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Addition of Small Molecules by Zn(II) and Cu(II) Dinuclear Complexes Obtained by an Amino-Phenolic Ligand. Crystal Structures of the Dinuclear Zinc Complex Assembling Butanolate and Azide Anions

Paolo Dapporto,[§] Mauro Formica,[‡] Vieri Fusi,[*,‡] Luca Giorgi,[‡] Mauro Micheloni,[*,‡]
Paola Paoli,[§] Roberto Pontellini,[‡] and Patrizia Rossi[§]

"S. Stecco" Department of Energetics, University of Florence, via S. Marta 3, I-50139 Florence, Italy,
and Institute of Chemical Sciences, University of Urbino, P.zza Rinascimento 6, I-61029 Urbino, Italy

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The coordination properties of the ligand 2,6-bis-{[bis-(2-aminoethyl)-amino]methyl}-phenol (**L**) toward the zinc ion were determined by means of potentiometric measurements in aqueous solution (298.1 ± 0.1 K, $I = 0.15$ mol dm^{-3}). **L** forms mono- and dinuclear complexes with zinc; the stable dinuclear complexes are practically the only existing species using **L**/Zn(II), molar ratio of 1:2. In these species, each dien subunit binds one zinc ion, while the phenolate moiety bound to both ions allows the two metal centers to be in close proximity with an incomplete coordination environment. The role of this metal−metal distance in binding secondary ligands was investigated for the dinuclear systems 2Zn/**L** and 2Cu/**L** by potentiometric (298.1 ± 0.1 K, I = 0.15 mol dm^{-3}) and NMR experiments in aqueous and methanol solution with a series of small guests having nitrogen donor atoms. The coordination sphere of the two metals was completed by adding 1 equiv of only those guests, which showed at least two contiguous donor atoms or two lone pairs on the same atom, to exactly fit the metal−metal distance without modifying the metal cluster. To do this, the imidazole molecule which shows the highest addition constants to the $[M_2H_{-1}\mathbf{L}]^{3+}$ species probably forms a μ-1,1-amino. These results are in agreement with the two crystal structures reported herein $[Zn_2(H_{-1}\mathbf{L})(CH_3CH_2CH_2CH_2O)](ClO_4)_2$ (space group $P2_1nb$, $a = 11.483(5)$, $b = 14.166(5)$, $c = 18.279(5)$ Å, $V = 2973(19)$ Å^3, $Z = 4$, R = = 0.0701, wR2 = 0.1611) and $[Zn_2(H_{-1}\mathbf{L})N_3](ClO_4)_2$ (space group C 2/c, $a = 14.460(3)$, $b = 12.814(3)$, $c = 14.875(3)$ Å, $\beta = 105.35(2)°$, $V = 2658(10)$ Å^3, $Z = 4$, R = 0.0783, wR2 = 0.1806). In fact, these structures display a butanolate or azide guest linked to both Zn(II) ions of the dinuclear complex, resulting in a μ-1,1-oxo and μ-1,1-azido bridge, respectively.

Introduction

Transition dinuclear metal complexes and ligands capable of yielding them have been attracting increasing interest in the field of synthetic and biological chemistry due to the key roles they play in many applications. In fact, dinuclear metal complexes have been used successfully for the recognition and assembly of external species of different natures, such as inorganic and organic substrates.[1−4] Many hydrolytic metalloenzymes contain two divalent transition metal ions in close proximity which together form their active site.[5−8] For example, urease catalyzes the hydrolysis of urea and small amine substrates around a dinuclear Ni(II) center,[9] alkaline phosphatase has Zn(II) as a divalent ion,[10] while tyrosinase is a monooxygenase enzyme that has a dinuclear copper active site, and it is responsible for the hydroxylation of substrates.[11] In this way, the distance between the two metals is crucial to allowing the cooperation of both 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] Recently, we reported the synthesis and coordination properties toward Ni(II) and Cu(II) of a

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[*] To whom correspondence should be addressed.

[§] University of Florence.

[‡] University of Urbino.

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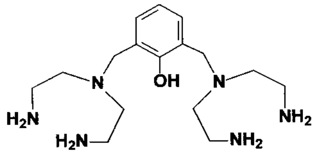
Chart 1



L

noncyclic ligand, **L**, which contains the phenol moiety separating two polyamine fragments (Chart 1).[13] Solid-state studies highlighted the ability of **L** to assemble two transition metal ions in close proximity; in this way, they cooperate to bind a new species which bridges the two metals, such as the OH^- or Cl^- anion in the case of the Cu(II) and Ni(II) complexes, respectively. To learn more about the structural parameters and the substrate that this type of bimetallic center can cooperatively bind, we performed thermodynamic studies in aqueous solutions for the Zn(II)/**L** system. The dinuclear Zn(II) complexes, together with those of the Cu(II), were successively investigated as hosts for a series of small molecules, mainly including the series of the mono- and di-aza-heterocyclic molecules with five or six members. These substrates were chosen for their rigid molecular structure and biological importance, in that they are part of many metal enzymes.

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 instrument, operating at 200.13 and 50.33 MHz, respectively. Peak positions are reported relative to TMS (MeOD) or HOD at 4.75 ppm (D_2O). Dioxane was used as a reference standard in ^{13}C NMR spectra ($\delta = 67.4$ ppm). IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer. UV absorption spectra were recorded at 298 K on a Varian Cary-100 spectrophotometer equipped with a temperature control unit. ESI mass spectra were recorded on a ThermoQuest LCQ Duo LC/MS/MS spectrometer. All reagents and solvents used were of analytical grade.

