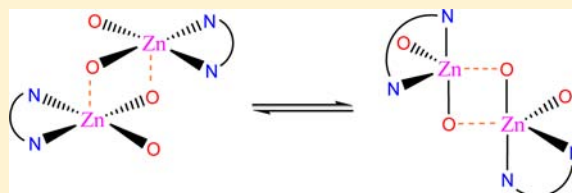


## An Unprecedented Structural Interconversion in Solution of Aggregate Zinc(II) Salen Schiff-Base Complexes

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## Supporting Information

**ABSTRACT:** This contribution explores the aggregation properties in solution of noncoordinating solvents of a series of amphiphilic Zn(salen) derivatives, through detailed <sup>1</sup>H NMR, DOSY NMR, and optical absorption spectroscopic studies. It is found that these aggregate species are involved in a unique structural interconversion between two defined dimers, A and B, driven by the concentration of water dissolved in chloroform. Dilute CHCl<sub>3</sub> solutions are characterized by the presence of dimeric species, A, in which both Zn<sup>II</sup> atoms of the Zn(salen) units mutually interact through a Zn...O axial coordination, likely adopting a square-base pyramidal structure. Investigations to higher concentrations indicate the existence of a new dimeric species, B, in equilibrium to that observed at lower concentrations, involving a coordination mode interconversion of an intermediate monomer presumably from a square-pyramidal to a trigonal bipyramidal structure. This behavior may be related to the nonconjugated, conformational flexible nature of the bridging diamine of the Schiff base, and is influenced by the solvent polarity. Variable-temperature <sup>1</sup>H NMR studies indicate the existence of a nonequivalent species B' in a fluxional equilibrium with species B.



## INTRODUCTION

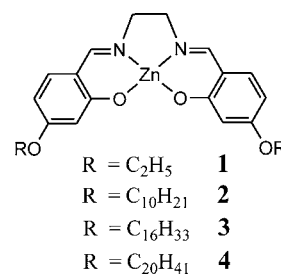
Tetracoordinated Zn<sup>II</sup> Schiff-base complexes are versatile substrates for the molecular aggregation, either in solution or in the solid state. Actually, they are Lewis acidic species that saturate their coordination sphere by coordinating a large variety of Lewis bases,<sup>1,2</sup> or in their absence, can be stabilized through intermolecular Zn...O axial coordination involving Lewis basic atoms of the ligand framework.<sup>3–5</sup> Alternatively, the appropriate design of ligands possessing flexible Lewis donor atoms as side substituents, suitable to axially coordinate the Zn<sup>II</sup> atom of another molecular unit, allows the achievement of new tailored Zn<sup>II</sup> supramolecular architectures.<sup>6</sup>

We have recently investigated a series of amphiphilic bis(salicylaldiminato)Zn Schiff-base complexes, having dipodal alkyl side chains in the salicylidene rings to allow a suitable solubility in a large variety of solvents. From these studies, a distinct behavior of these complexes in solution has been observed: in noncoordinating solvents, independent from the nature of the conjugated bridging diamine and the length of alkyl chains, these complexes form aggregates whose degree of aggregation is influenced by the nature of the bridging diamine and the concentration of the solution.<sup>2</sup> However, in coordinating solvents or via the addition of a Lewis base, there is the formation of monomer species having the solvent or the Lewis base axially coordinated to the Zn<sup>II</sup> ion.<sup>1,4,2</sup> Because the axial coordination of the Lewis base in these complexes is accompanied by sizable optical absorption variations and fluorescence enhancement, this has allowed the development of chromogenic and fluorogenic chemosensors,<sup>1,2,3b,7,8</sup> and the exploration of their unique second-order nonlinear optical

properties.<sup>9</sup> Moreover, a Zn<sup>II</sup> Schiff-base complex has been used as a reference Lewis acid to achieve a consistent, reliable scale of Lewis basicity for amines and nonprotogenic solvents.<sup>10</sup>

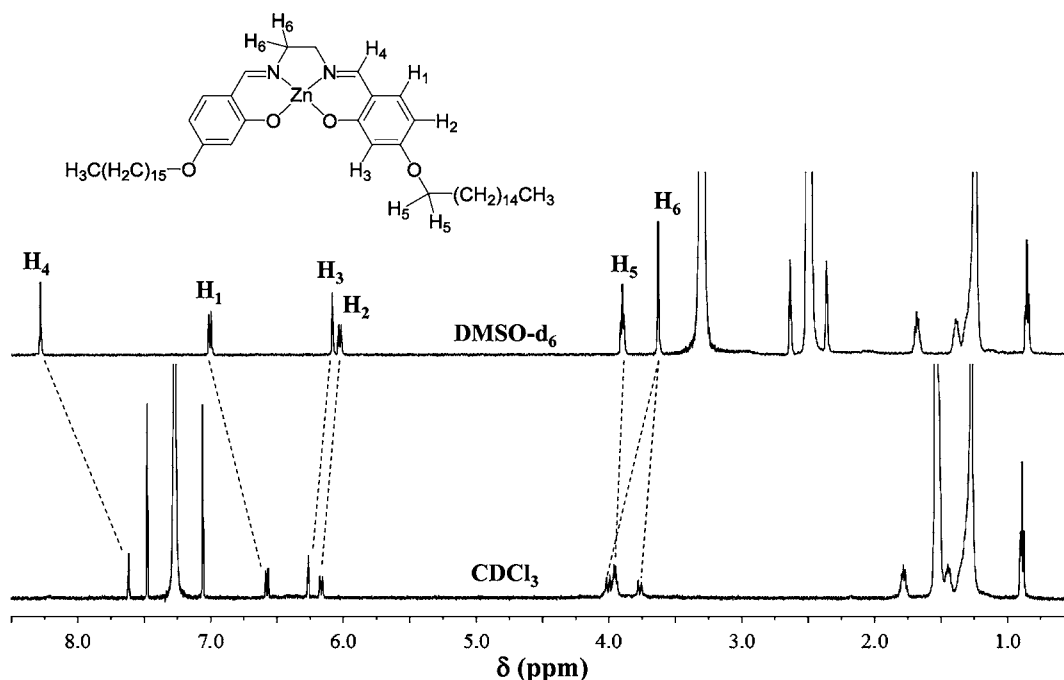
To further extend the study on the aggregation behavior of these complexes, we have synthesized a series of amphiphilic bis(salicylaldiminato)Zn<sup>II</sup> Schiff-base derivatives having nonconjugated, conformational more-flexible, bridging diamines, such as the ethylenediamine (salen), and investigated in detailed their <sup>1</sup>H NMR and optical spectroscopy properties in solution. The need to obtain sufficient solubility both in noncoordinating and coordinating solvents led to the synthesis of various amphiphilic derivatives upon changing the alkyl length chains (see Chart 1). It is found that these aggregate species are involved in a unique structural interconversion.

