Synthesis and Conformational Studies of a Chiral Octadentate Ligand Derived from (*R*)-1,1′-Binaphthyl-2,2′-diamine and its Dinuclear Zinc(II) and Nickel(II) Complexes

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The synthesis of the octadentate ligand (*R*)-(–)-*N*,*N*′-dimethyl-*N*,*N*′-bis{3-[bis(1-methyl-2-benzimidazolylmethyl)]-aminopropyl}-1,1′-binaphthyl-2,2′-diamine (**L**), containing a central 1,1′-binaphthalenediamine core connected to two aminobis(benzimidazole) arms by flexible trimethylene carbon chains, and its dinuclear complexes $[Zn_2\mathbf{L}](ClO_4)_4$ and $[Ni_2\mathbf{L}](ClO_4)_4$ is reported. The structural features of the free ligand and the metal complexes have been investigated by NMR, UV/Visible, CD, and computational methods, including simulated annealing-molecular mechanics and semiempirical PM3 calculations. The preferred conformation of the free ligand is characterized by a relatively small dihedral angle of about 75° between the two naphthyl rings, which is imposed by favorable stacking interactions between benzimidazole rings from different arms. In the dinuclear zinc(II) complex each metal ion is pseudotetrahedral and bound to three N donors of one aminobis(benzimidazole) arm and one N donor of the binaphthalenediamine residue. Coordination of the benzimidazole groups to the metal ions prevents the stacking interactions seen in the free ligand and, consequently, the dihedral angle between the naphthyl groups increases to the more usual ca. 90°. In the dinuclear nickel(II) complex, the ligand still provides four nitrogen donors to each metal centers, but the stereochemical preference of the nickel(II) ions imposes a ligand field of tetragonal symmetry, with pseudo-octahedral metal centers, and this occurs with pronounced flattening of the dihedral angle between the naphthyl groups. The change in conformation, from **L** to $[Zn_2\mathbf{L}]^{4+}$ to $[Ni_2\mathbf{L}]^{4+}$, of the critical 1,1′-binaphthalenediamine residue is clearly indicated by CD spectra.

Introduction

Polydentate ligands carrying nitrogen donor atoms have been extensively used in the biomimetic chemistry of metal enzymes, particularly those depending on copper and associated with oxidative processes, which typically contain dinuclear or trinuclear metal centers.[1] Surprisingly, though, few of the various ligands studied contain chiral centers. This is partly because of the difficulties encountered in synthesizing such polyfunctional molecules, as illustrated by our attempt to prepare biomimetic ligands containing L-histidine residues.[2] Nonetheless, chiral centers add a new dimension and open up interesting perspectives for synthetic active site analogues of metal enzymes, such as the possibility to perform asymmetric transformations.

We have, in particular, studied various copper complexes with polyamino-polybenzimidazole ligands to simulate structural and functional properties of dioxygen-activating copper enzymes.[3] Suitable dinucleating ligands usually contain a set of six nitrogen donors to be evenly distributed between the metal ions, whereas for trinuclear complexes the ligand must bind the metal ions with a total of eight nitrogen donors. A simple way to introduce a chiral moiety into the ligand scaffold is to use the 1,1′-binaphthalene residue. Chiral complexes of 1,1′-binaphthyl ligands have been extensively used in asymmetric catalysis; the complexes of 1,1′-bis(2-naphthol) (BINOL) and 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthalene (BINAP)[4,5] are recent examples. In addition, the chiroptical properties and the conformations of 2,2′-homosubstituted 1,1′-binaphthyl derivatives have been studied in detail,[6,7] and useful correlations between CD spectra and solution conformation for these C_2-symmetric chromophores are available. We therefore designed the new chiral ligand **L**, in which an (*R*)-(+)-1,1′-

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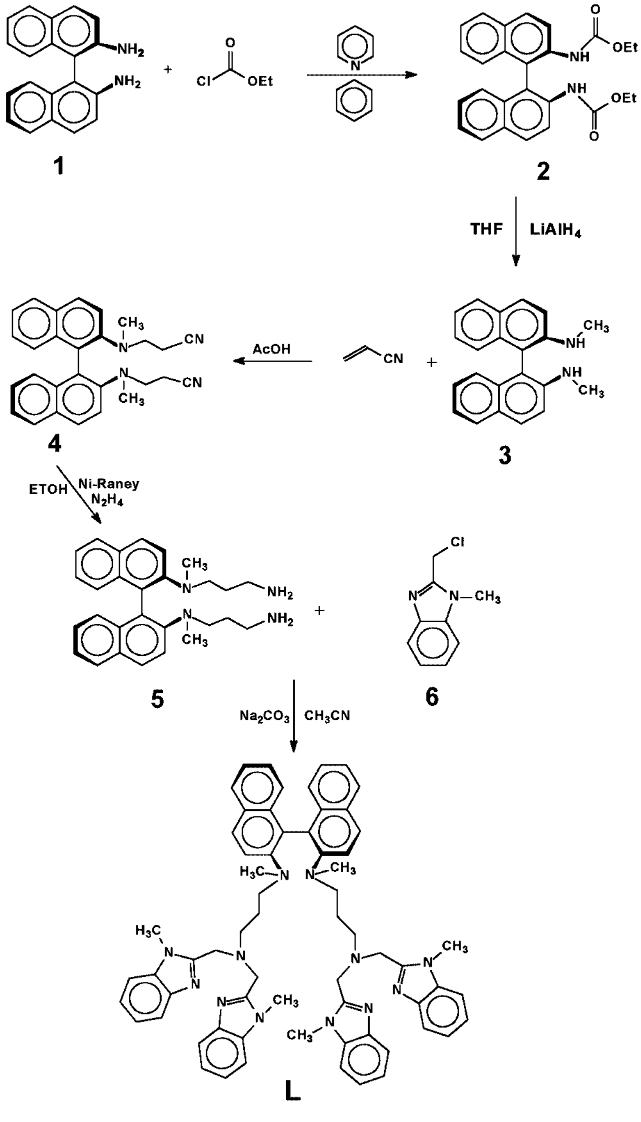
binaphthyl-2,2′-diamine residue acts as the spacer between two chelating arms containing tridentate aminobis(benzimidazole) donors (Scheme 1), and recently reported briefly that dinuclear and trinuclear copper(II) complexes derived from this ligand perform stereoselective catalytic oxidation of optically active diphenolic substrates.[8] We report here full synthetic details for the preparation of **L** and the conformational characterization of this new ligand and the corresponding dinuclear zinc(II) and nickel(II) complexes.



