu(1)−N(4) | 110.77(8) | N(2)−Cu(1)−N(4) | 118.5(7) |
| N(2a)−Zn(1a)−N(5a) | 108.3(3) | N(1)−Cu(1)−N(5) | 107.39(8) | N(2)−Cu(1)−N(5) | 102.3(7) |
| N(3a)−Zn(1a)−N(4a) | 76.3(4) | N(3)−Cu(1)−N(4) | 80.81(8) | N(3)−Cu(1)−N(4) | 79.8(7) |
| N(3a)−Zn(1a)−N(5a) | 155.7(3) | N(3)−Cu(1)−N(5) | 161.17(7) | N(3)−Cu(1)−N(5) | 160.7(7) |
| N(4a)−Zn(1a)−N(5a) | 79.4(4) | N(4)−Cu(1)−N(5) | 80.97(7) | N(4)−Cu(1)−N(5) | 81.1(7) |
| N(1b)−Zn(1b)−N(2b) | 116.8(3) | | | Cl(1)−Cu(2)−N(6) | 177.3(6) |
| N(1b)−Zn(1b)−N(3b) | 81.6(3) | | | Cl(1)−Cu(2)−N(7) | 94.0(6) |
| N(1b)−Zn(1b)−N(4b) | 118.4(3) | | | Cl(1)−Cu(2)−N(8) | 93.6(6) |
| N(1b)−Zn(1b)−N(5b) | 107.2(3) | | | Cl(1)−Cu(2)−Cl(1)′ | 85.7(2) |
| N(2b)−Zn(1b)−N(3b) | 83.0(3) | | | N(6)−Cu(2)−N(7) | 85.6(8) |
| N(2b)−Zn(1b)−N(4b) | 116.5(3) | | | N(6)−Cu(2)−N(8) | 86.1(8) |
| N(2b)−Zn(1b)−N(5b) | 112.5(3) | | | N(6)−Cu(2)−Cl(1)′ | 97.0(5) |
| N(3b)−Zn(1b)−N(4b) | 76.3(3) | | | N(7)−Cu(2)−N(8) | 158.3(8) |
| N(3b)−Zn(1b)−N(5b) | 154.1(3) | | | N(7)−Cu(2)−Cl(1)′ | 96.7(6) |
| N(4b)−Zn(1b)−N(5b) | 78.1(3) | | | N(8)−Cu(2)−Cl(1)′ | 104.1(5) |

[a] Equivalent position: (prime) −*x*, −*y*, −*z*.

buffered solution containing **L** with up to 3 equiv of M(II) with respect to the amount of **L**.

## Results and Discussion

**Synthesis.** The synthetic pathway used to obtain ligand **L** is outlined in Scheme 1. It consists in attaching two *N*,*N*-bis(2-phthalimidoethyl)amine (**2**) groups to the 2,9-bis(bromomethyl)-1,10-phenanthroline (**1**). The reaction, carried out in refluxing $CH_3CN$ in the presence of $K_2CO_3$ as a base, gave the fully protected intermediate (**3**). The final ligand **L** was obtained by removing the phthaloyl groups using HCl aqueous solution as acidic conditions. After the workup, **L** was further purified as hexahydrochloride salt.

The metal complexes reported can be easily obtained in the solid state by precipitating them from their aqueous solution. The starting materials are **L**·6HCl and M(II) as perchlorate salt; the pH of the solution, containing **L** and M(II) in a correct molar ratio, can be adjusted to the suitable pH values chosen by observing the distribution diagram of the species. Solid $NaClO_4$ can be added to the solution to accelerate the precipitation of the complexes which are always obtained as microcrystalline solid.

**X-ray Solid-State Structures. Mononuclear Complexes. [Zn($H_2$L)]($ClO_4$)$_4$·1.5$H_2O$ (4).** The crystal structure consists of [Zn($H_2$**L**)]$^{4+}$ cations, perchlorate anions, and water solvent molecules. In the asymmetric unit there are two independent complex cations, a and b, which essentially differ for the conformation of the uncoordinated diethylentriamine chain, whose primary nitrogen atoms [N(7) and (N8)] bear the acidic hydrogens. A very weak edge-to-face Ph−Ph interaction exists between the two independent complex cations: the hydrogen bound to the C(7a) (see inset of Figure 1 for atom labeling) is 3.9 Å from the aromatic centroid (M) of the C(9b)−C(17b) ring (the C(7a)−H(7a)−M angle being 164°).

In both the complex cations (Figure 1 shows the type a metal complex) the zinc ion is surrounded by five nitrogen atoms, two of which are provided by the phenanthroline residue and the others by one polyamine arm. The resulting geometry can be described as a distorted trigonal bipyramid [tbp; $\tau^{31}$ indexes 0.58 and 0.60 for a and b, respectively] with the metal cations slightly shifted toward the N(5) atom which, together with the tertiary nitrogen atom N(3), occupies the axial position of both the tbp. It is noteworthy (vide infra) that the distances Zn−axial donors are definitely longer than those with the equatorial nitrogen atoms (see Table 2).

Weak $\pi-\pi$ attractive interactions are present between the phenanthroline rings of symmetry-related [$H_2$**L**Zn]$^{4+}$ complexes (1 − *x*, −*y*, 1 − *z* for type a; 1 − *x*, 1 − *y*, 2 − *z* for type b). The closest 6-ring centroids are 3.8 and 3.9 Å apart for types a and b coupled cations.