Chart 1



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**Figure 1.** Comparison of  $^1\text{H}$  NMR spectra of complex **3** in  $\text{DMSO-d}_6$  and  $\text{CDCl}_3$  solutions ( $\sim 1 \times 10^{-4}$  M).

## RESULTS AND DISCUSSION

The amphiphilic  $\text{Zn}(\text{salen})$  complexes **1–4** were synthesized with standard procedures, as previously reported.<sup>2</sup> They were characterized by ESI-mass spectrometry and  $^1\text{H}$  NMR spectroscopy. Mass spectrometry analysis always indicates the presence of defined signals corresponding to the protonated dimer (see Figure S1 in the Supporting Information). Complexes **2** and **3** are moderately soluble in low-polarity solvents, such as chloroform, and in coordinating solvents, such as dimethylsulfoxide (DMSO). On the other hand, complex **1** is soluble in DMSO but shows very low solubility in  $\text{CHCl}_3$ , while derivative **4**, which possesses longer alkyl chains, has good solubility in  $\text{CHCl}_3$  but is almost insoluble in DMSO. This different solubility for alkyl derivatives **1** and **4** allows exploration of their behavior in solution at higher concentrations, in coordinating and noncoordinating solvents, respectively, which is otherwise inaccessible for derivatives **2** and **3**.

$^1\text{H}$  NMR spectra of  $\text{Zn}^{\text{II}}$  Schiff-base complexes **1–3** in a dilute solution of coordinating solvents ( $\text{DMSO-d}_6$ ,  $\sim 1 \times 10^{-4}$  M) indicate the presence of sharp signals with the expected multiplicity, according to their molecular structures and consistent with the existence of monomeric species. The  $^1\text{H}$  NMR spectrum of derivative **3**, chosen as a reference compound, is reported in Figure 1. As expected, the  $^1\text{H}$  NMR features in DMSO remain unaltered along the **1–3** series (see Figure S2 in the Supporting Information),<sup>11</sup> and are concentration-independent, as can be verified using derivative **1** (see Figure S3 in the Supporting Information).

On switching to noncoordinating solvents ( $\text{CDCl}_3$ ,  $\sim 1 \times 10^{-4}$  M), the maximum concentration achievable for complexes **2** and **3**, a substantial change in the  $^1\text{H}$  NMR spectra is noted (see Figure 1 and Figure S4 in the Supporting Information). In particular, a strong upfield shift, with respect to the coordinating solvent, of the  $\text{H}_4$  (0.67 ppm) and  $\text{H}_1$  (0.43 ppm) signals is found, while the  $\text{H}_2$  and  $\text{H}_3$  signals are shifted slightly downfield (ca. 0.15 ppm). Finally,  $\text{H}_6$  signals, which are equivalent in  $\text{DMSO-d}_6$ , are split into two different signals, one

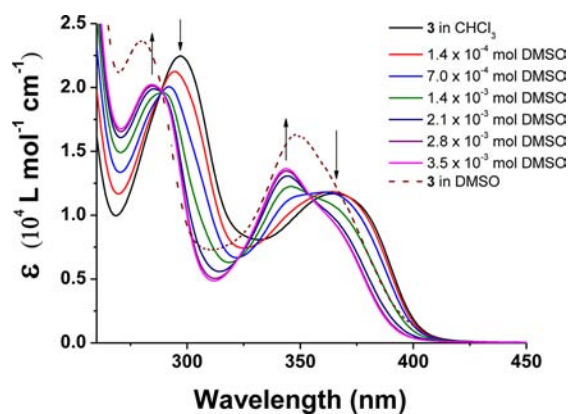
of which is shifted substantially downfield (0.38 ppm). These relevant upfield shifts upon switching from coordinating to noncoordinating solvents indicate that the involved hydrogens lie under the shielding zone of the  $\pi$  electrons of a conjugated system,<sup>2,12</sup> and the slight downfield shifts for some other hydrogen signals are consistent with the existence of aggregate species in solutions of noncoordinating solvents.

The alkyl side chains length is expected to play a very minor role in the aggregation properties, as the chemical shifts for all the aromatic,  $\text{CH}=\text{N}$  and the  $-\text{OCH}_2$  hydrogens remain unaltered along the **2–4** series ( $\text{CDCl}_3$ ,  $\sim 1 \times 10^{-4}$  M) (see Figure S5 in the Supporting Information).