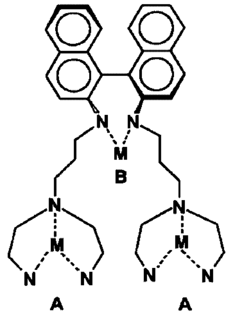
Scheme 1. Synthetic route for the preparation of ligand **L**

Results and Discussion

Synthesis

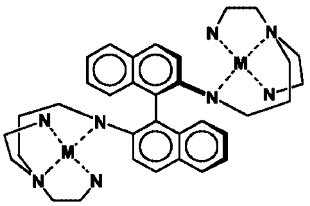
A particular challenge in the synthetic route to octadentate ligand **L** (Scheme 1) is to maintain an intact chiral moiety throughout the various reactions. To obtain a symmetric ligand containing a single arm attached to each nitrogen atom of the (*R*)-1,1′-binaphthyl-2,2′-diamine residue, compound **1** was initially derivatized with a double Benson-type monomethylation,[9] which gave the corresponding dicarbamate **2** in excellent yield (> 95%). The subsequent reduction using lithium aluminium hydride in anhydrous THF was also highly effective, since the *N*,*N*′-dimethyldiamine derivative **3** was isolated in high overall yield (> 70%). The diamine was then subjected to a Michael-type alkylation with acrylonitrile. This reaction was investigated under several conditions to avoid monoalkylation and/or oligomerization of the reagent. A good yield of the dialkylated compound proved difficult, but operating under nitrogen, and using acrylonitrile as solvent and a large excess of glacial acetic acid,[10] we obtained the dialkylated product **4** in > 80% yield. The pure compound was obtained by flash chromatography in 52% yield. The dicyano functionalities were reduced successfully to primary amines by reaction with Raney nickel and hydrazine hydrate in ethanol solution, and the resulting compound **5** was obtained in good yield (> 70%). Other reducing agents such as lithium aluminium hydride or sodium borohydride gave much poorer yields and formed by-products. Finally, the ligand **L** was obtained by condensation of an excess 2-(chloromethyl)-1-methylbenzimidazole, **6**,[11] with the diamine **5**. The use of *N*-methylated benzimidazoles increased the chemical stability of the resulting metal complexes in the oxidative reactions studied by us.[8]

The distribution of nitrogen donors of the ligand may allow one to obtain trinuclear metal complexes containing two equivalent metal coordination sites (**A**) within the tridentate units consisting of the aminobis(benzimidazole) residues and a third metal site at the binaphthalenediamine residue (**B**) (Scheme 2). This arrangement is adopted by the complex $[Cu_3\mathbf{L}]^{6+}$,[8] and reproduces the type of donor atom distribution among the metal centers in the trinuclear cluster of multicopper oxidases.[12] When the ligand **L** is used in a dinuclear complex several possibilities exist, according to the characteristics and stereochemical preferences of the metal ions, and the two sites may even result in non-equivalent coordination types. Since copper(II) is stereochemically flexible and a pair of Cu^{II} ions in close proximity can undergo electronic coupling interactions, unraveling the coordination environment of the two copper ions in $[Cu_2\mathbf{L}]^{4+}$ in solution[8] is difficult. The simplest situation occurs when the eight donor atoms of **L** are evenly distributed within the two metal ions (Scheme 3); a favored situation when the metal centers can adopt a tetrahedral geometry. Therefore, we anticipate that this structural ar-



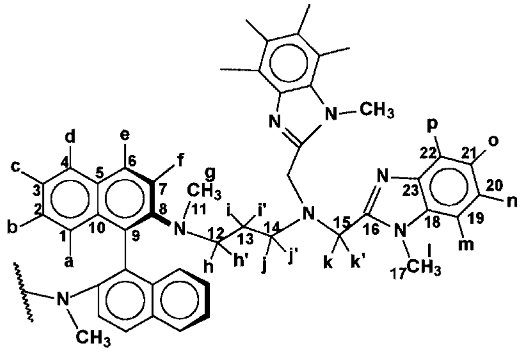
Scheme 2. Proposed structure for the trinuclear complexes of **L**

rangement will be present in the dinuclear zinc(II) complex $[Zn_2\mathbf{L}]^{4+}$; the diamagnetism of this metal ion is also useful since it enables a thorough investigation in solution by NMR spectroscopy. Only the dinuclear complex was isolated when we attempted to obtain a trinuclear zinc(II) complex, even upon reacting **L** with a large excess of Zn^{2+} at such high temperatures as boiling DMF, indicating that zinc(II) behaves differently from copper(II) in binding to **L**. This suggests that the binaphthalene-diamine nitrogen donors in the dinuclear complex $[Zn_2\mathbf{L}]^{4+}$ cannot be made available for binding a third metal ion. The investigation has been extended to the dinuclear nickel(II) complex $[Ni_2\mathbf{L}]^{4+}$, since the structural preferences of nickel(II) differ from those of zinc(II) and, in general, are relatively easy to assess on spectroscopic grounds. To this end, the spectral characteristics of $[Ni_2\mathbf{L}]^{4+}$ were compared with those of the mononuclear nickel(II) complex with the ligand *N*,*N*-bis[(2-*N*-methylbenzimidazol-2-yl)ethyl]benzylamine (**BzB**),[13] which essentially reproduces the tridentate donor set provided by the aminobis(benzimidazole) units present in each arm of **L**.



Scheme 3. Proposed structure for dinuclear complexes of **L** with metal ions in a tetrahedral geometry

Table 1. ^1H and ^{13}C NMR chemical shift assignments for ligand **L** in [D$_6$]acetone solution



^1H	δ	^1H	δ	^1H	δ
a	6.87	h	2.23	k	3.72
b	6.93	h′	2.33	l	3.64
c	7.07	i	1.13	m	7.47
d	7.72	i′	1.23	n	7.26
e	7.79	j	1.55	o	7.20
f	7.26	j′	1.62	p	7.58
g	2.28				
^{13}C	δ	^{13}C	δ	^{13}C	δ
1	126.0	9	129.0	17	29.0
2	126.0	10	134.4	18	136.9
3	124.0	11	39.3	19	109.9
4	128.1	12	55.5	20	122.4
5	130.4	13	23.3	21	121.5
6	128.7	14	51.2	22	119.6
7	121.7	15	51.0	23	143.1
8	150.8	16	151.9		

NMR Experiments

Deuterated acetone was chosen as solvent for comparative NMR experiments between **L** and the zinc(II) complex because both compounds are sufficiently soluble in it, and the best peak resolution was obtained. The assignment of the ^1H and ^{13}C signals of **L** (Table 1) was based on the expected chemical shifts and *J*-coupling patterns, and was confirmed by two-dimensional NMR experiments (Figure 1). An unambiguous assignment of the particularly challenging aromatic resonances of the binaphthyl and benzimidazole residues was obtained from the combination of ^1H-^{13}C HMQC, ^1H-^1H COSY, DEPT135, and ^1H-^{13}C HMBC spectra. With an ^1H-^{13}C HMQC experiment all the direct connections between protons and carbons could be detected. Long-range correlation with the known methyl protons **g** allowed the assignment of the quaternary carbon **8** resonance; then proton **e** could be recognized by correlations with carbons **8** and **10**. Signals belonging to the benzimidazole residues could be assigned from the long-range correlation between carbon **16** and protons **k** and **l**. Similarly, long-range correlations among protons and quaternary carbons, combined with the ^1H-^1H COSY spectrum, led to the identification of all the aromatic signals.

The assignment of protons **g**, **k**, and **l**, respectively, correlated with carbons **11**, **15**, and **17**, is consistent with the signal intensities and with the analysis of the DEPT135 spectrum. Due to the chirality of the compound, the three pairs of geminal protons **h**, **h′**, **i**, **i′**, **j**, **j′** give rise to three pairs of multiplets. Despite the overlap of signals **g** and **h′**, the analysis of the ^1H-^{13}C HMQC spectrum clearly showed the correlation of protons **h** and **h′** to the same carbon. The diastereotopic proton pairs **i**, **i′**, **j**, **j′** are connected in the same fashion to carbons **13** and **14**. Interestingly, the geminal protons **k** exhibit a singlet peak.