Synthesis of Complexes. 2,6-bis-{[bis-(2-aminoethyl)-amino]-methyl}-phenol (**L**) was prepared as previously described.[13]

$[Zn_2(H_{-1}L)(C_4H_9O)](ClO_4)_2$ (1). A sample of **3**, see below, (13.4 mg, 0.02 mmol) was dissolved in 10 cm^3 of methanol. Butanol (3 cm^3) was added to the solution, which was then stirred for 10 min at room temperature. The slow evaporation of the solvent led to crystallization of complex **1** as colorless crystals suitable for X-ray analysis. Anal. Calcd for $C_{20}H_{40}Cl_2N_6O_{10}Zn_2$: C, 33.08; H, 5.55; N, 11.57. Found: C, 33.0; H, 5.6; N, 11.5.

$[Zn_2(H_{-1}L)(N_3)](ClO_4)_2$ (2). A sample of $Zn(ClO_4)_2 \cdot 6H_2O$ (37.2 mg, 0.1 mmol) in methanol (20 mL) was slowly added to a methanol solution (30 mL) of **L** (16.2 mg, 0.05 mmol). The resulting solution was stirred at room temperature for 10 min, after which NaN_3 (3.2 mg, 0.05 mmol) was added. The slow evaporation of the solvent led to crystallization of the complex **2** as colorless crystals suitable for X-ray analysis. Anal. Calcd for $C_{16}H_{31}Cl_2N_9O_9Zn_2$: C, 27.65; H, 4.49; N, 18.13. Found: C, 27.7; H, 4.6; N, 18.1.

$[Zn_2(H_{-1}L)OH](ClO_4)_2$ (3). A sample of $Zn(ClO_4)_2 \cdot 6H_2O$ (186.2 mg, 0.5 mmol) in methanol (50 cm^3) was slowly added to a methanol solution (100 cm^3) of **L** (81.1 mg, 0.25 mmol). The resulting solution was stirred at room temperature for 10 min, after which NaOH (0.25 mmol) was added. After a few minutes, **3** precipitated as a microcrystalline white solid (125 mg, 75%). Anal. Calcd for $C_{16}H_{32}Cl_2N_6O_{10}Zn_2$: C, 28.68; H, 4.81; N, 12.54. Found: C, 28.7; H, 4.8; N, 12.6. MS (ESI) (*m/z*): 567 ($Zn_2(H_{-1}$**L**$)(OH)ClO_4^+$), 234 ($Zn_2(H_{-1}$**L**$)(OH)^{2+}$). ^1H NMR (CD_3OD, 25 °C): δ 2.85 (b, 16H), 3.51 (b, 2H), 4.38 (b, 2H), 6.91 (t, 1H), 7.24(d, 2H) ppm. ^{13}C NMR: δ 38.7, 53.6, 57.8, 121.7, 127.9, 134.3, 161.1 ppm.

$[Cu_2(H_{-1}L)(N_3)](ClO_4)_2$ (4). A sample of $Cu(ClO_4)_2 \cdot 6H_2O$ (74.1 mg, 0.2 mmol) in water (30 mL) was added to an aqueous solution (30 mL) containing **L**·6HBr (32.5 mg, 0.1 mmol). The pH of the resulting solution was adjusted to 6 with 0.1 M NaOH; after a few minutes, **4** precipitated as a microcrystalline green solid (57 mg, 82%). Anal. Calcd for $C_{16}H_{31}Cl_2Cu_2N_9O_9$: C, 27.79; H, 4.52; N, 18.23. Found: C, 27.9; H, 4.5; N, 18.3. MS (ESI) (*m/z*): 592 ($Cu_2(H_{-1}$**L**$)(N_3)ClO_4^+$), 549 ($Cu_2(H_{-1}$**L**$)(N_3)ClO_4^+ - HN_3$), 245.5 ($H_{-1}LCu_2N_3^{2+}$).

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

X-ray Crystallography. $[Zn_2(H_{-1}L)(CH_3CH_2CH_2CH_2O)(ClO_4)_2]$ (1). Data were collected, at 200 K, on a Siemens SMART CCD diffractometer equipped with a rotating anode and controlled using the SMART[14] software. The radiation used was Cu Kα ($\lambda = 1.5418$ Å). Five settings of ω were used, and narrow data "frames" were collected for 0.3° increments in ω. A total of 2500 frames of data were collected, providing a sphere of data. Data reduction was performed with the SAINT 4.0[15] program. The SADABS program[16] was used for absorption correction.

$[Zn_2(H_{-1}L)N_3(ClO_4)_2]$ (2). Data on intensity were collected on a Siemens P4 diffractometer, using graphite-monochromated Cu Kα radiation and the $\theta - 2\theta$ technique. Intensity data were corrected for Lorentz and polarization effects. An absorption correction was applied once the structure was solved by using the DIFABS program.[17]

The crystal structures of **1** and **2** were solved by direct methods, using the SIR-97[18] program, and subsequently refined by the full-matrix least-squares program SHELX-97.[19] All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the ligand, as well as those of the butanolate group, were introduced in calculated positions and refined accordingly to the linked atoms; the overall temperature factor converged to 0.052 and 0.065 Å^2 for **1** and **2**, respectively.

Crystal data and structure refinement are reported in Table 1. Geometrical calculations were performed using PARST97.[20] Molecular plots were produced by the ORTEP[21] program.