$^1\text{H}$  NMR studies of complex **3** in mixtures of noncoordinating/coordinating ( $\text{CDCl}_3/\text{DMSO-d}_6$ ) solvents further support the existence of aggregates in the former solvent. In fact, the addition of defined amounts of  $\text{DMSO-d}_6$  to  $\text{CDCl}_3$  solutions of complex **3** leads to substantial spectral changes. In particular, upon the addition of a 5000-fold mole excess of  $\text{DMSO-d}_6$ , the resulting solution shows a  $^1\text{H}$  NMR spectrum that can be compared to that recorded in  $\text{DMSO-d}_6$  (see Figure S6 in the Supporting Information).

The absorption spectrum of complex **3** in dilute solutions of noncoordinating solvents ( $\text{CHCl}_3$ ,  $1.0 \times 10^{-4}$  M) consists of two main bands, at 297 nm and  $\sim 365$  nm (see Figure 2). On switching to DMSO, unlike to our previous studies,<sup>2</sup> a blue shift ( $\sim 18$  nm) of both absorption bands is observed. The addition of defined amounts of DMSO to  $\text{CHCl}_3$  solutions of **3** leads to optical changes analogous to those observed on switching to solutions of DMSO. In particular, by addition of  $1.5 \times 10^4$ -fold mole excess, the optical absorption spectrum of the resulting solution is comparable to that recorded in the coordinating DMSO solvent (Figure 2).

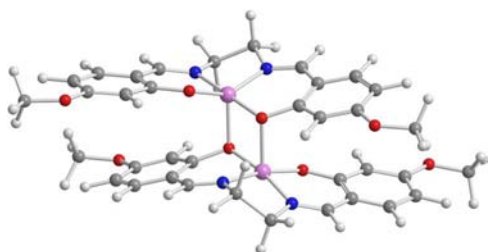
In summary, optical absorption and  $^1\text{H}$  NMR spectroscopic studies indicate that the behavior in dilute solutions of noncoordinating solvents for complexes **1–4** seems to be analogous to that previously found for derivatives having conjugated bridging diamines. In particular, on switching from



**Figure 2.** UV/vis absorption spectra of complex **3** ( $1.0 \times 10^{-4}$  M;  $2.0 \times 10^{-7}$  mol) in  $\text{CHCl}_3$ , and with the addition of DMSO. The absorption spectrum of **3** in DMSO (dotted line) is reported for comparison.

noncoordinating to coordinating solvents, the presence of sharp  $^1\text{H}$  NMR signals and the observed  $^1\text{H}$  NMR and optical absorption shifts are consistent with the existence of defined aggregate dimeric species (for example, in a pseudo-centrosymmetric fashion of the  $\text{Zn}(\text{salen})$  units, twisted in opposite directions to each other).<sup>13</sup> In such an arrangement, both  $\text{Zn}^{\text{II}}$  atoms mutually interact through a  $\text{Zn}\cdots\text{O}$  axial coordination, thus adopting a square-base pyramidal structure (**A**; see Chart 2).

#### Chart 2. Modeling (MM+) of the Proposed Structure **A** for Complexes **1**–**4** in Dilute Solutions of Non-Coordinating Solvents<sup>a</sup>



<sup>a</sup>Side alkyl chains were replaced by methyl groups for clarity of representation.

This is consistent with the dimeric X-ray<sup>3d</sup> or the optimized<sup>14</sup> structure found for the unsubstituted  $\text{Zn}(\text{salen})$  complex. A similar dimeric structure has been previously proposed in solution of noncoordinating solvents for analogous  $\text{Zn}^{\text{II}}$  complexes having conjugated bridging diamines.<sup>2</sup>

However,  $^1\text{H}$  NMR investigation of derivative **4** to higher concentrations in solution of noncoordinating solvents shows an unexpected behavior. In fact, the increase of the concentration ( $\text{CDCl}_3$ , up to  $5 \times 10^{-3}$  M) leads to the appearance of a new set of broad signals, which become progressively more intense with the increase of the concentration, while the sharp signals observed in dilute solutions undergo a parallel decrease (see Figure 3). This behavior is reversible, as demonstrated by dilution  $^1\text{H}$  NMR experiments using stock solutions of **4** ( $5 \times 10^{-3}$  M) in  $\text{CDCl}_3$ . This new set of broad signals is still consistent with the molecular structure of **4**. The detailed assignment of aromatic hydrogen signals was made by means of selected 1D T-ROESY experiments, which indicate that the  $\text{H}_1$  protons are spatially close to the  $\text{H}_4$  and  $\text{H}_2$  protons (see Figure S7 in the Supporting Information).

Therefore, chloroform solutions of the derivative **4** for concentrations greater than  $1 \times 10^{-4}$  M show evidence of the formation of a new species (**B**) in slow equilibrium, with respect to the NMR time scale, with the species **A** predominantly observed at lower concentrations. At the concentration of ca.  $5 \times 10^{-3}$  M, the maximum concentration achievable in  $\text{CDCl}_3$ , the species **B** becomes prevalent (ca. 70%, calculated by integration of  $^1\text{H}$  NMR signals) (see Figure 3).