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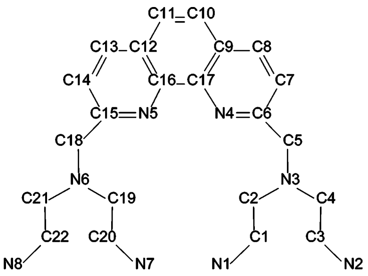

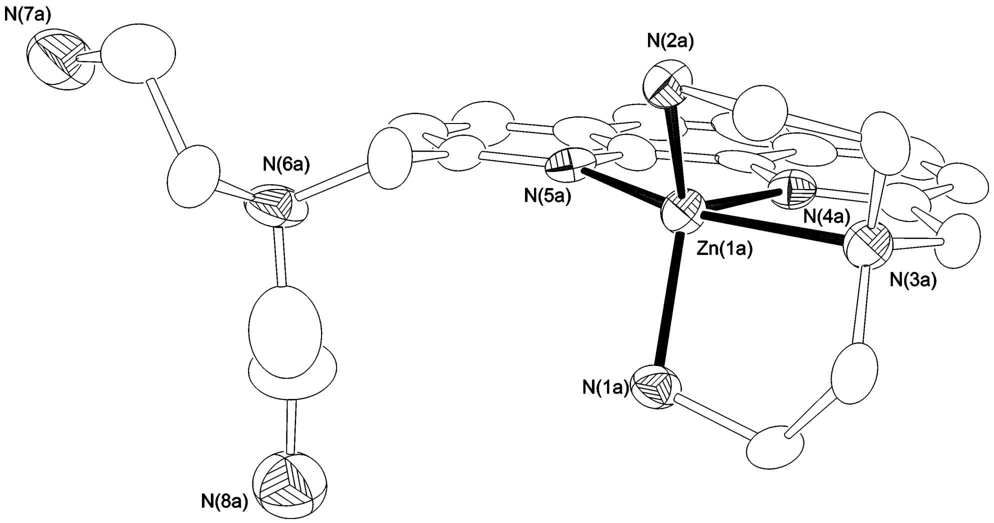

**Figure 1.** Complex cation $[Zn(H_2\mathbf{L})]^{4+}$. Ellipsoids are drawn at 20% probability.

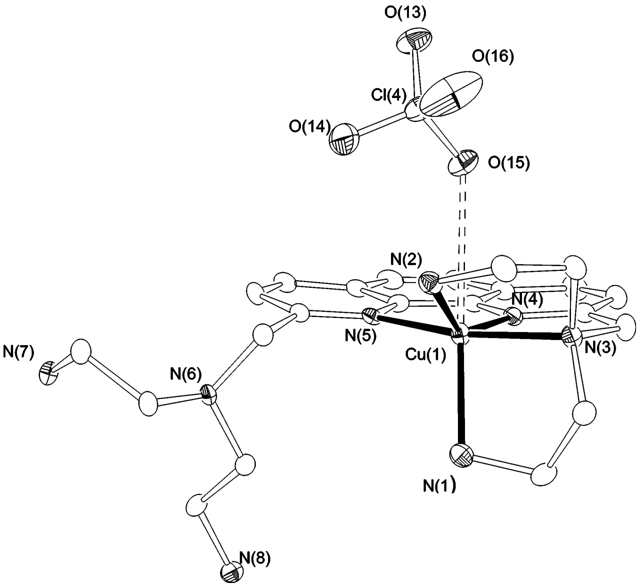

**Figure 2.** Complex cation $[Cu(H_2\mathbf{L})](ClO_4)^{3+}$. Ellipsoids are drawn at 40% probability.

Additionally, in the crystal lattice several H-bond contacts (N···O distances <3.0 Å) exist between the polyammonium groups of the uncoordinated amine arm of each complex cation and the perchlorate counterions as well as the crystallization water molecules. Analogous stabilizing interactions (O···O distances <3.0 Å) involve the latter solvent molecules and the perchlorate anions.

**$[Cu(H_2L)](ClO_4)_4{\cdot}3H_2O$ (5).** In the crystal lattice there are $[Cu(H_2\mathbf{L})]^{4+}$complex cations, perchlorate counterions, and crystallization water molecules. The conformation of the unbound polyamine arm makes the difference between the overall shape of the copper complex in **5** and those types a and b of the corresponding zinc adduct of **4**. The superimposition of the metal−ligands *core* of $[Cu(H_2\mathbf{L})]^{4+}$ and $[Zn(H_2\mathbf{L})]^{4+}$ (types a and b) gives a rms value of 0.19 Å in both cases. The coordination sphere around the copper ion is best described as a square pyramid (sp; $\tau$ index 0.32) with N(1) at the apex, the latter showing the usual axial elongation of the corresponding bond (Figure 2, Table 2). Opposite to the axial donor there is a perchlorate counterion, whose oxygen atom O(15), although definitely quite distant (3.128(2) Å is the Cu(1)−O(15) distance), points straight toward the metal ion (176.34(7)° is the O(15)−Cu(1)−N(1) angle). Thus, the copper ion can be described as 5 + 1 coordinated in a distorted octahedral environment.

Also in this case in the crystal packing there are weak $\pi-\pi$ attractive interactions between the phenanthroline rings; 3.7 Å is the distance between the centroids of the central rings of two symmetry-related complexes ($2 - x$, $1 - y$, $1 - z$).

Short interactions exist between the hydrogen atoms of the polyammonium groups and the oxygen atoms provided by the perchlorate counterions and a crystallization water molecule (N−H···O distances <2.17(2) Å, N−H···O angles >151(2)°). Finally the water solvent molecules act as H-bond donors toward the oxygen atoms of the perchlorate ions (O−H···O distances <2.32(3) Å, O−H···O angles >149(3)°).

**Dinuclear Complex $[Cu_2(L)Cl](ClO_4)_3$ (6).** The ligand **L** in its neutral form coordinates two copper ions (Figure