EMF Measurements. Equilibrium constants for the complexation reactions of **L** with the Zn(II) ion and for the ternary systems 2Cu(II)/**L**/substrate and 2Zn(II)/**L**/substrate were determined by pH-metric measurements (pH $= -\log [H^+]$) in 0.15 mol dm^{-3} NMe_4Cl aqueous solution at 298.1 ± 0.1 K, using the fully automatic equipment already described.[22] For the substrates investigated, basicity and their coordination properties toward Zn(II) and Cu(II) ions were determined under our experimental conditions; the data found were in agreement with those reported in the literature.[23] The EMF data were acquired with the PASAT computer program.[24] A 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,[25] which gives the standard potential $E°$ and the ionic product of water. At least three potentiometric titrations

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Table 1. Crystal Data and Structure Refinement for $[Zn_2(H_{-1}L)(CH_3CH_2CH_2CH_2O)(ClO_4)_2]$ (**1**) and $[Zn_2(H_{-1}L)N_3(ClO_4)_2]$ (**2**)

	1	**2**
empirical formula	$C_{20}H_{40}Cl_2N_6O_{10}Zn_2$	$C_{16}H_{31}Cl_2N_9O_9Zn_2$
fw	726.22	695.14
temp, K	200	298
wavelength, Å	1.5418	1.5418
cryst system	orthorhombic	monoclinic
space group	$P2_1$nb	$C2/c$
unit cell dimensions, Å, deg	$a = 11.483(5)$ $b = 14.166(5)$ $c = 18.279(5)$	$a = 14.460(3)$ $b = 12.814(3)$ $\beta = 105.35(2)$ $c = 14.875(3)$
V, Å^3	2973(19)	2658(10)
Z	4	4
D_c, Mg/m^3	1.622	1.737
abs coeff, mm^{-1}	4.165	4.637
cryst size, mm	0.30 × 0.45 × 0.50	0.35 × 0.50 × 0.60
reflns collected/unique	7961/2957	2858/2137
Data [$I > 2\sigma(I)$]/parameters	2593/364	1762/177
R indices [$I > 2\sigma(I)$]	[a]R1 = 0.0617 [b]wR2 = 0.1528	R1 = 0.0575 wR2 = 0.1585
R indices (all data)	R1 = 0.0701 wR2 = 0.1611	R1 = 0.0783 wR2 = 0.1806

[a] $R1 = \sigma||F_o| - |F_c||/\sigma|F_o|$. [b] $wR2 = [\sigma[w(F_o^2 - F_c^2)^2]/\sigma[w(F_o^2)^2]]^{1/2}$.

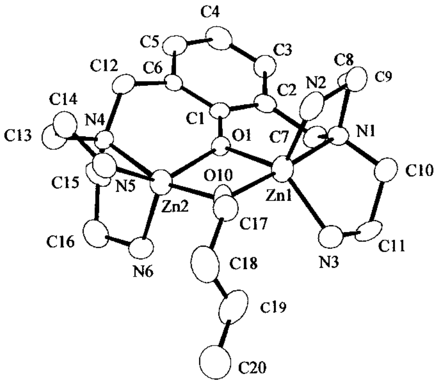


Figure 1. ORTEP view of compound **1** (50% probability).

were performed for each system in the pH range 2.5−11, using different molar ratio of M(II)/**L** ranging from 1:1 to 2:1. For the ternary systems, different molar ratios of the dinuclear complex/substrate were used, ranging from 1:1 to 1:3. 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.

Results and Discussion

X-ray Crystal Structures of $[Zn_2(H_{-1}L)(CH_3CH_2CH_2CH_2O)(ClO_4)_2]$ (1) and $[Zn_2(H_{-1}L)N_3(ClO_4)_2]$ (2). The crystal lattice of **1** is made up of dinuclear complex cations and perchlorate anions. Each zinc ion is coordinated by the three nitrogen atoms and the oxygen of the H_{-1}**L** ligand and by the oxygen atom of the butanolate moiety, reaching pentacoordination, which results, however, in different coordination geometries (Figure 1). In fact, the coordination polyhedron around the Zn1 atom can be described as a trigonal bipyramid (tbp), with the butanolate oxygen O10 and the N1 nitrogen occupying the axial positions, while a square pyramid (sp) well describes the coordination geometry of the Zn2 cation, with N6 at the apex. In both cases, the zinc donor atom distances are comparable. Comparison of the bond angles around the two cations revealed that the most significant difference concerns the <O1Zn1N3 angle and the corresponding <O1Zn2N5 angle, which differ by about 13°. In addition, the two binding moieties of the ligand are wrapped around the metal cations in a slightly different way, as shown by the angles between the mean least-squares planes described by the chelate rings. However, the overall arrangement of the ligands around the two metal moieties is quite symmetric, with the two zinc ions lying on the sides opposite the benzene ring, 3.086(2) Å apart, and correlated by a noncrystallographic two-fold axis passing through both the oxygen atoms, C1 and C4. The equatorial donors and Zn1 are well inside the plane, as provided by the sum of the bond angles around Zn1 (357°), which is shifted toward the butanolate oxygen atom O10 by 0.174(1) Å. The mean deviation of the four atoms defining the base of the sp about the Zn2 ion is 0.207(8) Å, with the metal cation lying at 0.475(1) Å from the mean plane and shifted toward the N6 donor. The butanolate moiety is in a gauche−trans conformation with respect to the C17−C18 and C18−C19 bonds. Many solid-state structures (ca. 450) were retrieved from a search performed using the CCDC[26] on dinuclear transition metal complexes that have an alcoholate (RO^-, R = methyl, ethyl, propyl, and butyl) as bridging unit, most of which were μ-2-methoxy complexes, while only one featured a μ-2-butyloxy pattern. Among these, about 10 complexes, none of which contained zinc ions, were found to have two metal cations bridged by a phenolate 2,6-disubstituted group with arms bearing the nitrogen donor atoms. A mean distance of 2.94 Å between the metal centers was estimated.

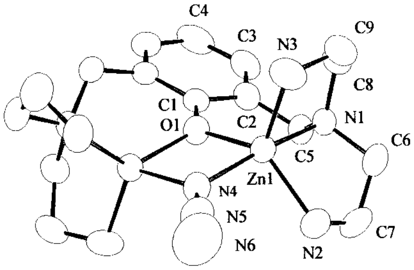
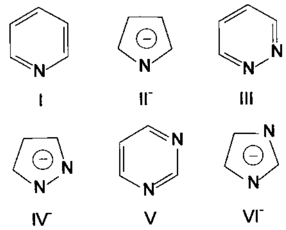


Figure 2. ORTEP view of compound **2** (50% probability).