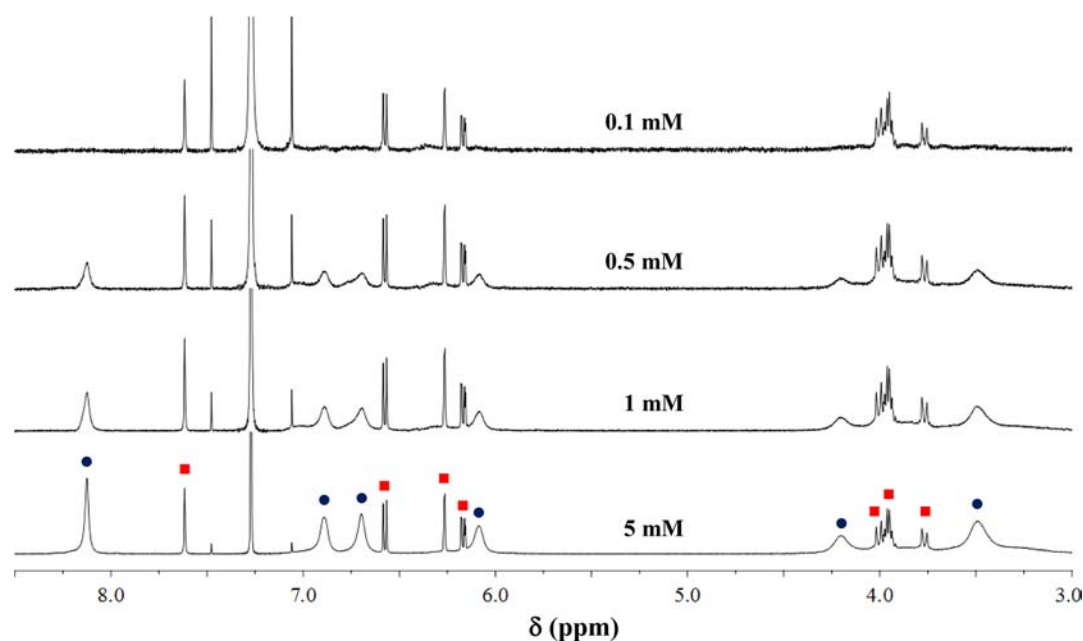
To further investigate this apparent concentration dependence behavior, a series of  $^1\text{H}$  NMR experiments were performed on  $\text{CDCl}_3$  solutions of **4** ( $1.0 \times 10^{-3}$  M) containing different concentration of water. Actually, upon passing from an unsaturated solution to a water-saturated  $\text{CDCl}_3$  solution, a decrease of the **B/A** concentration ratio and an incipient demetallation are observed. The successive addition of  $\text{D}_2\text{O}$ , with the formation of a two-phase system, results in a progressive disappearance of species **B** and the appearance of a set of new  $^1\text{H}$  NMR signals related to the demetallation of the complex. After 12 h, a complete disappearance of  $^1\text{H}$  NMR signals of **4** is observed, and the  $^1\text{H}$  NMR spectrum corresponds to that of the free ligand **4a** (see Figure S8 in the Supporting Information).<sup>15</sup> Analogous results are observed by even adding water or a DCl solution to  $\text{CDCl}_3$  solutions of **4**. In this last case, however, demetallation becomes faster.

These data indicate a role of the amount of water dissolved in chloroform in determining the equilibrium between the two species **A** and **B**. Despite this, we do not observe evidence for coordinated water in the  $^1\text{H}$  NMR spectra, presumably due to facile exchange. On the other hand, dimeric X-ray structures of bis(salicylaldiminato) $\text{Zn}^{\text{II}}$  Schiff-base derivatives always involve pentacoordinated  $\text{Zn}^{\text{II}}$  ions through intermolecular  $\text{Zn}\cdots\text{O}$  axial interactions,<sup>3</sup> while no dimeric structures with hexacoordination around the  $\text{Zn}^{\text{II}}$  ion are reported for tetradentate Schiff-base derivatives.<sup>16</sup> Monomeric structures that have axially coordinated water were reported, for example, for the unsubstituted  $\text{Zn}(\text{salen})$  derivative.<sup>17</sup> Moreover, it was recently demonstrated theoretically that starting from the monomeric  $\text{Zn}(\text{salen})\cdot\text{H}_2\text{O}$  adduct, the formation of the dimer  $[\text{Zn}(\text{salen})]_2$  involves a negative Gibbs energy.<sup>14</sup>