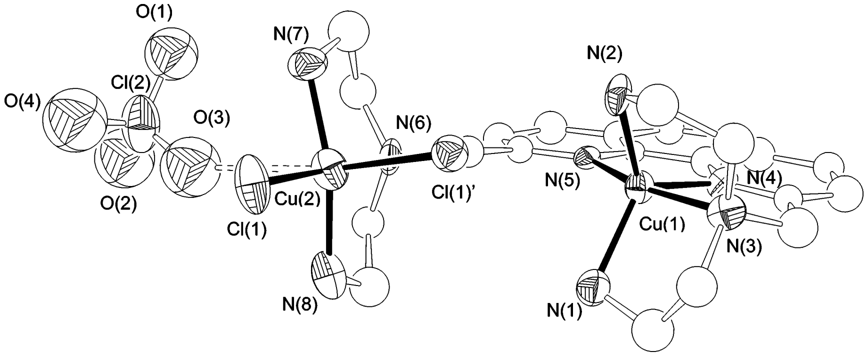

**Figure 3.** Complex cation $[Cu_2(\mathbf{L})Cl_2](ClO_4)^+$. Ellipsoids are drawn at 40% probability.

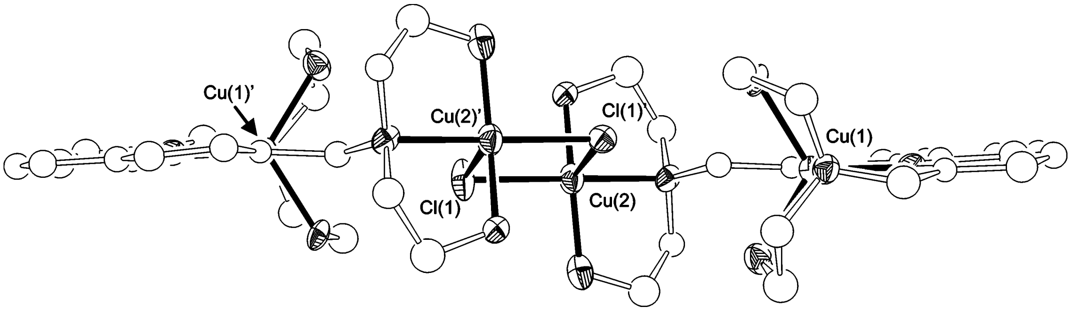

**Figure 4.** Dimer complex in the crystal lattice of **6**. Ellipsoids are drawn at 40% probability.

**Table 3.** Basicity Constants of **L** (log *K*) Measured by Potentiometry in Aqueous Solution at 298.1 ± 0.1 K ($I = 0.15$ mol dm$^{-3}$ $NMe_4Cl$)

| reacn | log *K* |
|---|---|
| $\mathbf{L} + H^+ = H\mathbf{L}^+$ | 10.51(1)[a] |
| $H\mathbf{L}^+ + H^+ = H_2\mathbf{L}^{2+}$ | 9.77(1) |
| $H_2\mathbf{L}^{2+} + H^+ = H_3\mathbf{L}^{3+}$ | 9.24(1) |
| $H_3\mathbf{L}^{3+} + H^+ = H_4\mathbf{L}^{4+}$ | 8.55(2) |
| $H_4\mathbf{L}^{4+} + H^+ = H_5\mathbf{L}^{5+}$ | 2.93(3) |

[a] Values in parentheses are the standard deviation on the last significant figure.

3). The overall shape of the complex around the copper cation labeled Cu(1) is not very different from those already observed in the crystal structures of **4** and **5** (the maximum rms value for the metal−ligand core superimposition is 0.2 Å with the mononuclear copper complex of **5**). At variance with the latter, the coordination sphere of Cu(1) can be described as a tbp ($\tau = 0.67$), with N(5) and N(3) occupying the axial positions. The copper atom Cu(2) is coordinated by the three nitrogen atoms of the other diethylenetriamine arm [N(6), N(7), and N(8)] and by two chloride ions (Cl(1) and Cl(1)′. The latter (reported by $-x$, $-y$, $-z$) occupies the apex of the sp ($\tau = 0.32$) around the metal ion, 2.682(7) Å apart from Cu(2). A sixth donor opposite to Cl(1)′, namely the oxygen atom O(3) provided by a perchlorate ion, even if quite distant, completes the coordination sphere about the metal cation (2.93(3) Å is the Cu−O distance, the angle O(3)−Cu(2)-Cl(1)′ is 168.3(6)°).

The chloride ions Cl(1) and Cl(1)′ both work as bidentate ligands toward Cu(2) and Cu(2)′ (reported by $-x$, $-y$, $-z$), which are held together 3.673(4) Å apart. In this way dimers of the complex cation $[Cu_2\mathbf{L}Cl]^+$ are formed in the crystal lattice (Figure 4). A pseudo symmetry plane can be recognized in the complex as well as in the dimer: this plane contains the phenanthroline moiety and the metal ions together with the coordinated chlorine and oxygen atoms. The four chelating arms of the diethylentriamine moieties are almost perpendicular to this plane. Weak $\pi-\pi$ interactions can be spotted in the crystal lattice: the closest 6-ring centroids are 3.7 Å apart.

As a concluding remark, the metal centers of the mononuclear complexes **4** and **5** and the Cu(1) ion of **6** are coordinated by the two nitrogen atoms provided by the 1,-10-phenanthroline and the three donors provided by one diethylenetriamine arm, forming two coplanar fused five-membered rings having quite acute $N-M^{2+}-N$ angles. Also in this case, as already noticed both in mono- and dinuclear transition metal complexes with 1,10-phenanthroline-bearing chains in 2,9 positions providing additional nitrogen donors,[32−34] the large heteroaromatic moiety stiffens the ligand, usually preventing the simultaneous coordination of both benzylic nitrogens [N(3) and N(6)] and heteroaromatic ones to the same metal ion.

**Solution Studies. Basicity.** The protonation equilibria of **L** were studied by potentiometry in 0.15 M $NMe_4Cl$ aqueous solution at 298.1 K, and the measured basicity constants are reported in Table 3. **L** can bind up to five protons, behaving as a pentaprotic base under the experimental condition employed. The high values of the first four protonation constants clearly indicate that the nitrogen atoms involved in the protonation are the amine functions of the dien units. In fact, all four values are much higher (see Table 3) than

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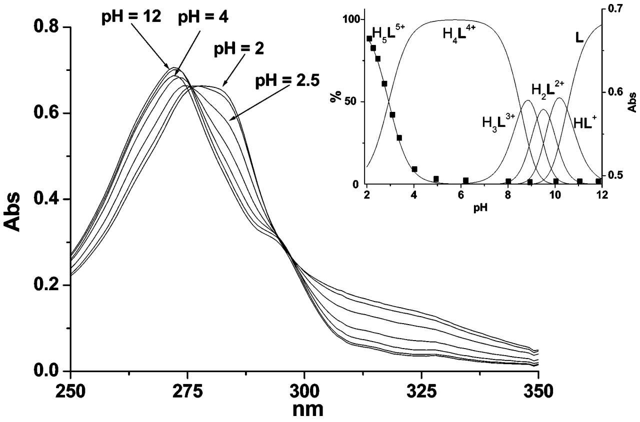

**Figure 5.** Absorption spectra of **L** at different pH values ([**L**] = 2.0 × $10^{-5}$ M). Inset: Absorption titration (■, absorbance at $\lambda = 282$ nm) and distribution curves of the **L** species (line) in aqueous solution at 298.1 K in 0.15 M $NMe_4Cl$.