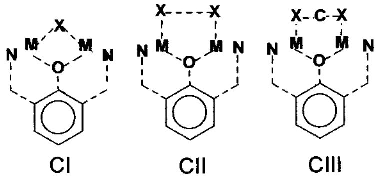
The asymmetric unit of **2** contains half a complex cation and a perchlorate anion. A two-fold symmetry axis, passing through the phenolate oxygen atom O1 and the azide moiety, relates the two halves, with the zinc ions disposed on the opposite sides of the aromatic ring and 3.098(1) Å apart. The zinc environment can be described as a trigonal bipyramid with N1 and N4 occupying the axial positions, with the other two nitrogen atoms and the O1 oxygen atom provided by the ligand completing the coordination sphere on the equatorial plane (Figure 2). The sum of the bond angles of this plane about Zn1 is 358°, with the metal shifted toward the azide nitrogen atom N4 by 0.1403(7) Å. The arrangement of the chelate rings around the metal is comparable to that found in **1** (tbp coordination sphere), as are the zinc-donor atom bond distances. Many dinuclear transition metal complexes (ca. 170) that have the azide group acting as monodentate bridging unit were retrieved in the CCDC, few of which featured zinc ions. In 10 dinuclear complexes, a phenolate group, 2,6-disubstituted with arms bearing donor atoms, bridges two copper cations (mean Cu−Cu distance 3.05 Å), giving a coordination pattern very similar to that found in **2**.

Search of the Cambridge Crystallographic Data Center (CCDC) Database. An analysis of the structures deposited at the CCDC was performed both to check the coordination behavior with respect to two metal centers of the substrates investigated by means of potentiometric titrations (Scheme 1) and to gain some information concerning the ability of the $[M_2(H_{-1}\mathbf{L})]^{3+}$ complex to recognize external species (Scheme 2).

Scheme 1



Scheme 2



A search was performed to retrieve molecular fragments featuring dinuclear metal complexes with the species depicted in Scheme 1 which are involved in the coordination of two metal ions. For pyrazole and imidazole, the neutral species were also searched. Analogous coordination patterns were expected for the heterocycles I/II$^-$, III/IV$^-$, and V/VI$^-$, given their geometry around the donor atoms and the disposition of the lone pairs.

Only for I (5 refcodes), II$^-$ (3 refcodes), and IV$^-$ (1 refcode), the solid-state structures retrieved in the CCDC featured a nitrogen atom as a bridging unit in linking two transition metal ions.

In complexes in which the nitrogen atom of the pyridine ligand acts as a bridge between two metal cations, the latter are rather close each other, about 3.0 Å, with the heterocyclic aromatic ring quite perpendicular with respect to the metal$\cdots$metal direction.[27]

A different coordination behavior was observed for the pyrrolate (II$^-$) grouping; three μ-2, η-5-bound pyrrolyl complexes were found with II$^-$ involved in the coordination of two metal cations at the same time.[28]

A structure was found featuring the nitrogen atom of the pyrazolyl moiety acting as bidentate donor for two Cu(I) cations, which were 2.660 Å apart, with the heterocyclic ring perpendicular to the metal$\cdots$metal direction, as observed for the pyridine ligand.[29]

The III/IV$^-$ species can act as bidentate ligands, maintaining the two metal ions about 3.4 Å apart. In addition, many of the structures retrieved had the two cations bridged by an oxygen atom,[30,31] which, in most cases, was provided by a hydroxide grouping. The two metal ions bound by each nitrogen atom of the pyrimidine (V) species are about 6 Å apart, and a similar structure was found for the imidazolate ligand (VI$^-$, 5.9 Å). Many fragments were found to have a pyrazole or imidazole acting as a monodentate donor. The coordination properties of the azide ligand as a monodentate bridging unit linking the two metal cations have been already discussed in the previous section.

Concerning fragment CI, 47 structures were found, many of which show hydroxy or methoxy bridging units, μ-2-chloro, bromo, and azido coordination patterns are also rather common. The mean metal$\cdots$metal observed distance was 3.03 Å.

In the few complexes (4) showing the pattern CII that were retrieved, the peroxo or pyrazolyl anion links the two metal cations, which are about 3.36 Å apart.

Finally, 57 solid-state structures show the coordination pattern depicted in CIII. Most of them feature a μ-2-carboxylate bridging unit, with the two metal ions 3.36 Å apart, and none of them have X = N.

On the basis of the results obtained from the CCDC, the following conclusions can be drawn: *i*) the pyridine substrate could fit into the cavity of the $[M_2(H_{-1}\mathbf{L})]^{3+}$ complex, thus acting as bridging unit and completing the coordination of the two metal cations with a spatial disposition for the pyridine, with respect to the $[M_2(H_{-1}\mathbf{L})]^{3+}$ complex, similar to that found in the X-ray structure featuring the butanolate moiety reported. Nevertheless, potentiometric titrations did not reveal pyridine capture, probably because of a low affinity of the pyridine for the $[M_2(H_{-1}\mathbf{L})]^{3+}$ complex or because of the competition with the hydroxide group (see solution studies). *ii)* The solid-state structures retrieved from the CCDC, featuring a bridging pyrrolyl substrate between two metal ions, are characterized by a μ-2, η-5 bond type. Because copper(II) and zinc(II) have a very low tendency to form π-bonds, the recognition of the pyrrolyl substrate by the $[M_2(H_{-1}\mathbf{L})]^{3+}$ complex appears rather unlikely. The solution study results are in agreement with this conclusion. *iii*) Solution studies showed that the $[Cu_2(H_{-1}\mathbf{L})]^{3+}$ complex, unlike that of zinc, binds pyridazine and pyrazole substrates. The analysis of the solid-state structures deposited at the CCDC suggests that the $[M_2(H_{-1}\mathbf{L})]^{3+}$ complex could bind both substrates, with minor rearrangement of the dinuclear receptor, so as to push the two metal ions slightly away. The resulting coordination pattern could be very similar to that observed in the crystal structures retrieved from the CCDC, which feature both a phenolate grouping and a pyrazolate anion. *iv)* The bite of the V and VI species appear to be too large to coordinate both metal cations of the $[M_2(H_{-1}\mathbf{L})]^{3+}$ complex acting as a bidentate ligand. As a consequence, in the recognition of the V and VI species by the complex, a different coordination pattern than that of the structures retrieved from database must be hypothesized.