The NMR spectra of **L** are strongly affected by the coordination of Zn^{2+} ions. When Zn^{2+} is added to the solution of **L** in a 1:1 stoichiometry, several isomeric species are formed, because the metal ion can bind in different coordination modes, and this gives a proton NMR spectrum dominated by broad, poorly defined envelopes as the result of many superimposed resonances. The addition of Zn^{2+} to the ligand in a 2:1 stoichiometry removes the coordinative vacancies and gives the dinuclear complex $[Zn_2\mathbf{L}]^{4+}$ consisting of a single species. In the ^1H NMR spectrum, the broad envelopes are replaced by well-resolved peaks. Compared with the spectrum of the ligand, several signals undergo apparent splittings and many of them are shifted either downfield or upfield. Thus, the full assignment of the signals required the combination of one- and two-dimensional spectra (Figure 2). For the ^1H and ^{13}C NMR spectra

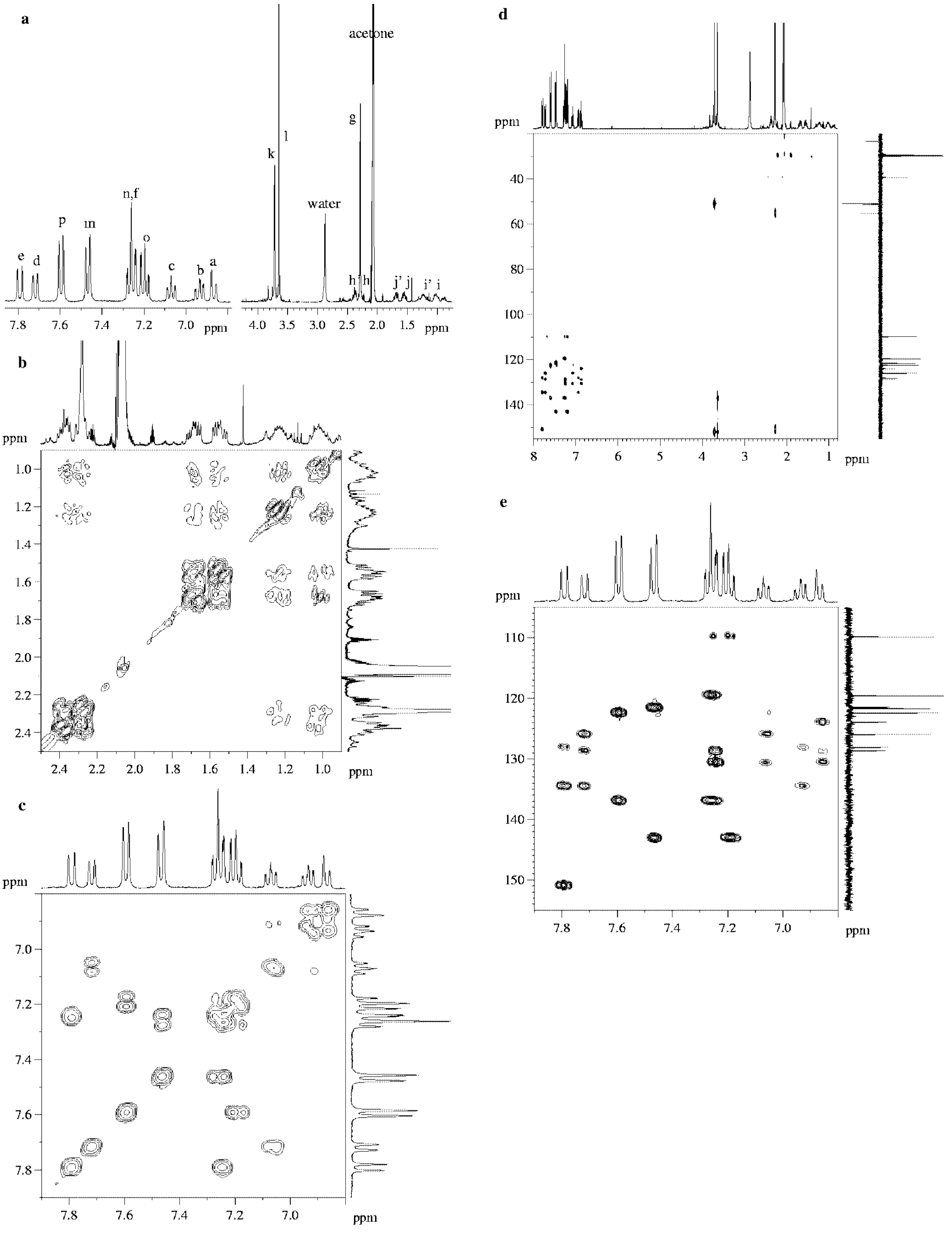


Figure 1. NMR spectroscopic data for **L** in [D$_6$]acetone solution: (a) proton NMR spectrum; (b) expanded plot of the aliphatic portion of the ^{1}H-^{1}H COSY spectrum; ^{1}H NMR spectrum of **L** at the right-hand edge and top of the map; (c) expanded plot of the aromatic portion of the spectrum of **L**; (d) long-range H-C correlated spectrum, with the ^{1}H NMR spectrum at the top edge and DEPT135 ^{13}C NMR at the right edge; (e) expanded plot of the aromatic portion of (d)

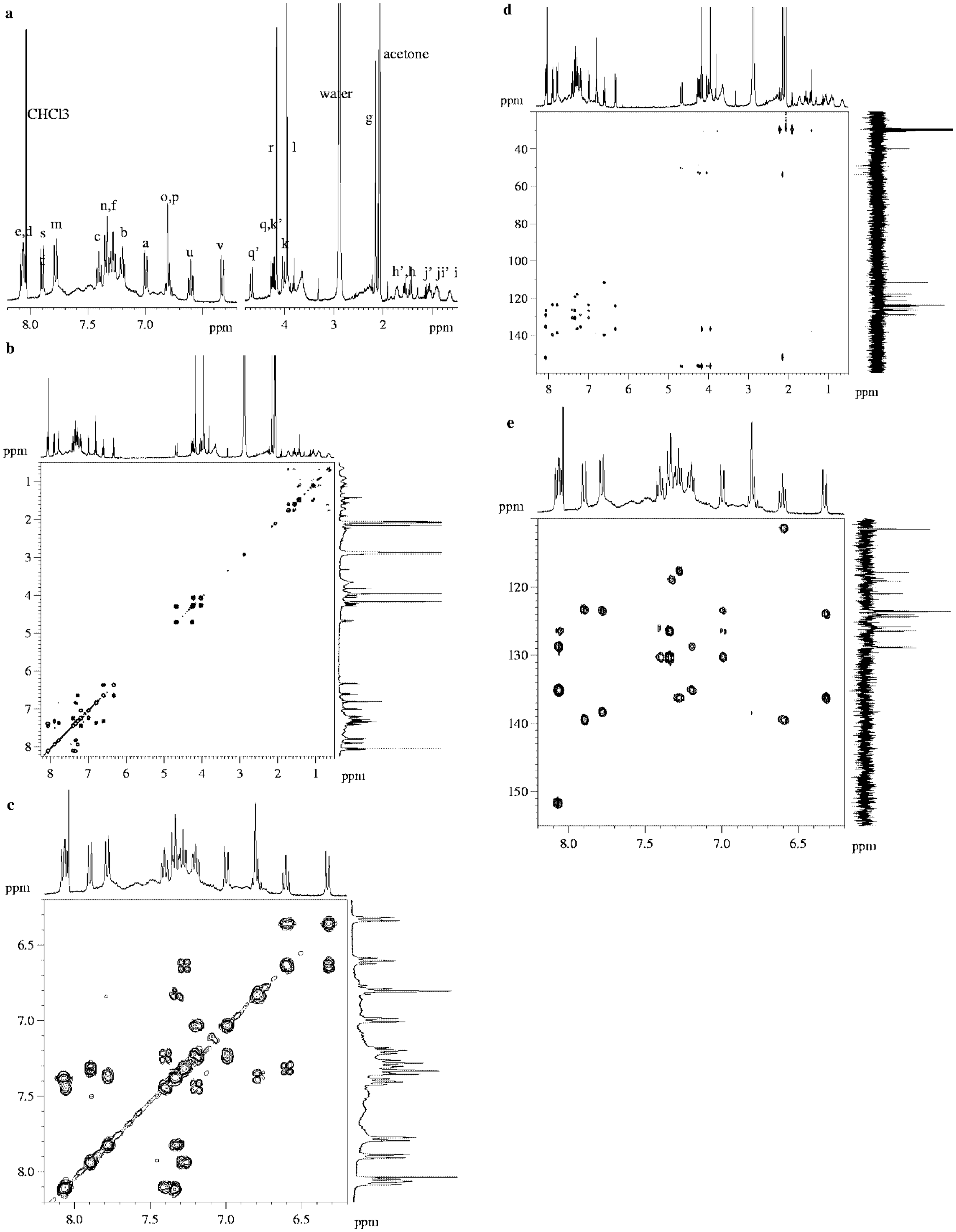
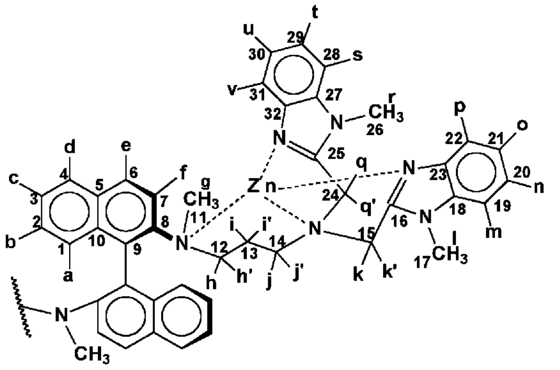