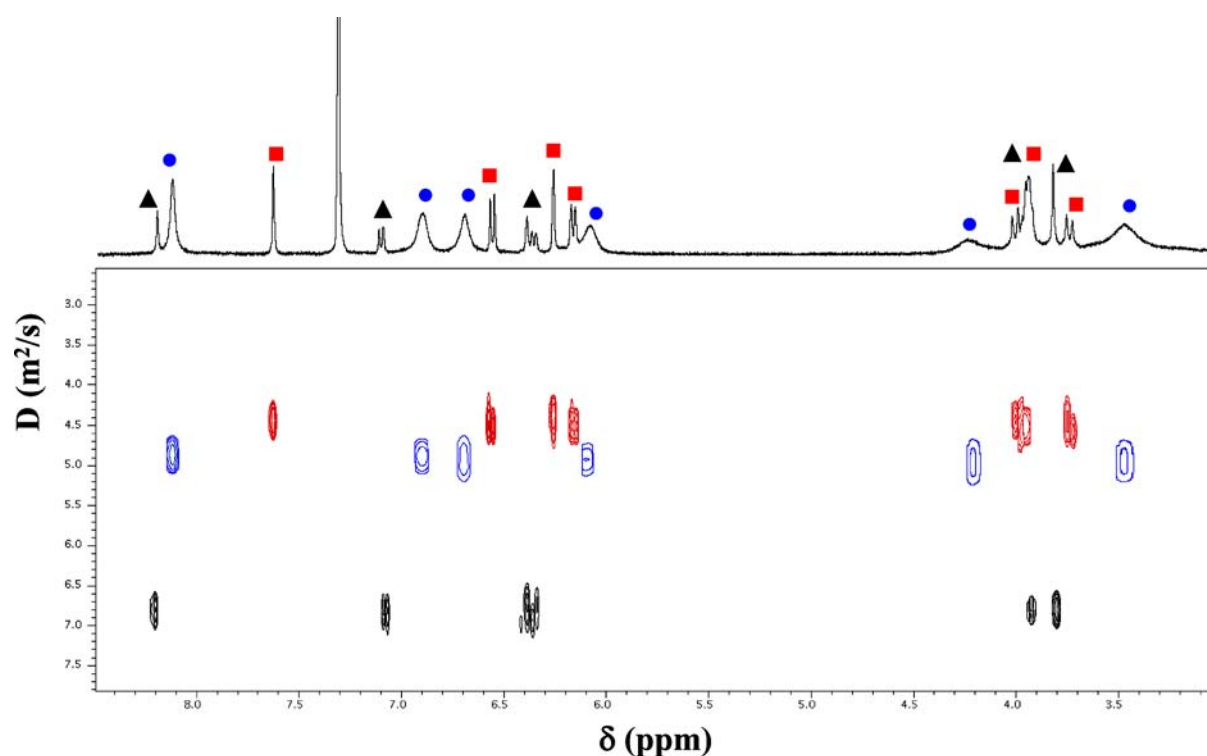
These observations suggest that the species **A** is stabilized by the concentration of water dissolved in chloroform, although experimental data and the above observations suggest that the water is presumably involved in an intermediate species.

As far as species **B** is concerned, the broad nature of related  $^1\text{H}$  NMR signals would suggest the presence of oligomeric aggregates or, alternatively, the existence of a slow (in the NMR time scale) conformational equilibrium involving species **B**. Therefore, we have used diffusion-ordered NMR spectroscopy (DOSY) to estimate the molecular mass of the species present in solution.<sup>18</sup> However, the nonspherical nature of the involved molecules does not allow any straightforward application of the Stokes–Einstein equation, as normally used to estimate the molecular size through the measurement of the diffusion coefficient ( $D$ ).<sup>19</sup> Thus, to achieve reliable molecular masses from DOSY measurements, we have chosen to estimate them by using a known internal reference species having an analogous molecular shape, thus obtaining the molecular mass by their relative diffusion coefficient.<sup>2,20</sup> In our case, we have properly chosen the uncomplexed ligand (**4a**) of derivative **4**.

The  $^1\text{H}$  NMR DOSY spectrum of **4** in  $\text{CDCl}_3$  ( $5.0 \times 10^{-3}$  M) is separated into two components in the diffusion dimension, associated to the set of signals related to species **A** and **B**, in addition of signals at larger  $D$  values, because of the presence of



**Figure 3.** Concentration dependence of  $^1\text{H}$  NMR spectra of complex **4** in  $\text{CDCl}_3$ . The labeling of  $^1\text{H}$  NMR signals related to the 5 mM solution refers to species **A** (denoted by the red square, ■) and **B** (denoted by the dark blue circle, ●).



**Figure 4.**  $^1\text{H}$  NMR DOSY spectrum of **4** in  $\text{CDCl}_3$  ( $5.0 \times 10^{-3}$  M) in the presence of the free Schiff-base ligand **4a** ( $5.0 \times 10^{-3}$  M). The labeling of  $^1\text{H}$  NMR signals refers to species **A** (denoted by the red square, ■), **B** (denoted by the dark blue circle, ●), and the free ligand (denoted by the black triangle, ▲).

the uncomplexed ligand used as reference. For both species, the estimated molecular mass clearly indicates the existence of dimers, although to the set of broad signals, species **B** is associated with a slightly larger  $D$  value and, hence, a smaller molecular mass (see Figure 4 and Table 1).

$^1\text{H}$  NMR studies of **4** in mixtures of noncoordinating/coordinating ( $\text{CDCl}_3/\text{DMSO-d}_6$ ) solvents further support the

existence of an equilibrium between the two species (**A** and **B**). In fact, the progressive addition of defined amounts of  $\text{DMSO-d}_6$  to  $\text{CDCl}_3$  solutions ( $5.0 \times 10^{-4}$  M) of **4** leads to the predominant disappearance of signals associated with species **A**, with respect to those associated with species **B** (see Figure S9 in the Supporting Information). Finally, via the addition of a 5000-fold mole excess of  $\text{DMSO-d}_6$  to a  $\text{CDCl}_3$  solution of **4**,



**Table 1.** Diffusion Coefficients and Estimated Molecular Mass ( $m$ ) for **4** and **4**:DMSO- $d_6$  Adduct at 27 °C in  $CDCl_3$  ( $5.0 \times 10^{-3}$  M)

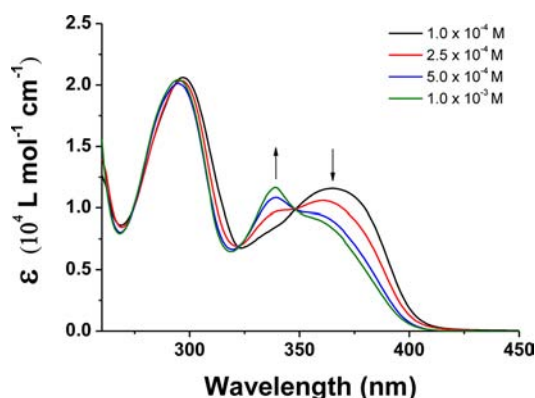
	Diffusion Coefficient, $D$ ( $\times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ )		Molecular Mass, $m$ (Da)		
	<b>4</b>	<b>4a</b>	estimated <sup>a</sup>	expected <sup>b</sup>	error (%)
<b>A</b>	4.50	6.80	1967	1849.5	6.3
<b>B</b>	4.80	6.80	1729	1849.5	6.5
<b>4</b> :DMSO- $d_6$ <sup>c</sup>	5.55	5.80	958	1008.9	5.0