Solution Studies. Coordination of Zn(II). The coordination behavior of **L** toward the Zn(II) ion was studied in 0.15 mol dm^{-3} NMe_4Cl aqueous solution at 298.1 K. The stability constants for the equilibrium reactions of **L** with Zn(II) were potentiometrically determined and are reported in Table 2. **L** forms mono- and dinuclear complexes with zinc; the mononuclear species are quite important in solution only at **L**/Zn(II) molar ratios equal to or greater than 1, although dinuclear species are also present at this molar ratio. Dinuclear complexes are, instead, virtually the only existing species with a **L**/Zn(II) molar ratio of 1:2 (see Figure 3). This behavior is analogous to that reported for the complexes of **L** with Co(II), Ni(II), and Cu(II) ions, and the discussion of the values of the formation constant can be outlined in the same way;[13,32] however, some other

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Table 2. 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 Zn(II) and Cu(II) Ions

reaction	Log K	
	Zn(II)	Cu(II)
$M^{2+} + \mathbf{L} + 3H^+ = M\mathbf{L}H_3^{5+}$	–	36.61[b]
$M^{2+} + \mathbf{L} + 2H^+ = M\mathbf{L}H_2^{4+}$	28.67 (2)[a]	33.02
$M^{2+} + \mathbf{L} + H^+ = M\mathbf{L}H^{3+}$	23.51 (3)	28.27
$M^{2+} + \mathbf{L} = M\mathbf{L}^{2+}$	14.87 (4)	21.01
$M^{2+} + \mathbf{L} + H_2O = M(H_{-1}\mathbf{L})^+ + H_3O^+$	5.63 (2)	11.60
$2M^{2+} + \mathbf{L} = M_2\mathbf{L}^{4+}$	–	30.27
$2M^{2+} + \mathbf{L} + H_2O = M_2(H_{-1}\mathbf{L})^{3+} + H_3O^+$	17.64 (1)	25.95
$2M^{2+} + \mathbf{L} + 2H_2O = M_2(H_{-1}\mathbf{L})OH^{2+} + 2H_3O^+$	9.08 (4)	19.87
$M(H_{-1}\mathbf{L})^+ + M^{2+} = M_2(H_{-1}\mathbf{L})^{3+}$	12.01	14.35
$M_2(H_{-1}\mathbf{L})^{3+} + OH^- = M_2(H_{-1}\mathbf{L})OH^{2+}$	5.17	7.65

[a] Values in parentheses are the standard deviations on the last significant figure. [b] Reference 13.

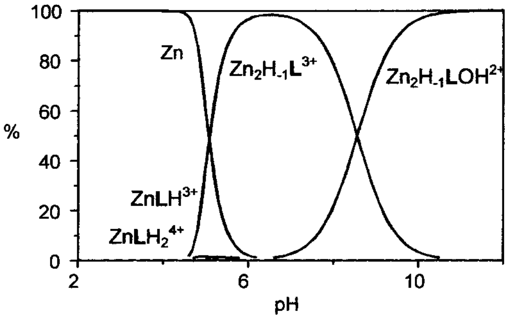

Figure 3. Distribution diagrams of the species for the **L**/Zn(II) systems as a function of pH in aqueous solution, $I = 0.15$ mol dm^{-3} NMe_4Cl, at 298.1 K. $[\mathbf{L}] = 1 \times 10^{-3}$ mol dm^{-3}, $[Zn^{2+}] = 2 \times 10^{-3}$ mol dm^{-3}.

important aspects can also be highlighted. **L** forms stable mononuclear complexes, with a log K of 14.87 for the addition of Zn(II) to the neutral species **L** (see Table 2). This value of the formation reaction is about 6 logarithmic units higher than that reported for the same speciation of Zn(II) with the ligand 1,4,7-triazaheptane (dien), leading us to suppose that at least one other atom is involved in the coordination of the metal.[22] The topology of the ligand suggests that the phenol oxygen is involved in the formation of the mononuclear species together with the triamine subunit in a coordination arrangement similar to that found in the crystal structures reported herein. Moreover, due to the presence of the metal ion, the ligand reaches the anionic form in the $[ZnH_{-1}\mathbf{L}]^+$ species, with the presence of the phenolate group, as confirmed by the UV–vis absorption spectra. In fact, the two typical bands of the phenolate group appear at a pH greater than 5, reaching their maximum values at pH 6.5 (λ_{max} 242 ($\epsilon = 8800$ cm^{-1} mol^{-1} dm^3) and 293 ($\epsilon = 4800$ cm^{-1} mol^{-1} dm^3)). These values are preserved for higher values of pH or for **L**/Zn(II) molar ratios equal to or greater than 1, evidencing that the deprotonation of the phenol occurs in all the complexed species formed. The log K value of 12.01 logarithmic units obtained for the addition of the second Zn(II) to the $[ZnH_{-1}\mathbf{L}]^+$ species indicates the great tendency of **L** to coordinate another Zn(II) ion, and it lends further support, as already reported, for the deduced potential of **L** to form stable dinuclear species. Also, in this case, we can hypothesize a similar coordination environment for the two zinc ions, each stabilized by a dien unit and by the oxygen of the phenolate moiety, as found in the crystal structures reported here. It was possible to detect at least one hydroxylated species, with a value of 5.17 logarithmic units, for the addition of the OH^- anion to the $[Zn_2H_{-1}\mathbf{L}]^{3+}$ species. This high value indicates a strong binding of the hydroxide ion in the dinuclear complex and can be ascribed to a bridge disposition of the hydroxide similar to that found in the crystal structure of the $[Cu_2(H_{-1}\mathbf{L})OH]^{2+}$ species,[13] which saturates the coordination requirement of the two Zn(II) ions. This hydroxylated species $[Zn_2(H_{-1}\mathbf{L})OH](ClO_4)_2$ was isolated in the solid state from alcoholic solution (see Experimental Section) and used for the addition of substrates in the ^1H NMR studies.