**Table 4.** Logarithms of the Equilibrium Constants Determined in 0.15 mol dm$^{-3}$ $NMe_4Cl$ at 298.1 K for the Complexation Reactions of **L** with Cu(II) and Zn(II) Ions

| reacn | log *K*<br>M = Cu(II) | <br>M = Zn(II) |
|---|---|---|
| $M^{2+} + \mathbf{L} = M\mathbf{L}^{2+}$ | 20.15(2) | 16.89(2) |
| $M\mathbf{L}^{2+} + H^+ = MH\mathbf{L}^{3+}$ | 9.06(2) | 9.56(1) |
| $MH\mathbf{L}^{3+} + H^+ = MH_2\mathbf{L}^{4+}$ | 8.32(1) | 8.43(1) |
| $MH_2\mathbf{L}^{4+} + H^+ = MH_3\mathbf{L}^{5+}$ | 3.18(4) | 4.14(2) |
| $M\mathbf{L}^{2+} + OH^- = M\mathbf{L}OH^+$ | 1.69(7) | |
| $M\mathbf{L}^{2+} + M^{2+} = M_2\mathbf{L}^{4+}$ | 9.50(3) | 6.10(3) |
| $M_2\mathbf{L}^{4+} + OH^- = M_2\mathbf{L}OH^{3+}$ | 6.90(3) | 5.25(2) |
| $M_2\mathbf{L}OH^{3+} + OH^- = M_2\mathbf{L}(OH)_2{}^{2+}$ | 4.21(5) | 3.61(3) |
| $M_2\mathbf{L}(OH)_2{}^{2+} + OH^- = M_2\mathbf{L}(OH)_3{}^+$ | 3.33(6) | |

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

those reported for the 1,10-phenanthroline (log *K* = 4.89),[35] indicating that its nitrogen atoms are not involved in the first four protonation steps; in addition, they are similar to the first two protonation constants of the dien unit.[36] In other words, the first four protonation steps occur on both dien subunits and the nitrogen atoms involved are the four primary amine functions; in this way, the positive charges are located as far as possible thus minimizing the charge repulsion. The slight decreases in basicity between the successive steps of protonation support this hypothesis. The sharp decrease in basicity in the fifth protonation step indicates that the fifth proton undergoes a strong charge repulsion. The low value of the last protonation constant does not allow us to hypothesize the localization of the fifth acidic proton. UV−vis experiments were performed at different pH values to obtain further information about the fifth protonation step.

It is known that protonation of the aromatic amine nitrogens of 1,10-phenanthroline gives rise to a new red-shifted band in its UV absorption spectrum.[37] In this case, a marked shift of the **L** UV band from 271 to 282 nm is observed below pH = 4 with formation of the pentaprotonated $H_5\mathbf{L}^{5+}$ species (Figure 5). This indicates that the fifth protonation step mainly involves the heteroaromatic nitrogen atoms. The absorption trend at 282 nm is reported as a function of pH together with the distribution diagram of the **L** species in the inset of Figure 5; the figure highlights that, due to protonation, the perturbation of the phenanthroline spectrum occurs with the formation of the $H_5\mathbf{L}^{5+}$ species; similar behavior was observed by Bencini et al. with an amino−phenathroline ligand.[18a] Fluorescence experiments were also carried out in all ranges of pH, but **L** did not show any emission properties under alkaline (up to 1 M NaOH solution) as well as under strong acidic conditions (up to 1 M HCl solution). Many amino ligands containing the phenanthroline unit become emissive at acidic pH but are not fluorescent in the alkaline field of pH.[17c,38] It is known that, in those ligands, emission depends on the degree of protonation of the amine functions in the benzylic position of the aromatic group.[17c,38] The fluorescence of the group is enhanced if these nitrogen atoms are both protonated (ammonium group), while if they have a lone pair (amine function), fluorescence is quenched. In our case, the latter situation should persist also at strongly acidic pH and the presence of at least one lone pair on the amine functions in the benzylic position gives the ligand not fluorescent throughout the pH range investigated.

**Metal Complexes.** The coordination behavior of **L** toward the metal cations Cu(II), and Zn(II) was studied in 0.15 mol dm$^{-3}$ $NMe_4Cl$ aqueous solution at 298.1 K. The stability constants for the equilibrium reactions were potentiometrically determined and are reported in Table 4.

Before discussion of any results, it is necessary to have a clear understanding of the topology of the ligand, which consists of two branched triaminic arms connected by a rigid spacer such as the aromatic 1,10-phenanthroline moiety. The resulting molecule is symmetric with two different kinds of nitrogen donor atoms, three aliphatic nitrogen per side and two aromatic nitrogens belonging to the spacer. In other words, **L** shows plenty of donor atoms for one metal ion to form mononuclear species and enough to fully coordinate two metal ions to form dinuclear species. Indeed, **L** forms mono- and dinuclear species with both the Cu(II) and Zn(II) ions examined. The mononuclear species are virtually the only species existing in aqueous solution when the ligand−metal ratio is 1:1; when the **L**/M(II) molar ratio is 1:2, the mononuclear species remain prevalent in acidic solution while the dinuclear species are prevalent at alkaline pH values. Figure 6 reports the distribution diagrams of the species for the **L**/M(II) system in 1:1 and 1:2 molar ratios as a function of pH.