<sup>a</sup>Estimated molecular mass with eq 1 using **4a** as internal reference species (see Experimental Section for more details). <sup>b</sup>Expected molecular mass. <sup>c</sup>Obtained upon the addition of a 5000-fold molar excess of DMSO- $d_6$  to a  $CDCl_3$  solution of  $5.0 \times 10^{-3}$  M.<sup>11</sup>

both sets (**A** and **B**) of the proton signals merge in a unique set of signals (see Figure 5), comparable to that recorded for complexes **1**–**3** in DMSO- $d_6$  (see Figure S2 in the Supporting Information).

UV/vis absorption spectra of complex **4** in  $CHCl_3$  are concentration-dependent (Figure 6). While the absorption spectrum of the dilute solution ( $1.0 \times 10^{-4}$  M) is almost identical to that recorded for complex **3** at the same concentration (Figure 2), more-concentrated solutions are characterized by the progressive appearance of a new, blue-shifted band at  $\sim 338$  nm, while the band at 365 nm becomes a shoulder. Moreover, the presence of multiple isosbestic points clearly indicates the existence of an equilibrium between two different species.

Overall, experimental data suggest that, in chloroform solution, derivative **4** is involved in an equilibrium between two different dimeric species, **A** and **B**, driven by the concentration of water dissolved in chloroform. In particular, we propose that the equilibrium between **A** and **B** presumably implies the interconversion of an intermediate monomer from a square-pyramidal (SP) to a trigonal bipyramidal (TBP) structure,<sup>21,22</sup>

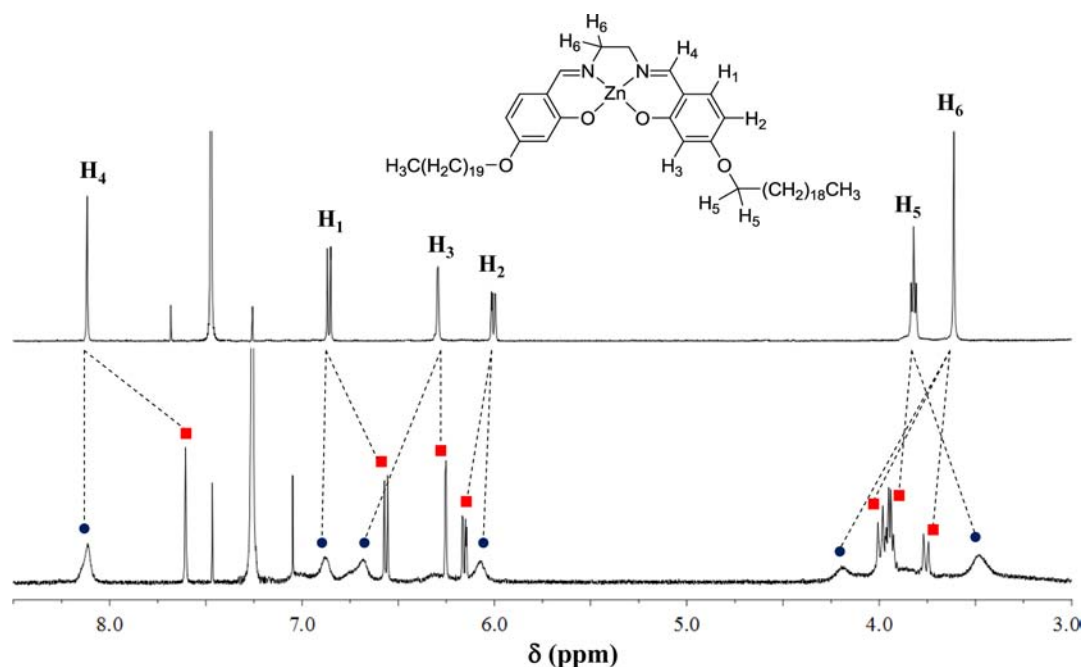


**Figure 6.** Concentration dependence of UV/vis absorption spectra of **4** in chloroform. Absorption spectra were recorded on the solutions used for concentration-dependent  $^1\text{H}$  NMR experiments in Figure 3.

through a pseudo-rotation<sup>23</sup> (see Scheme 1). The water is likely involved in the intermediate monomeric SP species, which rapidly evolves toward the formation of the more-stable dimer, **A**.<sup>14,24</sup> On the other hand, water-saturated  $CDCl_3$  solutions lead to demetallation with the formation of the free ligand **4a**.