In conclusion, the aqueous solution studies underline the capability of **L** to form stable dinuclear species with the Zn(II) ion. This is due to the presence of the phenolate group, the oxygen of which has the capability to bridge the two zinc ions, forming a rigid dinuclear cluster. In this way, the two metal ions are assembled very close to each other (3.08 and 3.10 Å for butanolate and azide complexes, respectively) with a similar coordination environment, given by the dien subunit and the oxygen of the phenolate group in a bridge disposition. The short distance between the two Zn(II) ions and their incomplete coordination sphere in the $[Zn_2(H_{-1}\mathbf{L})]^{3+}$ species should permit the dinuclear complex to host new species, preferring those able to simultaneously bridge the two metal ions.

Substrate Addition. The capability of **L** to form stable dinuclear species with various bipositive transition metal ions led us to explore their use as hosts for secondary ligands. In this case, the binding potential of 2Cu/**L** and 2Zn/**L** systems toward mono- and di-aza heterocyclic molecules with five or six members and toward azide anion in aqueous and methanol solution was investigated. Besides N_3^-, the guests (G) added were pyridine, pyrazine, pyridazine, pyrimidine, pyrrole, imidazole, and pyrazole. The 2M/**L**/G systems were potentiometrically studied in 0.15 mol dm^{-3} NMe_4Cl aqueous solution at 298.1 K, using different $M_2\mathbf{L}$/G molar ratios. Not all of the substrates interacted with the dinuclear systems under the experimental conditions used; the stability constants for the ternary systems formed are reported in Table 3.

For the 2Cu/**L**/G system, it was possible to calculate the formation constants with the Cu(II) dinuclear species of **L** only for the substrates imidazole, pyrazole, and pyridazine; the precipitation of the adduct $[Cu_2H_{-1}\mathbf{L}N_3]Cl_2$, occurring at pH values above 6, prevented the determination of the stability constants for the 2Cu/**L**/N_3^- system.

With regard to the 2Zn/**L**/G system, it was possible to determine the formation constants only for the imidazole and azide substrates; the other guests do not interact with the Zn(II) dinuclear species of **L** under the experimental conditions used.

Analysis of the data from the potentiometric measurements showed that only adducts with 1:1 stoichiometries between the dinuclear complexes and G are formed under our experimental conditions. By examining the stability constants for the systems formed and comparing the 2Cu/**L**/G and 2Zn/**L**/G systems, some shared features were identified. Imidazole and azide substrates are bound by both dinuclear systems, even if it was not possible to determine the values of the addition constant of N_3^- to the 2Cu/**L** system (vide infra); moreover, the Cu_2/**L** system also binds pyridazine and pyrazole. This different behavior of Cu(II) and Zn(II) can be ascribed to the higher affinity of Cu(II) toward the nitrogen donor atom of these substrates. The addition constants of substrates for the dinuclear systems are higher by about one logarithmic unit than those reported in the literature for the G/Cu(II) and G/Zn(II) systems. For example, the formation constant for the Zn/imidazole species is log K =

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Table 3. Logarithm of the Formation Constants for the 2Cu(II)/L and 2Zn(II)/L Systems with the Guests (G) Imidazole (G1), Pyrazole (G2), Pyridazine (G3), and N_3^- (G4), Determined in 0.15 mol dm^{-3} NMe_4Cl at 298.1 K

	Log K				
	Cu			Zn	
reaction	G1	G2	G3	G1	G4
$2M^{2+} + \mathbf{L} + G = [GM_2H_{-1}\mathbf{L}]^{3+} + H^+$	30.57 (3)[a]	29.10 (4)	28.54 (2)	21.68 (3)	20.45 (2)
$2M^{2+} + \mathbf{L} + G = [H_{-2}GM_2\mathbf{L}]^{2+} + 2H^+$	23.64 (4)	24.24 (4)	23.90 (3)	13.06 (3)	−
$2M^{2+} + \mathbf{L} + G = [H_{-3}GM_2\mathbf{L}]^{+} + 3H^+$	12.51 (3)	13.08 (3)	−	2.97 (4)	−
$[M_2(H_{-1}\mathbf{L})]^{3+} + G = [GM_2(H_{-1}\mathbf{L})]^{3+}$	4.6	3.2	2.6	4.0	2.8