**Mononuclear Complexes.** **L** forms stable mononuclear complexes with both metal ions examined. In a comparison of the species having the same stoichiometry, the Cu(II)

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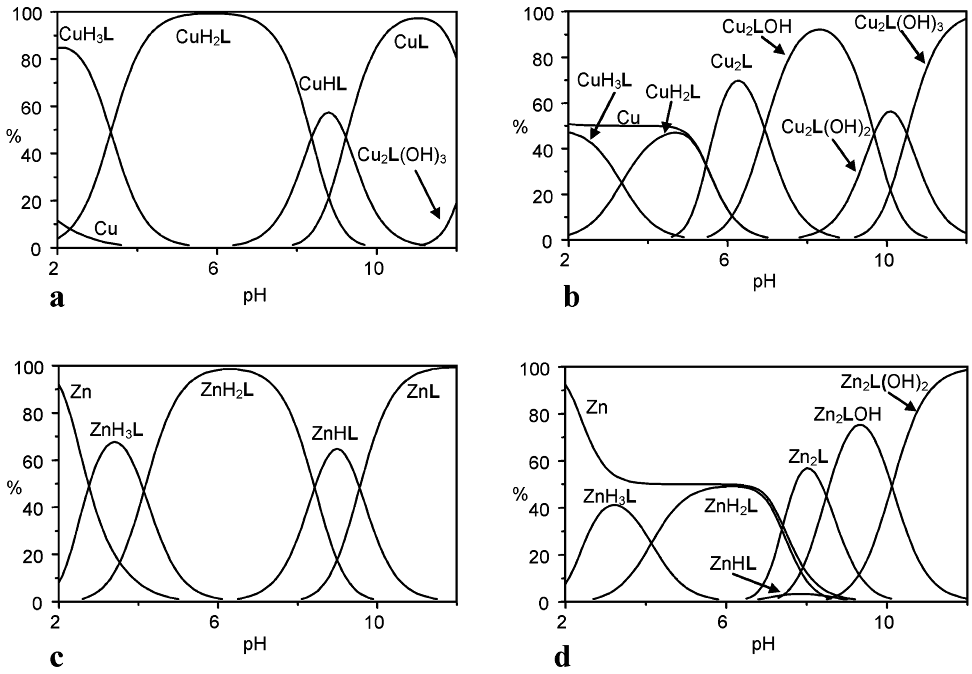

**Figure 6.** Distribution diagrams for the systems **L**/$Cu^{2+}$, (a) ratio 1:1 and (b) ratio 1:2, and **L**/$Zn^{2+}$, (c) ratio 1:1 and (d) ratio 1:2, in aqueous solution 0.15 mol $dm^{-3}$ $NMe_4Cl$ at 298.1 K as a function of pH.

species show higher stability than the Zn(II) ones. The formation constants of the mononuclear $[M\mathbf{L}]^{2+}$ species are very high: log $K = 20.15$ and 16.89 for Cu(II) and Zn(II), respectively. These values are higher with respect to the addition of both M(II) to the dien subunit;[39] thus, M(II) must be coordinated by more than three nitrogen atoms of the dien subunit in each $[M\mathbf{L}]^{2+}$. This consideration is also supported by the lower values of the stability constants reported for ligand **L1** (Chart 1), in which only a dien unit was supposed to be involved in the stabilization of the M(II).[16b]

The mononuclear $[M\mathbf{L}]^{2+}$ species easily undergo protonation; constants for the addition of the two first protons to $[M\mathbf{L}]^{2+}$ forming the $[MH\mathbf{L}]^{3+}$ and $[MH_2\mathbf{L}]^{4+}$ species are very high and, for both metal ions, similar to the values found for the protonation of the $H_2\mathbf{L}^{2+}$ species of the free ligand (see Table 3). All this indicates that the two nitrogen atoms involved in protonation are not involved in metal ion coordination. Only in the third protonation step of the mononuclear species to form $[MH_3\mathbf{L}]^{5+}$ there is a sharp decrease in the protonation constant, log $K = 3.18$ and 4.14 for Cu(II) and Zn(II), respectively, indicating that charge repulsions and/or binding intersection are present.

Considering these data and the molecular framework of **L**, and keeping in mind the two crystal structures of the $[MH_2\mathbf{L}]^{4+}$ species obtained from aqueous solution reported in Figure 1 and 2 (M = Zn(II) and Cu(II), respectively), it is possible to safely affirm that in solution both M(II) ions show the same coordination environment in all mononuclear species; this is the same environment reported in both crystal structures formed by the three nitrogen atoms belonging to one of the dien subunits and by both nitrogen atoms of the phenanthroline unit. The other dien unit is not involved in metal ion coordination and easily undergoes protonation. This quite close coordination environment around Cu(II) and Zn(II) in the mononuclear species affects the poor tendency of $[M\mathbf{L}]^{2+}$ to give hydroxylated species; in fact a $[M\mathbf{L}OH]^{+}$ species with a low $OH^-$ addition constant (log $K = 1.69$) was detected only for the Cu(II) system.

**Dinuclear Complexes.** The dinuclear species are in general quite stable (log $\beta = 29.65$ and 22.99 for Cu(II) and Zn(II), respectively). They are the most important species in solution when the **L**/M(II) ratio is 1:2; under these conditions, the dinuclear species are largely prevalent in aqueous solution at pH values higher than 6.5 or 8 for Cu(II) and Zn(II), respectively (Figure 6b,d). However, although the overall stability of the dinuclear species is rather high, the stepwise addition constant of the second metal ion to the mononuclear species to form the dinuclear one is quite low, being log $K = 9.50$ and 6.10 for Cu(II) and Zn(II), respectively. This indicates that the coordination environment of the second M(II) is not the same as that of the first M(II) or that its addition induces a drastic rearrangement of the mononuclear species. The crystal structure of the $[Cu_2\mathbf{L}]^{4+}$ species (Figure 3) supports the first hypothesis, that is, that the second M(II) is coordinated by a lesser number of donor atoms than the first one. The coordination pattern of the second M(II) is provided by the three nitrogen atoms of the unbound dien subunit of the mononuclear species as shown in both the mononuclear crystal structures reported. The two M(II) ions are thus coordinated in a different way: the first by one of the dien units and by the phenanthroline moiety; the second by the other dien unit, giving rise to unsymmetrical metal complexes in which the two metals are in an arrangement similar to that retrieved in the crystal structure reported in Figure 3.