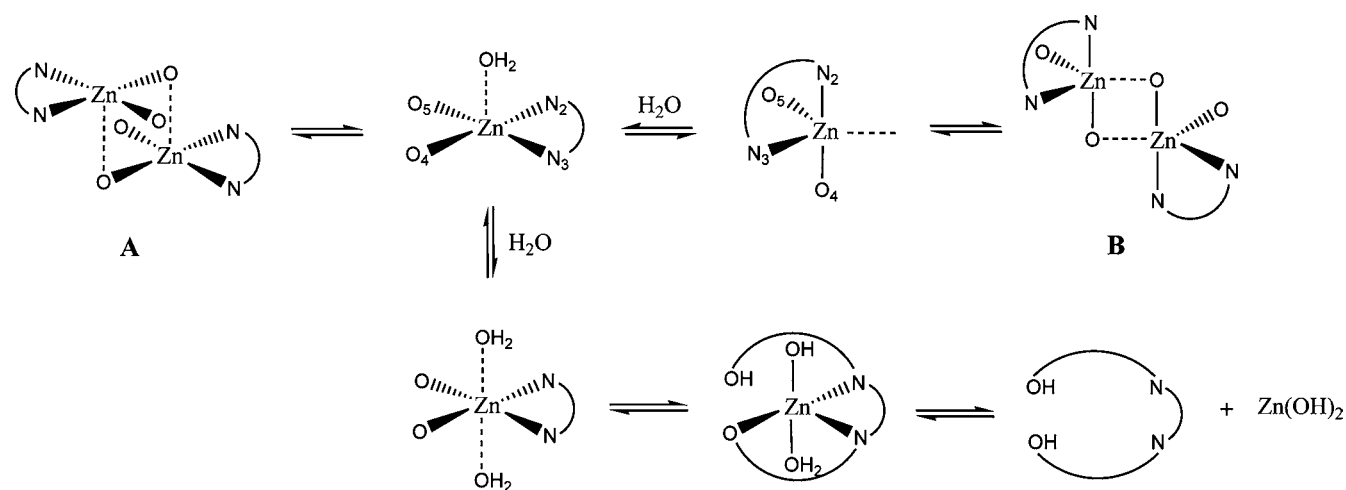
Thus, for species **B**, we suggest a structure in which both  $\text{Zn}^{\text{II}}$  atoms mutually interact through a  $\text{Zn}\cdots\text{O}$  equatorial coordination, in a TBP arrangement, in which the  $\text{Zn}(\text{salen})$  units lie orthogonal to each other (see Chart 3). An analogous TBP configuration has been found in the X-ray structure of related  $\text{Zn}^{\text{II}}$  diamino-aliphatic derivatives,<sup>3f,g</sup> thus supporting our proposed structure.

The proposed structure **B** is consistent with UV/vis,  $^1\text{H}$  NMR, DOSY NMR results, and deaggregation studies. In fact, the  $^1\text{H}$  NMR chemical shifts of the broad signals related to species **B** ( $CDCl_3$ ,  $5.0 \times 10^{-4}$  M), except the  $\text{H}_3$  signals that are downfield-shifted (0.40 ppm), are almost identical to those found upon

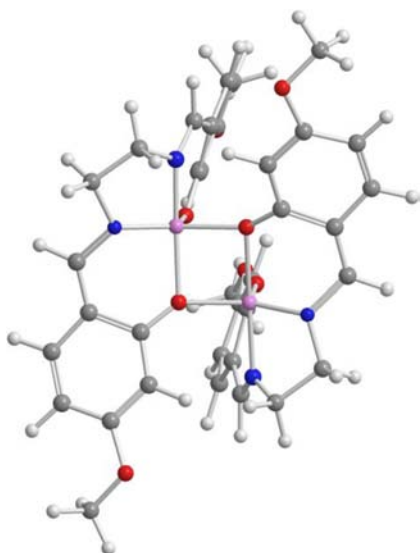


**Figure 5.**  $^1\text{H}$  NMR spectra of **4** in  $CDCl_3$  ( $5.0 \times 10^{-4}$  M;  $3.0 \times 10^{-7}$  mol) (bottom) and with the addition of  $1.5 \times 10^{-3}$  mol of DMSO- $d_6$  (top). The labeling of  $^1\text{H}$  NMR signals related to the  $CDCl_3$  solution refers to species **A** (denoted by the red square, ■) and **B** (denoted by the dark blue circle, ●).

**Scheme 1.** Proposed Equilibrium Involving the  $SP \rightleftharpoons TBP$  Interconversion of Complex 4 in Concentrate Solutions of Noncoordinating Solvents



**Chart 3.** Modeling (MM+) of the Proposed Structure B for Complex 4 in Concentrated Solutions of Noncoordinating Solvents<sup>a</sup>



<sup>a</sup>Side alkyl chains were replaced by methyl groups for the sake of clarity of representation.