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

2.56, while the addition of imidazole to $[Zn_2(H_{-1}\mathbf{L})]^{3+}$ species gave log K = 4.0 (see Table 3). This behavior indicates that the close proximity of the two metals favors the addition of the guest, moreover, suggesting that the two metal ions cooperate to bind the substrate. The guests interacting with the dinuclear systems in the pH range investigated have at least two donor atoms; on the contrary, the substrates containing only one donor atom, besides holding a lone pair, do not interact. Furthermore, the previous condition is not sufficient for binding; in fact, pyrazine and pyrimidine (the two N atoms are in the 1,4 and 1,3 positions, respectively) are not bound by both $M_2\mathbf{L}$ systems. This can be explained taking into account the fact that G probably binds the two metal centers in a bridge disposition, and for this reason the presence of at least two lone pairs in the guest is necessary. Nevertheless, the guests are not recognized as having two donor atoms which are, however, located too far away to fit the distance between the two metal centers well (this interpretation is in agreement with the CCDC analysis). For this reason, the structure of the bimetallic cluster $[M_2H_{-1}\mathbf{L}]^{3+}$ seems to be rigid and preorganized, coordinating only secondary ligands able to fit this distance well. In fact, the azide has two possibilities to bridge the two metal ions, the μ-1,1 and the μ-1,3-azido bridges. In our case, the μ-1,1-azido bridge is preferred, as shown by the crystal structure of the cation $[Zn_2(H_{-1}\mathbf{L})(N_3)]^{2+}$; moreover, the IR spectrum shows only one asymmetric stretch of the azide at 2080 cm^{-1} attributed to the μ-1,1-azido bridge between the two Zn(II) ions.[33] A band at 2082 cm^{-1} was also observed for the $[Cu_2(H_{-1}\mathbf{L})(N_3)](ClO_4)_2$ complex isolated as a solid, revealing a similar azide arrangement in the copper complex. The addition of imidazole, which shows the highest addition constants to the $[M_2H_{-1}\mathbf{L}]^{3+}$ species of all the guests, seems to contradict the hypothesis that the guest has to have two close nitrogen atoms or two lone pairs on the same donor atom to bind the dinuclear host, and besides, it is not supported by the results of the CCCD analysis unless only one of the two nitrogen atoms of imidazole binds the two metals in a μ-1,1-amino bridge, as has been shown in some cases for pyridine when it binds two metals in close proximity (see CCDC analysis). Moreover, for the systems with imidazole and pyrazole there is the appearance of a further degree of deprotonation in ternary systems with respect to the binary 2M/L systems (Tables 2 and 3). This can be explained by the addition of another hydroxyl group and by the deprotonation of the guests, as reported in some cases in the literature,[34] which would yield the imidazolate or pyrazolate species. This latter hypothesis is supported by the different speciation patterns for the addition of azide or pyridazine, which do not have any acidic protons. In other words, the potentiometric data and the CCDC analysis suggest that the coordination of imidazole and pyrazole molecules to the dinuclear species $M_2\mathbf{L}$ can favor the deprotonation of the guest; furthermore, at least for imidazole, a μ-1,1-amino bridge between one of the two nitrogen atoms of the guest and the two M(II) ions is proposed.

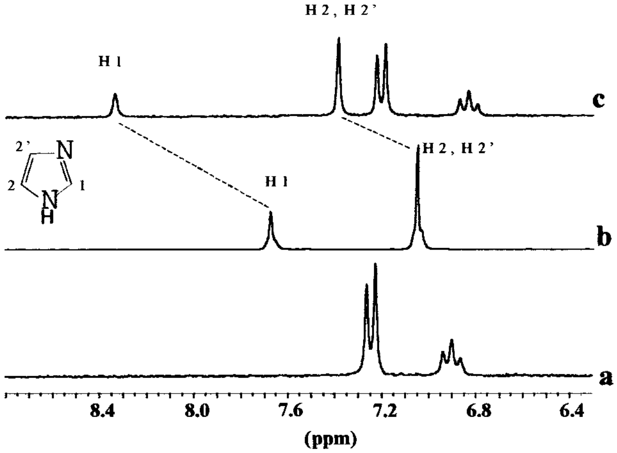

Figure 4. ^1H NMR spectra (aromatic protons) in CD_3OD of **L** (a); imidazole (b); L/imidazole system in 1:1 molar ratio (c).

NMR Studies. ^1H NMR experiments were carried out for the 2Zn/**L**/imidazole system in aqueous and methanol solutions to better understand how imidazole is involved in the coordination of the dinuclear species. The ^1H NMR spectrum, recorded in methanol, of the $[Zn_2(H_{-1}L)OH](ClO_4)_2$ species isolated in the solid state (see experimental part) is very similar to that recorded in aqueous solution at pH 6.4, where the same species is prevalent. When such studies are performed in methanol solution and increasing amounts of imidazole are added to the $[Zn_2(H_{-1}\mathbf{L})(OH)]^{2+}$ species, the Job plot of the ^1H NMR chemical shift for the signals of the protons of the imidazole against the imidazole/$[Zn_2(H_{-1}\mathbf{L})(OH)]^{2+}$ ratio shows a sharp break at imidazole/$[Zn_2(H_{-1}\mathbf{L})(OH)]^{2+} = 1$. This means that only 1 equiv of imidazole coordinates the dinuclear complex. Moreover, the shifts in those resonances show that the complex is completely formed by adding 1 equiv of imidazole. Figure 4 reports the spectrum of the aromatic part of the $[Zn_2(H_{-1}\mathbf{L})(OH)]^{2+}$ species (Figure 4a) together with those of free imidazole (Figure 4b) and the complexed species (Figure 4c) formed by adding 1 equiv of imidazole to $[Zn_2(H_{-1}\mathbf{L})(OH)]^{2+}$ species. Figure 5 reports the complexed species formed with imidazole and recorded at different temperatures. By comparing the spectra recorded at 25 °C (Figure 4), it was found that the resonances of **L** did not change appreciably when imidazole was added to the $[Zn_2(H_{-1}\mathbf{L})(OH)]^{2+}$ species, while the signals of imidazole show a marked downfield shift ($\Delta\delta$ is 0.34 and 0.67 ppm for H2, H2′ and H1, respectively). This evidence indicates an interaction between imidazole and the $[Zn_2(H_{-1}\mathbf{L})]^{3+}$ species; however, the coordination of imidazole does not affect the $H_{-1}\mathbf{L}$