Figure 2. NMR spectroscopic data for $[Zn_2L]^{4+}$ in [D$_6$]acetone solution: (a) proton NMR spectrum; (b) ^{1}H-^{1}H COSY spectrum; ^{1}H NMR spectrum of $[Zn_2L]^{4+}$ at the right-hand edge and at the top; (c) expanded plot of the aromatic portion of the spectrum of $[Zn_2L]^{4+}$; (d) long-range H-C correlated spectrum, with the ^{1}H NMR spectrum at the top edge and DEPT135 ^{13}C NMR at the right-hand edge; (e) expanded plot of the aromatic portion of (d)

Table 2. ^1H and ^{13}C NMR chemical shift assignments for the $[Zn_2\mathbf{L}]^{4+}$ complex in [D$_6$]acetone solution



^{1}H	δ	^{1}H	δ	^{1}H	δ
a	7.00	i	0.66	o	6.80
b	7.20	i′	0.90	p	6.80
c	7.40	j	0.90	q	4.20
d	8.06	j′	1.06	q′	4.70
e	8.07	k	4.00	r	4.10
f	7.35	k′	4.15	s	7.90
g	2.10	l	3.90	t	7.29
h	1.57	m	7.78	u	6.60
h′	1.72	n	7.35	v	6.37
^{13}C	δ	^{13}C	δ	^{13}C	δ
1	125.5	12	52.0	23	138.5
2	126.0	13	23.0	24	48.0
3	123.5	14	53.0	25	157.0
4	128.5	15	50.0	26	29.0
5	130.5	16	157.0	27	137.0
6	128.5	17	29.0	28	111.2
7	121.0	18	137.0	29	124.0
8	152.0	19	111.0	30	123.3
9	130.8	20	124.0	31	117.2
10	135.1	21	123.5	32	139.5
11	38.0	22	119.0		

of the zinc complex (Table 2), as with **L**, the long-range correlations among protons and quaternary carbons combined with the $^1H-^1H$ COSY spectrum led to the identification of the signals of binaphthyl and benzimidazole residues. Analysis of the spectra of the cation $[Zn_2\mathbf{L}]^{4+}$ gave many clues about the coordination mode of the Zn^{2+} ions, which is consistent with the computed structure of the complex (see below).

In general, the coordination of metal ions makes the ligand more rigid: consequently, in the complex $[Zn_2\mathbf{L}]^{4+}$ there is no rapid exchange of nuclei and the signals of the methyl-benzimidazoles residues are split into two sets of resonances. As reported by Quiroz-Castro et al.,[14] the shift to higher frequencies of the **k** and **q** methylene groups indicates that the tertiary amine nitrogen atom is bonded to the metal center. The coordination of each Zn^{2+} ion with two benzimidazole *N*-donors is consistent with the downfield shift of the resonances of protons **m**, **n**, (at δ = 7.78, 7.35 ppm) and **s**, **t**, (7.90, 7.29) when compared with the corresponding protons **m** and **n** of the free ligand (at δ = 7.47, 7.26 ppm). Conversely, protons **o**, **p**, **u**, **v** undergo highfield shifts that can be explained by considering the computed structure of the complex. In fact, coordination of Zn^{2+} brings the aromatic protons **m**, **n**, **s**, **t** to an outer position with respect to the core of the molecule, while protons **o**, **p**, **u**, **v** occupy an inner position, where they are shielded by the aromatic binaphthyl residue.

The coordination of each Zn^{2+} ion to one naphthylamino nitrogen donor is shown by the downfield shift of all the ^1H signals of the naphthyl residue, with the strongest effect on proton **d** ($\Delta\delta = +0.34$, with respect to the free ligand), and on carbon **8** ($\Delta\delta = +1.2$). Interestingly, the two naphthylamine fragments still give a unique set of signals as for the free ligand: probably, the mobility of the molecule averages the signals in the dinuclear complex. Finally, the aliphatic chain with the carbon skeleton indicated as **12**, **13**, **14** undergoes some important modifications: strong positive shielding effects are observed on carbon **12** ($\Delta\delta = -3.5$ ppm) and on **h** and **h′** multiplets ($\Delta\delta = -0.66$ and -0.61 ppm, respectively), as well as on **j** and **j′** multiplets (-0.65 and -0.56, respectively), while a slight positive shielding effect occurs on carbon **13** ($\Delta\delta = -0.3$ ppm) and on **i** and **i′** multiplets (-0.47 and -0.33, respectively), and a deshielding effect is observed on carbon **14** ($+2.8$). The Δδ between geminal protons of these groups increases; the strongest effect is for the **i**, **i′** multiplets (Δδ of $+0.33$). The reported values arise from the opposing effects of coordination to a metal ion and interaction with the positive shielding zone of the binaphthalene and benzimidazole rings.