Given the results shown in Table 4, another general consideration can be made: both dinuclear species show a

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great tendency to add the hydroxide species and up to three or two $OH^-$ anions can be added to the $[M_2\mathbf{L}]^{4+}$ dinuclear species for M = Cu(II) or Zn(II), respectively. All stepwise addition constants of $OH^-$ to the dinuclear species are favorable, indicating a strong tendency of $[M_2\mathbf{L}]^{4+}$ dinuclear species to add this guest. This is in agreement with a low number of coordination of at least one of the two coordinated metal ions in the species as previously suggested and found in the solid state (Figures 3 and 4). However, the first stepwise addition constants of $OH^-$ to $[M_2\mathbf{L}]^{4+}$ species ($\log K = 6.90$ and 5.25 for M = Cu(II) and Zn(II), respectively) are very high in both cases, suggesting that very likely both metal ions are involved in the coordination of such species.

A direct comparison between the stability constants of **L** with those reported for **L2**, and **L3** (see Chart 1) is quite difficult in that **L2** and **L3** mainly bind in their anionic form;[16b,c] however, the addition constants of the second M(II) is always higher for **L2** and **L3** than **L**. This can be explained taking into account that while in **L2** and **L3** the spacer (i.e., phenol and biphenol for **L2** and **L3**, respectively) is also involved in the coordination of the second M(II) by forming symmetrical dinuclear species, this can be excluded in the case of **L**.

It is also interesting to briefly compare between the binding properties of **L** with those potentiometrically evaluated with an analogous ligand in which the two dien units have been substituted by the cyclic dien counterpart, the $[9]aneN_3$ macrocyclic unit.[18a] In this latter case, the authors did not report any crystal structures; thus, they were only able to suggest a coordination environment around the Cu(II) and Zn(II) ions. However, some differences in the stability constants and thus in coordination between such ligands can be underlined: (i) **L** shows stability constants that are more than 3 logarithmic units higher in the formation of the mononuclear species. (ii) The $[M\mathbf{L}]^{2+}$ species does not easily form hydroxylated species while this is favored with the other ligand. (iii) **L** gives stable $[M_2\mathbf{L}]^{4+}$ dinuclear species while these species were not detected in the other case and only dinuclear hydroxylated species were found in solution. All these differences can be attributed to a greater flexibility of the dien function with respect to the $[9]aneN_3$ macrociclic unit which permits, in ligands in which the spacer also cooperates in binding the metal, an easier adaptation of both dien and aromatic units in binding the metal. This produces not only more stable complexes with **L** but above all higher binucleating capability of **L**.

**Spectroscopy.** $^1H$ and $^{13}C$ NMR, UV−vis, and fluorescence experiments in aqueous solution were performed to obtain further information about the coordination environment in the mono- and dinuclear species. The fluorescence experiments highlighted that **L** does not emit fluorescence not only as free ligand but also in the presence of 1 or 2 equiv of both metal ions. While this aspect is common with the quenching ion Cu(II), it was not completely expected with Zn(II); in fact, other amino−phenanthroline ligands show some fluorescent Zn(II) species. As previously mentioned, it must be taken into account that the fluorescence properties in these ligands are mainly due to the amine functions in the benzylic position with respect to the phenanthroline and that, as above-reported, it is the presence of a lone pair on the nitrogen atom which quenches the fluorescence.[17c,38] The absence of emission denotes that at least one of the two benzylic amine functions is not strongly involved in the coordination of the Zn(II) ions and in protonation both in the mono- and dinuclear Zn(II) species; the long Zn(II)−N3 distance in the crystal structure reported justifies this hypothesis and thus the absence of fluorescence in all Zn(II) species of **L**.

$^1H$ and $^{13}C$ NMR experiments were performed for the Zn(II)/**L** system in $D_2O$ solution at different molar ratios and pH. The $^1H$ NMR spectrum of the system Zn(II)/**L** in a 1:1 molar ratio recorded at pH = 6.2, where the $[ZnH_2\mathbf{L}]^{4+}$ species is prevalent in solution (see Figure 6c), is reported in Figure 7 together with that of **L** in the absence of Zn(II) recorded at the same pH value (i.e., $H_4\mathbf{L}^{4+}$ species; see Figure 5). The main differences between the two spectra are retrieved in the downfield shift of the aromatic and benzylic resonances as well as the broadening of some signals mainly in the aliphatic range. The downfield shift of the phenanthroline and the benzylic protons can be justified by the involvement of the phenanthroline as well as of all nitrogen atoms of one of the dien units in the coordination of the Zn(II), as previously suggested by potentiometric data. In this way, in solution the $[ZnH_2\mathbf{L}]^{4+}$ species preserves an arrangement similar to that depicted for the solid state as shown in the crystal structure of Figure 1. The broadening of the spectrum is attributable to a slow exchange in the Zn(II) coordination of the two dien units, on the NMR time scale. In other words, one of them is involved in coordination while the other is protonated on the two terminal amine functions, and they slowly exchange their role in solution. This consideration is supported by the sharpening of the signals, both by increasing the temperature (see below and Figure S1) and changing the pH up to 11 to obtain the $[Zn\mathbf{L}]^{2+}$ species (Figure 7c). At this pH, all resonances become sharper due to an easier exchange of the two dien units, on the NMR time scale. The absence of the two acidic protons of the $[ZnH_2\mathbf{L}]^{4+}$ species favors in the $[Zn\mathbf{L}]^{2+}$ species the exchange between the two dien units in Zn(II) coordination. However, the previous coordination environment around the Zn(II) ion is also preserved in the $[Zn\mathbf{L}]^{2+}$ species; in fact, the chemical shifts of the aromatic part and the benzylic protons remain substantially unchanged while the ethylenic protons shift upfield due to the loss of protonation of two primary amine functions. This exchange in coordination between the two dien units is confirmed by the $^{13}C$ NMR spectra of the $[ZnH_2\mathbf{L}]^{4+}$ and $[Zn\mathbf{L}]^{2+}$ species which both show (see Experimental Section for the $[ZnH_2\mathbf{L}]^{4+}$ species) nine signals due to a $C_{2v}$ symmetry mediated on the NMR time scale; this symmetry is preserved throughout the entire range of pH in the dinuclear Zn(II) species as well. An example of the $^1H$ NMR spectra of the dinuclear species is reported in Figure 7d with the spectrum recorded at pH = 8, where the $[Zn_2\mathbf{L}]^{4+}$ species is prevalent in solution (Figure 5d). The spectrum preserves a similar profile and chemical shift for the aromatic resonances while the aliphatic