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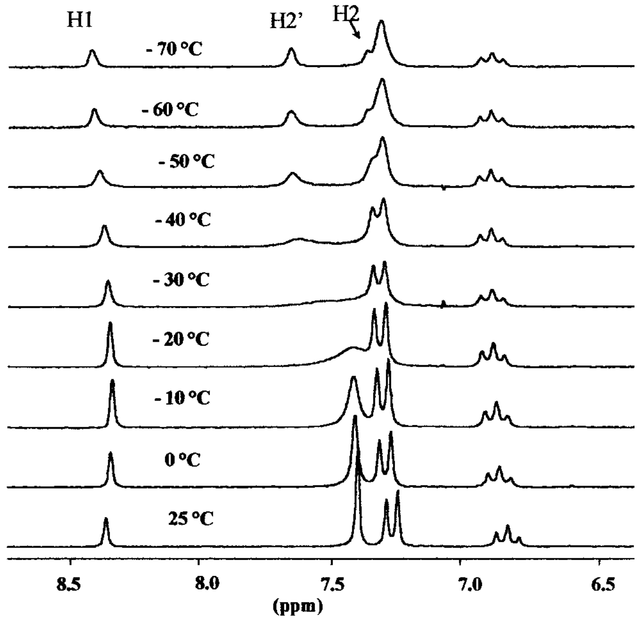

Figure 5. ^{1}H NMR spectra (aromatic protons) in CD_3OD of L/imidazole system in 1:1 molar ratio at various temperatures.

moiety or, in other words, the $[Zn_2(H_{-1}\mathbf{L})]$ cluster, suggesting that imidazole probably replaces the hydroxide ion in the complex without modifying the coordination sphere of the two Zn(II) ions. When the temperature was lowered, the sharp resonance at 7.38 ppm attributed to the two equivalent protons H2 and H2′ of imidazole became broad, and at − 30 °C it was near to coalescence. At lower temperatures, two new broad resonances appear, and at −70 °C they are sharp signals, integrating for one proton each. These two resonances can be ascribed to the protons H2 and H2′, which lose their magnetic equivalence on the NMR time scale below −30 °C. It is of interest that the resonance attributed to the proton H2′ exhibits a more marked downfield shift than H2 ($\Delta\delta$ are 0.59, 0.51, and 0.21 at −70 °C for H1, H2′, and H2, respectively). This loss of symmetry in the complexed imidazole, together with the different shifts exhibited by the three protons, indicates a bridged disposition of the imidazole between the two metal centers involving only one of its nitrogen atoms in a μ-1,1-amino bridge, as previously suggested by the potentiometric data. This situation is averaged between the two nitrogen atoms at room temperature on the NMR time scale but is blocked at lower temperature. Furthermore, the experimental data suggest that the addition of the imidazole (G) to the $[Zn_2(H_{-1}\mathbf{L})(OH)]^{2+}$ species takes place, forming the imidazolate adduct $[(H_{-1}G)\text{-}Zn_2(H_{-1}\mathbf{L})]^{2+}$ and H_2O; in other words, the presence of the hydroxide anion in the $[Zn_2(H_{-1}\mathbf{L})(OH)]^{2+}$ can favor the deprotonation of the imidazole. This ability to deprotonate substrates having one weak acidic proton is also supported by the deprotonation of butanol by the same species, as found in the solid state. This aspect makes the $[Zn_2(H_{-1}\mathbf{L})(OH)]^{2+}$ species attractive for use as a catalyst, for example in the hydrolysis of phosphate monoesters, mimicking the alkaline phosphatase enzyme.

Similar experiments performed with the other substrates did not give any significant variations in the NMR spectra of either the substrate or the dinuclear species, confirming that they do not interact with the dinuclear species in this medium.

Concluding Remarks

The ligand **L**, which contains two diethylenetriamine units linked to the central nitrogen atom by 2,6 dimethylphenol, forms stable dinuclear complexes with Zn(II) ions in aqueous solution. Each tri-aza subunit binds one zinc ion, while the oxygen atom of the phenolate binds both ions in a bridge disposition, making it possible to have the two metal centers in close proximity. In this way, the dinuclear species show an unsaturated coordination environment, which is taken up by secondary ligands, as shown by the two crystal structures reported. In these structures, both Zn(II) ions show a pentacoordinated environment in which the fifth position is occupied by a secondary ligand that bridges the two metals centers. The substrates bound to the dinuclear species are the azide and butanolate anions, respectively; the latter is obtained by the deprotonation of butanol from the $[Zn_2(H_{-1}\mathbf{L})(OH)]^{2+}$ species, revealing the strong binding ability of the dinuclear species and suggesting that the hydroxide anion cooperates in the deprotonation of the substrate. The azide anion prefers a μ-1,1-azido bridge, as the μ-1,3 bridge is unfavorable due to the short distance between the two Zn(II) ions in the cluster. The influence of the metal−metal distance on the binding of substrates in the dinuclear complexes of **L** with Cu(II) and Zn(II) was studied by adding small aza-molecules to the 2M(II)/**L** system over all the series of the mono- and diaza-heterocyclic molecules with five or six members. These studies performed in solution, together with the search in the CCCD database, highlighted the rigidity and selectivity of the $M_2\mathbf{L}$ cluster toward assembling the substrate. In fact, it binds only one molecule of only those substrates which show at least two contiguous donor atoms or two lone pairs on the same donor atom able to exactly fit the metal−metal distance without modifying the metal cluster. This ability can be ascribed to the cooperation of the two metal centers in binding the guest, which is coordinated in a bridge disposition between the two metals. The imidazole molecule is the substrate that gives the highest addition constants to the $[M_2\mathbf{L}]^{3+}$ species, suggesting in this case a μ-1,1-amino bridge, because a μ-1,3-amino bridge is precluded by the short distance between the two metals; in this case the presence of the imidazolate anion is also presumed.

The ability of the Zn(II) dinuclear species to deprotonate substrates makes the $[Zn_2(H_{-1}\mathbf{L})(OH)]^{2+}$ species attractive to us as catalysts for hydrolytic processes, such as the hydrolysis of phosphate monoesters, mimicking the alkaline phosphatase enzyme.

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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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