The proton NMR spectra of both $[Ni_2\mathbf{L}]^{4+}$ and $[Ni(\mathbf{BzB})]^{2+}$ exhibit paramagnetically shifted resonances up to about 90 ppm (Figure 3). This precludes the metal centers having a four-coordinate, square-planar coordination environment as this would result in a diamagnetic species. The broad peaks downfield indicate an orbitally nondegenerate ground state, with excited states well separated in energy, for both complexes. This can occur with six-coordinate (pseudo-octahedral) or five-coordinate (both TBP and SP) nickel(II) complexes. By contrast, pseudo-tetrahedral nickel(II) complexes exhibit sharper NMR resonances due to fast electronic relaxation caused by the low energy excited states originating from the orbitally degenerate $^3T_1$ ground state of a pure tetrahedral symmetry.[15] Furthermore, in pseudo-tetrahedral nickel(II) complexes, the dipolar and spin polarization contributions to the paramagnetic shift generates both downfield and upfield shifts in the NMR resonances. The spectrum of $[Ni(\mathbf{BzB})]^{2+}$ exhibits sharper NMR lines than that of $[Ni_2\mathbf{L}]^{4+}$, and also some upfield signals. The whole spectrum resembles those of five-coordinate, trigonal bipyramidal, nickel(II) complexes,[16] in which an unpaired electron in the equatorial plane accounts for the moderately intense spin-polarization and dipolar contributions. The donor groups for nickel(II) in $[Ni(\mathbf{BzB})]^{2+}$ are the two benzimidazoles, the central amine and two solvent molecules, as in structurally characterized copper(II) complexes with related aminobis(benzimidazole) ligands.[17] On the other hand, the NMR spectrum of

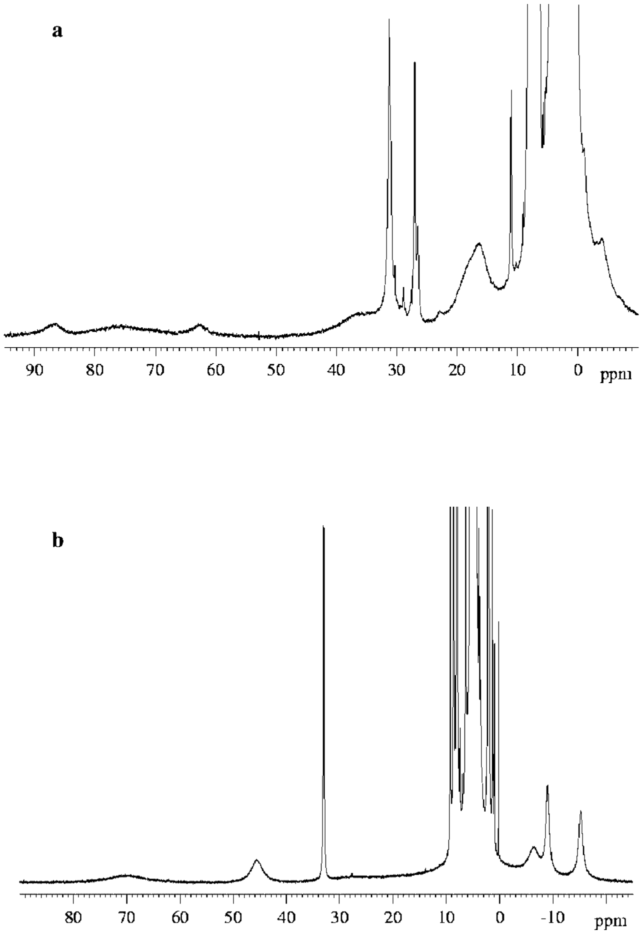


Figure 3. Paramagnetic NMR spectra recorded in [D$_6$]acetone solution at 25 °C of (a) [Ni$_2$**L**]$^{4+}$ and (b) [Ni(**BzB**)]$^{2+}$ complexes

[Ni$_2$**L**]$^{4+}$ shows essentially downfield shifts, indicating that the Fermi-contact is the predominant contribution to the paramagnetic NMR shifts. This situation is characteristic for electron configurations with a nondegenerate ground state, with unpaired electrons in σ-type d orbitals, as it occurs in six-coordinate, pseudo-octahedral or tetragonally distorted nickel(II) complexes.[15] The difference in metal coordination environment observed for [Ni$_2$**L**]$^{4+}$ with respect to [Ni(**BzB**)]$^{2+}$ clearly arises from the additional binding of the binaphthalenediamine nitrogen donors in the former complex, which provide the tetragonal equatorial field for each metal ion.

Optical and CD Spectroscopy

The electronic spectrum of **L** consists of transitions associated with both the 1,1′-binaphthyl and the benzimidazole chromophores. The former is mostly responsible for the absorptions at 305 and 258 nm, and the latter for the multicomponent bands at 286, 278, and 271 nm, while both chromophores contribute to the band at 352 nm and the intense absorption at highest energy.[7a,11] The CD spectrum of **L** is dominated by the features of the (*R*)-1,1′-binaphthyl moiety (Figure 4), and from a comparison with the pattern of CD bands of (*R*)-*N,N,N′,N′*-tetramethyl-[1,1′-binaphthalene]-2,2′-diamine[7a] the replacement of a methyl group of each NMe$_2$ residue of the latter compound with the methylene chain carrying the aminobis(benzimidazole) arm in **L** clearly maintains the *cisoid* conformation (M helicity) of the naphthalene rings. This arrangement is determined by the steric hindrance between the amino substituents and the naphthyl group, which prevents their coplanar disposition maximizing conjugation of the nitrogen lone pair with the naphthalene ring.[7a]

In addition to the CD bands attributable to the binaphthyl chromophore, the CD spectrum of **L** displays a clearly defined positive peak at 248 nm (inset of Figure 4). This corresponds to a distinctive CD feature detected, or deduced from the CD lineshape, at 240 nm in the spectra of chain-bridged (*R*)-1,1′-binaphthyl derivatives.[7b] The latter feature, attributed to an inter-naphthalenic CT transition, witnesses that the dihedral angle between the naphthalene rings of the chromophore reduces to significantly below 90°.[7b] This unexpected arrangement for **L** is confirmed by the minimum energy conformation of the ligand resulting from the computations described below.

The CD spectrum of [Zn$_2$**L**]$^{4+}$ is qualitatively similar to, though appreciably less intense than, that of the free ligand (Figure 4). Clearly, the M chirality of the (*R*)-1,1′-binaphthyl chromophore is maintained in the complex, but the spectrum lacks the distinctive positive CD peak at 248 nm which is present in the spectrum of **L**. This suggests that in the complex the dihedral angle between the naphthalene rings must increase to around 90°, which typically characterizes the conformation of unstrained 1,1′-binaphthyl chromophores.[7b] The decrease in intensity of the CD couplet, from **L** to [Zn$_2$**L**]$^{4+}$, agrees with the increase in dihedral angle between the naphthalene rings.[6] The change in conformation undergone by the ligand on metal binding must be associated with the fact that the amino groups linked to the naphthalene rings are now involved in the coordination to the metal centers.

The reduction in CD amplitude of the exciton coupled binaphthalene transitions in the 210−230 nm range becomes drastic for the [Ni$_2$**L**]$^{4+}$complex (Figure 4). Here, the ligand conformation must meet the coordination requirements of the metal ions, which tend to arrange the four nitrogen donor atoms in a nearly coplanar disposition. This apparently imposes a marked flattening of the dihedral angle between the naphthalene planes, as indicated by the much weaker intensity of the CD couplet.[6,7b] Also for [Ni$_2$**L**]$^{4+}$ the CD spectrum has a positive peak in the 245 nm range, but the assignment to an intraligand transition is less certain, because LMCT transitions involving the Ni^{II} ions may occur in the same wavelength range. The optical and CD spectra of the [Ni$_2$**L**]$^{4+}$complex exhibit additional weak absorptions in the visible region, which can be assigned to LF transitions. The reduced molar absorptivity observed in this range excludes pseudo-tetrahedral coordination, in agreement with the NMR spectrum of the complex. The LF spectrum (λ_{max} at 566 and 980 nm) is con-