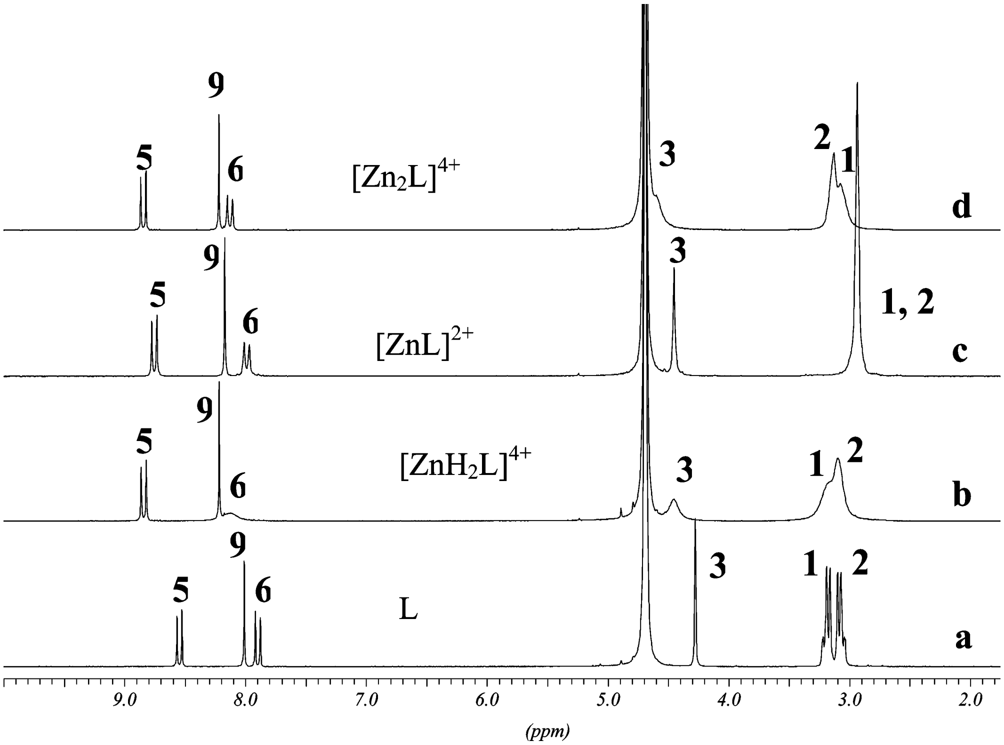

**Figure 7.** $^1H$ NMR spectra in aqueous solution of **L** at pH = 6.2 ($H_4L^{4+}$ species) (a), Zn/**L** system of 1:1 molar ratio at pH = 6.2 ($[ZnH_2L]^{4+}$ species) (b), Zn/**L** system of 1:1 molar ratio at pH = 11 ($[ZnL]^{2+}$ species) (c), and Zn/**L** system of 2:1 molar ratio at pH = 8 ($[Zn_2L]^{4+}$ species) (d).

part broadens once again and, due to the coordination of the second Zn(II) ion, shifts downfield with respect to the spectrum of the mononuclear $[Zn\mathbf{L}]^{2+}$ species. Therefore, the entrance of the second Zn(II) mainly perturbs the dien part while the phenanthroline remains unchanged, highlighting the involvement of the unbound dien unit in the stabilization of the second Zn(II); the aromatic part remains involved together with the other dien unit in the stabilization of the first Zn(II), in an arrangement similar to that retrieved at the solid state for the dinuclear Cu(II) species (see Figure 3). The $C_{2v}$ symmetry is also preserved for the dinuclear species, as underlined by the nine resonances exhibited by the $^{13}C$ NMR spectra of these species; the broad $^1H$ NMR signals of the aliphatic part highlight a slow exchange of the asymmetric complex on the NMR time scale. This aspect is supported by the sharpening of the signals that occurred at higher temperature (complete fast exchange at 343 K; see Figure S1) both for the $[ZnH_2\mathbf{L}]^{4+}$ as well as for the $[Zn_2\mathbf{L}]^{4+}$ species.

It is interesting to note the differences occurring in the NMR experiments upon substitution of the phenanthroline with the 2,2′-biphenol function as in **L3**.[16c] In particular, the Zn−**L3** mononuclear species showed sharp signals due to a reduced $C_s$ symmetry both in $^1H$ and $^{13}C$ NMR spectra and not only a broadening of the signals as occurs in the Zn−**L** species. This can be attributed to a different role played by the binding spacers; in fact, while in both systems only one dien unit is involved in coordination of Zn(II), both nitrogen atoms of the phenathroline in **L** and one oxygen atom of the biphenol in **L3** are involved. This affects the mechanism of the fast exchange in solution to achieve the higher $C_{2v}$ symmetry; in **L** only the role of the dien unit has to be exchanged while in **L3** it is the Zn(II) that has to move from one part of the molecule to the other; the latter needs more energy, and the exchange does not occur on the NMR time scale. This also produces the coexistence of the mono- and dinuclear species for **L3**, on the NMR time scale, which does not occur for **L**. In addition, the dinuclear species of **L3** show sharp signals due to a $C_{2v}$ symmetry having both Zn(II) ions the same coordination environment.