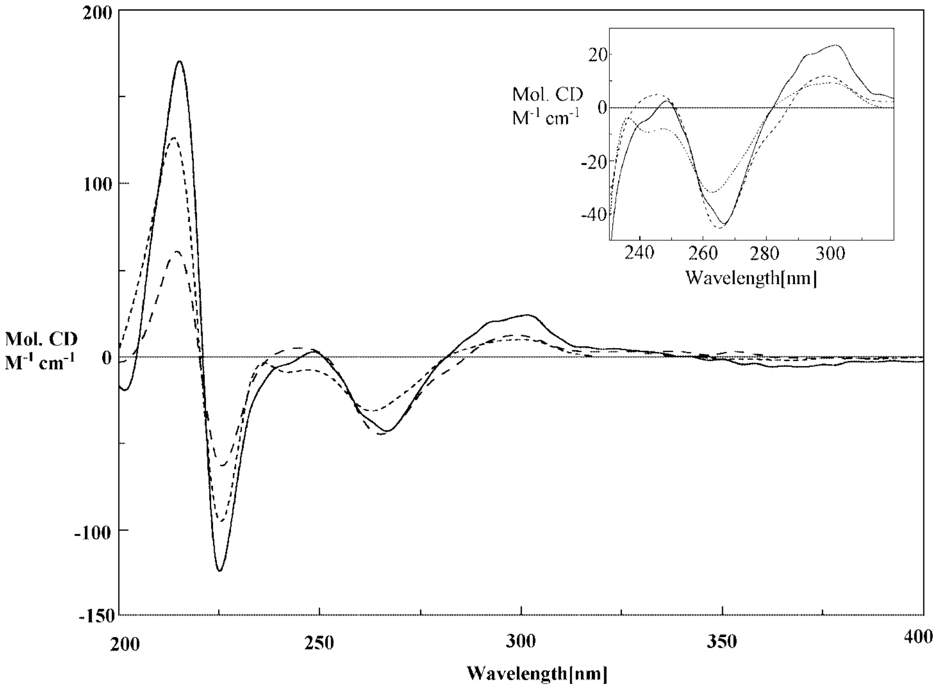


Figure 4. Circular dichroism spectra in CH_3CN solution of (—) **L**, (- - - -) $[Zn_2\mathbf{L}]^{4+}$, and (— — —) $[Ni_2\mathbf{L}]^{4+}$

sistent with six-coordinate, pseudo-octahedral metal centers,[18] which generally exhibit three absorption bands in the range 300−1200 nm. In the present case, the LF band at highest energy is clearly buried under the strong intraligand bands of **L**. The LF spectrum of $[Ni(\mathbf{BzB})]^{2+}$ contains absorptions of low intensity at 605, 920 and 1020 nm, which are consistent with a five-coordinate species and agree with the characteristics of the NMR spectrum. However, the optical spectrum cannot distinguish between trigonal bipyramidal and square-pyramidal configuration, due to the relatively high number of energy terms of the nickel(II) ion produced by even small geometric distortions from regular geometries.[19]

Computational Studies

Being unable to obtain crystals suitable for X-ray investigations, the structures of the ligand **L** and the binuclear complex $[Zn_2\mathbf{L}]^{4+}$, for which the conformational preferences deduced from CD are more reliable, were investigated by simulated annealing (SA) molecular mechanics (MM) and semiempirical calculations (see Exp. Sect.). The best structures obtained are shown in Figure 5. In **L** the benzimidazole rings from different arms are involved in favorable stacking interactions and this forces the dihedral angle θ defining the conformation of the 1,1′-binaphthyl group to close to 75° (Figure 5, a). A very similar arrangement is observed in all the most stable **L** structures obtained by the computational procedure (θ = 77±4°). In the binuclear complex $[Zn_2\mathbf{L}]^{4+}$ the benzimidazole rings are involved in Zn coordination. Both metal ions are in a slightly distorted tetrahedral environment, characterized by bond lengths ranging from 2.02 (Zn-*N*-benzimidazole) to 2.16 Å (Zn-*N*-binaphthyl). As a consequence of metal coordination, the benzimidazole rings fold around the two metal ions (Figure 5, b), which does not allow the stacking interactions observed in **L**, and relaxes the dihedral angle defining the conformation of the 1,1′-binaphthyl group to close to 90° (θ = 91±3°). In addition, the steric constraints imposed by the nitrogen ligand result in a distorted tetrahedral coordination geometry, suggesting that an extra ligand could bind to the metal forming a trigonal bipyramidal complex. To investigate this possibility we added a water molecule to the metal coordination environment and optimized the structure using semiempirical calculations. It turns out that a water molecule can bind (albeit weakly) to the metal center without affecting significantly the spatial disposition of the nitrogen ligands (data not shown). However, the slightly unfavourable reaction energy associated with its binding (0.2 kcal mol^{-1}) and the relatively long computed Zn−O distance (2.43 Å) indicate that it is more appropriate to consider the water molecule as only solvating the metal ion. Computed models of the $[Ni_2\mathbf{L}]^{4+}$complex could not be investigated because the electronic structure of the metal ion

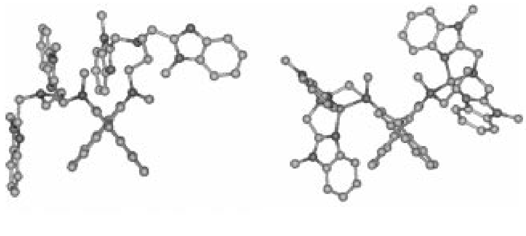

(a) (b)

Figure 5. Best structures for **L** (a) and $[Zn_2\mathbf{L}]^{4+}$ (b) as obtained by the combined SA-MM + PM3 procedure. Hydrogen atoms not shown for clarity

precluded reliable results with MM and semiempirical methods.

Conclusion

We have shown that (*R*)-1,1′-binaphthyl-2,2′-diamine provides a useful starting point for the synthesis of polyfunctional chiral ligands. The conformational features of the octadentate ligand **L** markedly change when it folds around the metal ions in the dinuclear zinc(II) and nickel(II) complexes. The spectroscopic and CD features of these complexes are consistent with the adoption of pseudo-tetrahedral structures for the zinc(II) centers and pseudo-octahedral structures for the nickel(II) centers. The stereochemical arrangement of the critical binaphthalenediamine portion of the molecule carrying the chiral unit can be clearly assessed on the basis of the CD spectra.

Experimental Section

Materials and Physical Methods: All reagents and solvents were obtained from commercial sources and used without further purification. The ligand *N*,*N*-bis[(2-*N*-methylbenzimidazol-2-yl)ethyl]benzylamine (**BzB**) was synthesized according to a published procedure,[13] while the corresponding nickel(II) complex was prepared in situ by mixing equimolar amounts of the ligand and nickel(II) salt. Tetrahydrofuran was dried by refluxing and distilling from metallic sodium. Elemental analyses were performed at the microanalytical laboratory of the Chemistry Department in Milan. Optical rotations were obtained from a Perkin−Elmer 241 polarimeter at 25 °C using a quartz cell of 10 cm path length. Optical spectra were obtained with HP 8452A and 8453 diode array spectrophotometers. MS spectra were obtained from a VG 7070 EQ spectrometer. Circular dichroism (CD) spectra were recorded with Jasco J-500 or J-710 spectropolarimeters, using quartz cells of 0.01−2 cm path length. ^{1}H and ^{13}C NMR spectra were recorded with Bruker AC 300 or Bruker AVANCE 400 spectrometers operating at 7.03 and 9.37 T, respectively. For solubility reasons, comparative NMR studies of **L** and $[Zn_2\mathbf{L}](ClO_4)_4$ were performed on CD_3COCD_3 solutions. A concentrated solution of the complex was obtained by mixing solutions of the ligand **L** and $Zn(ClO_4)_2{\cdot}7H_2O$ in [D$_6$]acetone and stirring for a few min in the NMR tube. The paramagnetic NMR spectra of $[Ni_2\mathbf{L}]^{4+}$ and $[Ni(\mathbf{BzB})]^{2+}$ complexes were recorded in the same solvent at 25 °C; the spectral width was increased to 50000 Hz and the pulse length reduced to 3 μs.

Ligand Synthesis. (*R*)-(+)-*N*,*N*′-(Ethoxycarbonyl)-1,1′-binaphthyl-2,2′-diamine (2): Compound **2** was prepared in accordance with Benson et al.[9] Commercial (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine, **1**, (2.0 g, 7.19 mmol) was dissolved in benzene (25 mL) and pyridine (5 mL, 62.14 mmol) under N_2 and cooled to 0 °C. A solution of ethyl chloroformate (1.8 mL, 18.89 mmol) in benzene (5 mL) was then added dropwise during 15 min. The mixture was subsequently warmed to room temperature and stirred for 2 h. The reaction, followed by TLC (silica gel) using light petroleum/ethyl acetate (8:2, v:v) as eluent, was then quenched by the addition of 2 N KOH (40 mL); the organic layer was separated, and the aqueous layer was extracted with benzene (3 × 20 mL). The organic layers were dried with Na_2SO_4 and the solvent was removed by rotary evaporation. After drying, a slightly pink powder was obtained, with sufficient purity for the subsequent reaction (yield 97%). $[\alpha]_D^{20} = +86.68$ ($c = 4.28{\cdot}10^{-3}$, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.18$ (t, $J_{H,H} = 7.1$ Hz, 6 H, CH_3), 4.1 (q, $J_{H,H} = 7.1$ Hz, 4 H, CH_2), 6.28 (br., 2 H, NH), 6.98 (d, $J_{H,H} = 8.5$ Hz, 2 H, CH), 7.24−7.30 (m, 2 H, CH), 7.41−7.46 (m, 2 H, CH), 7.94 (d, $J_{H,H} = 8.1$ Hz, 2 H, CH), 8.08 (d, $J_{H,H} = 9.1$ Hz, 2 H, CH), 8.57 (d, $J_{H,H} = 9.1$ Hz, 2 H, CH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 14.7$, 61.8, 117.8, 119.7, 125.2, 125.5, 127.7, 128.7, 130.7, 131.0, 132.9, 135.7, 154.0 ppm.

(*R*)-(+)-*N*,*N*′-Dimethyl-1,1′-binaphthyl-2,2′-diamine (3): $LiAlH_4$ (2.65 g, 69.83 mmol) was suspended in dry THF (40 mL) under N_2, and cooled to 0 °C. The dicarbamate **2** (2.71 g, 6.33 mmol) dissolved in dry THF (15 mL) was then slowly added via addition funnel, and the mixture was warmed and then refluxed for 24 h. The reaction was followed by TLC (silica gel) using light petroleum/ethyl acetate (8:2, v:v) as eluent. After cooling to room temperature, excess $LiAlH_4$ was quenched with MeOH (2 mL), NaOH 15% (2 mL), and finally water (2 mL). The resultant gray precipitate was filtered off through Celite and washed with diethyl ether. The filtrate and washings were combined and the solvent was removed by rotary evaporation under vacuum, giving a pale yellow solid. The crude compound was purified by silica gel flash chromatography using light petroleum/ethyl acetate (8:2, v:v) as eluent, furnishing a white compound in 72% yield. $[\alpha]_D^{20} = +182.82$ ($c = 4.08{\cdot}10^{-3}$, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.84$ (s, 6 H, CH_3), 6.96−7.00 (m, 2 H, CH), 7.14−7.23 (m, 4 H, CH), 7.27 (d, $J_{H,H} = 8.9$ Hz, 2 H, CH), 7.79−7.84 (m, 2 H, CH), 7.93 (d, $J_{H,H} = 8.9$ Hz, 2 H, CH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 32.1$, 113.1, 114.5, 122.8, 124.4, 127.5, 128.6, 130.5, 134.3, 145.6 ppm. MS (70 eV, EI): *m*/*z* (%) = 312 (100) $[M]^+$.

(*R*)-(−)-*N*,*N*′-Dimethyl-*N*,*N*′-[bis(2-cyanoethyl)]-1,1′-binaphthyl-2,2′-diamine (4): Glacial acetic acid (7 mL, 12.24 mmol) was added to compound **3** (1.5 g, 4.80 mmol) dissolved in acrylonitrile (35 mL). The resulting mixture was then heated to reflux whilst stirring in a nitrogen atmosphere for 72 h. Some signs of polymerization were evident on heating, and the initial yellow solution turned brown. The reaction was followed by TLC (silica gel) using light petroleum/ethyl acetate (8:2, v:v) as eluent. Excess acrylonitrile was removed by rotary evaporation and the remaining residue was extracted with aqueous Na_2CO_3 and CH_2Cl_2. The organic layer was anhydrified with Na_2SO_4. After filtration, the solvent was removed by rotary evaporation to give a brown, oily product. Silica gel flash chromatography using light petroleum/ethyl acetate (8:2, v:v) as eluent afforded a light yellow product in 52% yield. $[\alpha]_D^{20} = -173.48$ ($c = 6.60{\cdot}10^{-3}$, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.46$−1.70 (m, 4 H, CN-CH_2-CH_2-N), 2.80 (s, 6 H, CH_3), 2.80−2.89 (m, 4 H, CN-CH_2-CH_2-N), 7.12 (d, $J_{H,H} = 8.5$ Hz, 2 H, CH), 7.23−7.29 (m, 2 H, CH), 7.38−7.43 (m, 2 H, CH), 7.55 (d, $J_{H,H} = 8.9$ Hz, 2 H, CH), 7.90 (d, $J_{H,H} = 8.1$ Hz, 2 H, CH), 7.98 (d, $J_{H,H} = 8.9$ Hz, 2 H, CH) ppm. ^{13}C (75.5 MHz, $CDCl_3$, 25 °C, TMS) $\delta = 16.6$, 41.2, 53.1, 118.9, 121.6, 125.4, 126.1, 127.6, 128.6, 129.9, 130.1, 131.2, 134.7, 148.9 ppm. MS (70 eV, EI): *m*/*z* (%) = 418 (100) $[M]^+$.

(*R*)-(−)-*N*,*N*′-Dimethyl-*N*,*N*′-bis[(3-aminopropyl)]-1,1′-binaphthyl-2,2′-diamine (5): Compound **4** (600 mg, 1.43 mmol) was dissolved in EtOH (30 mL) by heating to 60 °C. A water suspension of Ni-Raney (12 g) and $N_2H_4{\cdot}H_2O$ (8 mL, 257 mmol) was added and the mixture maintained at 60 °C. After 3 h, complete nitrile consumption was evident by TLC (silica gel); excess Ni-Raney was removed by filtration through Celite and the solvent distilled off under vacuum. The remaining residue was purified by silica gel flash chromatography eluting with CH_2Cl_2/*i*PrOH (60:40, v:v) and an increasing amount of concentrated NH_3 (0 to 7%). A light yellow oil was obtained in > 70% yield. $[\alpha]_D^{20} = -95.11$ ($c = 1.00\cdot10^{-2}$, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) $\delta = 0.85-0.95$ (m, 2 H, CH_2-CH_2-CH_2), 1.16−1.27 (m, 2 H, CH_2-CH_2-CH_2), 1.82−1.94 (m, 4 H, CH_2), 2.52−2.64 (m, 4 H, CH_2), 2.64 (s, 6 H, CH_3), 7.09−7.22 (m, 4 H, CH), 7.26−7.36 (m, 2 H, CH), 7.53 (d, $J_{H,H} = 8.3$ Hz, 2 H, CH), 7.83−7.93 (m, 4 H, CH) ppm. ^{13}C NMR (75.5 MHz, [$CDCl_3$, 25 °C, TMS): $\delta = 32.0$, 40.4, 40.8, 56.0, 121.9, 124.6, 126.6, 126.9, 128.5, 129.1, 131.0, 135.1, 151.2 ppm. MS (FAB): *m*/*z* (%) = 428 (100) $[M+1]^+$.