The UV−vis spectra of **L**, recorded in aqueous solution containing Cu(II) or Zn(II) ions at different pH values and molar ratio, once again highlight the involvement of the phenanthroline unit in the stabilization of the first metal ion while the chromophore is not perturbed by the coordination of the second metal in both cases. The UV−vis spectra in the range 250−350 nm, obtained by adding increasing amounts of Cu(II) to a MES buffer pH = 6.1 solution, are reported in Figure 8 to underline this behavior. A pH of 6.1 was chosen since at this pH it is possible to obtain both mono- and dinuclear species, i.e., $[CuH_2\mathbf{L}]^{4+}$ and $[Cu_2\mathbf{L}]^{4+}$ species, depending on the amount of Cu(II) present in solution (see Figure 6a,b). In the range reported, the absorption is due to the phenanthroline chromophore. As shown in the figure, the spectral profile of the Cu(II)/**L** system changes when increasing amounts of Cu(II) are added up to the addition of 1 equiv of the ion, while the second Cu(II) ion does not produce a significant change in the spectral profile. The spectrum obtained by adding 1 equiv of Cu(II) to the **L** solution shows the shift of the $\lambda_{max}$ of the band toward lower energy with a slight decrease in absorptivity with respect to that of the free ligand. In particular, the main band shifts from 273 ($\epsilon = 32\,600$ cm$^{-1}$ mol$^{-1}$ dm$^3$) in the absence of Cu(II) to 277 nm ($\epsilon = 31\,300$ cm$^{-1}$ mol$^{-1}$

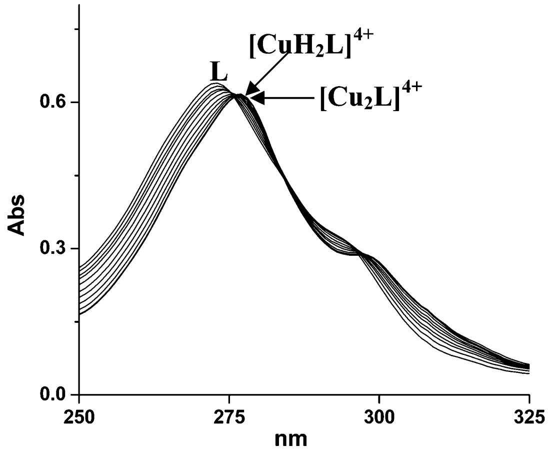

**Figure 8.** Absorption spectra of Cu$^{2+}$/**L** system in aqueous buffer (MES, $5 \times 10^{-2}$ M) solution at pH = 6.1 in the range 250−325 nm, obtained by adding several different amounts of Cu$^{2+}$ to **L** up to 3 equiv with respect to [**L**] = $2 \times 10^{-5}$ M.

dm$^3$) in presence of Cu(II); moreover, a shoulder at 294 nm, present in the spectrum of the free ligand, also shifts up to 299 nm in the complex. The invariance of the spectra following the addition of the second equiv of Cu(II) supports the hypothesis that the phenanthroline contributes to the stabilization of the first metal ion only, while it is not involved in the coordination of the second one. Similar spectral features were also obtained for the addition of Zn(II), confirming the previous assertion.

In conclusion, the UV−vis and NMR experiments highlighted the formation of unsymmetrical mono- and dinuclear species in solution in which the phenanthroline and one of the dien units participate in the stabilization of the first coordinated metal ion, while the other dien unit remains unbound and undergoes protonation in the mononuclear species while binds the second M(II) ion, giving rise to a coordination arrangement in solution similar to that retrieved at the solid state for the mono- and dinuclear M(II) species. The two dien units exchange their role in solution, and this exchange is, in the protonated mononuclear and in the dinuclear species, on the NMR time scale. However, one of the nitrogen atoms in the benzylic position must be weakly bound to the metal at least in the Zn(II) system, since the ligand is never fluorescent in all ranges of pH and using different M(II)/**L** molar ratios.

## Conclusions

The new ligand **L** is a ditopic compartmental ligand that can be inserted in the class of ligands acting to separate two amine binding units by an aromatic spacer, in this case, the 1,10-phenanthroline group. **L** behaves as a pentaprotic base in aqueous solution under the experimental conditions used; the phenanthroline is involved in protonation only in the pentaprotonated H$_5$**L**$^{5+}$ species binding one of the five acidic protons, while in the other steps only the secondary amine functions are protonated. The lack of involvement of the tertiary amine functions of the dien units in protonation produces the absence of fluorescence in the opposite field of pH.

The ligand is able to form mono- and dinuclear species with both Cu(II) and Zn(II) metal ions. The phenanthroline is always involved in the coordination of the first metal ion bound, by coordinating it through both nitrogen atoms; this metal is also stabilized by one of the dien units in a pentacoordination environment. The other dien unit undergoes easy protonation in the mononuclear complex while it binds the second metal in the dinuclear species. For this reason, **L** behaves as a compartmental ligand providing two binding areas for metal ion coordination, one of which is formed by a dien unit and by the phenanthroline nitrogen atoms and the other by the other dien unit. This produces unsymmetrical metal complexes both for the mono- and dinuclear species; however, the role of the binding areas is to permit exchanging in aqueous solution, at least on the NMR time scale. This unsymmetrical compartmental behavior in complex formation was revealed by the analysis of the stability constants as well as by the three crystal structures reported herein and by the NMR studies carried out on the Zn(II)/**L** system. As for the free ligand, the metal complexes are also not fluorescent in all ranges of pH and using different M(II)/**L** molar ratios; this points to a weak involvement in metal ion coordination of at least one of the amine nitrogen atoms in the benzylic position which quenches the fluorescence of the phenanthroline. The two binding units do not saturate the coordination requirements of the coordinated M(II) ions which are thus prone to add exogenous ligands, which, in this case, are hydroxide anions or water molecules as well as chloride and perchlorate.

In conclusion, this study has highlighted the ability of **L** to form unsymmetrical metal complexes that can be used as potential metalloreceptors for external species in solution. Therefore, it will be of interest to study the hosting properties of the dinuclear species and determine if and how the differently coordinated metal centers contribute in adding guests, particularly those of biological relevance. Seen from this standpoint, it will also be interesting to compare the hosting properties of **L** with similar but symmetrical dinuclear species such as those formed by a ligand as **L2** and **L3** of Chart 1.

**Supporting Information Available:** $^1$H NMR spectra of the [ZnH$_2$**L**]$^{4+}$ species at different temperatures and listings of crystallographic data, positional parameters, isotropic and anisotropic thermal factors, 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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