(*R*)-(−)-*N*,*N*′-Dimethyl-*N*,*N*′-bis{3-[bis(1-methyl-2-benzimidazolylmethyl)]aminopropyl}-1,1′-binaphthyl-2,2′-diamine (L): (*R*)-(−)-*N*,*N*′-Dimethyl-*N*,*N*′-bis[(3-aminopropyl)]-1,1′-binaphthyl-2,2′-diamine (**5**, 332.5 mg, 0.78 mmol) was dissolved in anhydrous acetonitrile (40 mL). 2-(Chloromethyl)-1-methylbenzimidazole (**6**)[11] (365.7 mg, 3.45 mmol) and dry sodium carbonate were then added and the stirred mixture was boiled under reflux for 6 h under N_2. The reaction was followed by TLC (silica gel) using CH_2Cl_2/MeOH (9:1, v:v), as eluent. The mixture was then cooled to room temperature and the so-obtained precipitate filtered off; it consisted of product and inorganic salts and thus was treated with $CHCl_3$ and filtered again. The combined filtrates were finally dried under vacuum to afford a yellow powder in 65% yield. $C_{64}H_{66}N_{12}\cdot1.5CHCl_3$ (1182.34): calcd. (%) C 66.53, H 5.80, N 14.22; found C 66.41, H 5.90, N 14.21. $[\alpha]_D^{20} = -87.40$ ($c = 5.00\cdot10^{-3}$, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.70-0.90$ (m, 2 H, CH_2-CH_2-CH_2-N), 1.00−1.30 (m, 2 H, CH_2-CH_2-CH_2-N), 1.45−1.65 (m, 4 H, CH_2-CH_2-CH_2), 2.10−2.37 (m, 4 H, CH_2-*N*-binaphthyl), 2.37 (s, 6 H, CH_3-*N*-binaphthyl), 3.45 (s, 12 H, CH_3-*N*-benzimidazole), 3.51−3.64 (d, 8 H, CH_2-benzimidazole), 6.98−7.13 (m, 4 H, CH), 7.20−7.26 (m, 16 H, CH), 7.65−7.72 (m, 8 H, CH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 24.1$, 30.1, 40.1, 51.2, 52.2, 55.5, 109.4, 113.7, 120.0, 121.4, 122.4, 123.1, 124.3, 126.4, 126.5, 128.0, 128.6, 129.1, 129.6, 130.5, 134.6, 136.4, 142.4, 150.7, 151.7 ppm. MS (FAB): *m*/*z* (%) = 1003 (100) $[M+1]^+$. UV/Vis (CH_3CN): λ_{max} (ε) = 208 (239000), 258 (71000), 271 sh (54400), 278 sh (43500), 286 (32400), 305 sh (11900), 352 nm (6300 $mol^{-1}\cdot dm^3\cdot cm^{-1}$). CD ($CH_3CN$): λ_{max} ($\Delta\varepsilon$) = 214 (+169.8), 225 (−124.5), 240 sh (−3.8), 248 (+2.7), 260 sh (−36.1), 266 (−44.7), 301 (+23.2), 368 nm (−5.9 $mol^{-1}\cdot dm^3\cdot cm^{-1}$).

Caution! *1,1′-Binaphthyl-2,2′-diamine derivatives are not stable in solution; after a few hours a deeper color orange is observed. These compounds should be kept dry and protected from light.*

Synthesis of the Metal Complexes. $[Zn_2L](ClO_4)_4$: A methanolic solution of $Zn(ClO_4)_2\cdot7H_2O$ (0.038 mmol) (4 mL) was added dropwise to a solution of the ligand **L** (0.019 mmol) in $CHCl_3$/MeOH (1:5, v:v) (20 mL). The mixture was stirred for 3 h at room temperature, and then the solvent was removed by rotary evaporation. The residue was washed with a little water, filtered, and dried under vacuum. Elemental analysis for $C_{64}H_{66}Cl_4N_{12}O_{16}Zn_2$ (1530.14): calcd. (%) C 50.20, H 4.31, N 10.98; found C 50.33, H 4.41, N 10.95. UV/Vis (CH_3CN): λ_{max} (ε) = 220 sh (99000), 254 (46300), 264 (44400), 272 (43000), 280 (37200), 300 sh (10500), 350 nm (3000 $mol^{-1}\cdot dm^3\cdot cm^{-1}$). CD ($CH_3CN$): λ_{max} ($\Delta\varepsilon$) = 213 (+122.5), 225 (−95.1), 240 sh (−8.2), 263 (−31.9), 298 (+9.3), 365 nm (−2.8 $mol^{-1}\cdot dm^3\cdot cm^{-1}$).

$[Ni_2L](ClO_4)_4\cdot2H_2O$: This compound was prepared in a similar way as for the zinc complex, but using $Ni(ClO_4)_2\cdot6H_2O$ as metal salt. A pale green precipitate was obtained after addition of the metal salt to the ligand solution. The complex was separated by centrifugation, washed several times with MeOH, and dried under vacuum. Elemental analysis for $C_{64}H_{66}Cl_4N_{12}Ni_2O_{16}\cdot2H_2O$ (1552.77): calcd. (%) C 49.50, H 4.54, N 10.83; found C 49.22, H 4.63, N 10.78. UV/Vis (CH_3CN): λ_{max} (ε) = 222 sh (97800), 260 (67500), 272 (56800), 282 (42600), 304 (15300), 356 (5400), 566 (8), 980 nm (2 $mol^{-1}\cdot dm^3\cdot cm^{-1}$). CD ($CH_3CN$): λ_{max} ($\Delta\varepsilon$) = 214 (+61.0), 225 (−63.2), 245 (+4.72), 265 (−45.8), 278 sh (−13.0), 298 (+11.7), 331 sh (+1.9), 373 (−2.6), 583 nm (−0.1 $mol^{-1}\cdot dm^3\cdot cm^{-1}$).

Caution! *Perchlorate complexes with organic ligands are potentially explosive and should be handled with great care. Only small amounts of material should be prepared. We had no problems working with the small amounts of perchlorate complex described here.*

Molecular Modelling: The structures of the ligand and the corresponding dinuclear zinc(II) complex were derived as follows. Starting structures were submitted to SA calculations carried out in vacuo over 200 ps, starting from 10 K, heating the system to 500 K in 80 ps, and then cooling it to 10 K in 110 ps. The time step was set to 1 fs. The final structures were optimized by MM calculations, using the conjugate gradient algorithm and requiring that the residual gradient of energy did not exceed 0.01 $kcal\cdot mol^{-1}\cdot Å^{-1}$. SA and MM calculations were carried out using the Universal Force Field.[20] This cycle was repeated 50 times both for the ligand and the dinuclear zinc(II) complex. The families of structures generated were clustered according to RMSD and ranked by relative energies. The conformers within 10 $kJ\cdot mol^{-1}$ above the computed global minimum conformation were further optimized by semiempirical calculations using the PM3 method.[21] All calculations were performed on a Silicon Graphics Indigo workstation using the software packages InsightII and Cerius2 [Biosym/MSI 9685, Scranton Road, San Diego, CA, USA].

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