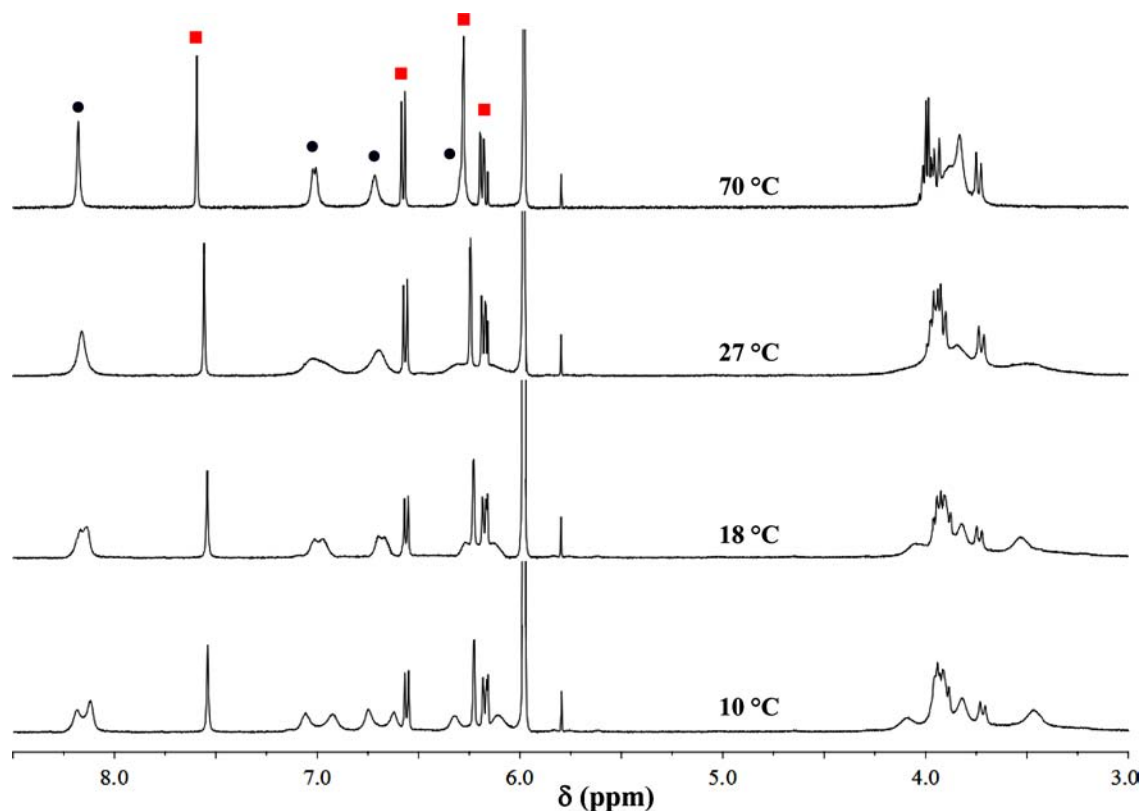
the addition of a large mole excess of DMSO- $d_6$  (Figure 5). This is indicative that, at variance of the sharp signals related to species A, upon switching from species B to the monomer, these involved protons are almost in the same chemical and magnetic environment, thus excluding any structure in a twisted arrangement between the Zn(salen) units, as in the case of structure A (see Chart 2). Accordingly, in structure B, except for H<sub>3</sub> hydrogens, which are deshielded, the remaining aromatic and CH=N hydrogens would not be influenced by the ring current effect of the salicylidene moieties of the other molecular unit (Chart 3). The observed blue shift of the longer wavelength band in UV/vis absorption spectra of concentrated CHCl<sub>3</sub> solutions of 4 (Figure 6) is also consistent with a structure in which the two Zn(salen) units of the dimer are barely interacting. Actually, these UV/vis spectra resemble those achieved upon deaggregation of dilute CHCl<sub>3</sub> solutions of 3 where species A is predominant.

Finally, the different molecular shape associated with the two (A and B) structures may account for the different observed diffusion coefficient values. In particular, the larger diffusion coefficient associated with structure B may be related to a more oblate spheroid shape of this dimeric aggregate (Chart 3), with respect that of structure A (Chart 2).<sup>19</sup>

<sup>1</sup>H NMR studies on changing the polarity of the non-coordinating solvent may be of interest to get further insights into the nature of the involved species A and B. Actually, upon switching from chloroform to the slightly more polar tetrachloroethane (TCE) solvent, a decrease of the B/A concentration ratio is observed. Conversely, in the nonpolar tetrachloromethane solvent, B becomes the only observed species (see Figure S10 in the Supporting Information). In other words, independent from the concentration, species B seems to be favored upon decreasing the solvent polarity. This reflects a more hydrophobic nature of species B, with respect to A. Note that, independently from the amount of water dissolved in the solvent, CCl<sub>4</sub> solutions of 4 are much more stable than those in CDCl<sub>3</sub>, since no appreciable demetallation is observed after 24 h. This suggests that species B is not influenced by the presence of water, thus supporting the above involved equilibria (Scheme 1).

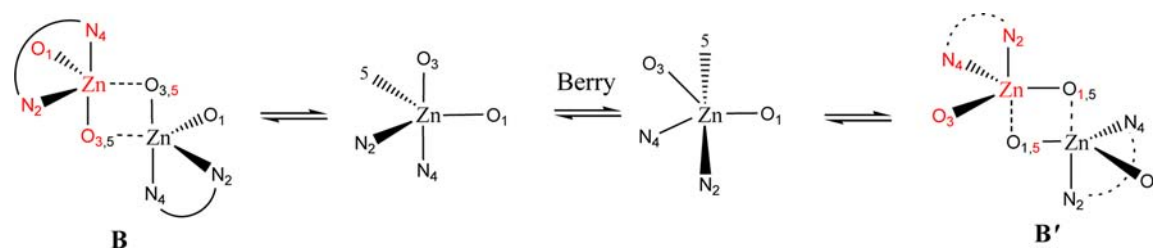
Overall, these results are in strict contrast to our previous studies in solution of noncoordinating solvents on related bis(salicylaldiminato)Zn<sup>II</sup> derivatives having conjugated bridging diamines.<sup>2</sup> In fact, we have found that they are always characterized as single dimeric species, while in the cases where a concentration dependence occurs, it affects the degree of aggregation. Thus, for present complexes, the existence of two different species, A and B, may be related to an improved conformation flexibility of the salen ligand, by virtue of the nonconjugated diamine bridge.

Variable-temperature <sup>1</sup>H NMR studies deserve further interesting investigations. Two noncoordinating solvents, CDCl<sub>3</sub> and TCE- $d_2$ , were considered. In particular, the latter solvent allows exploring at a higher temperature. Thus, <sup>1</sup>H NMR spectra of 4 either in CDCl<sub>3</sub> or TCE- $d_2$  ( $5.0 \times 10^{-3}$  M) indicate that, while the set of the sharp signals related to species A is almost temperature-independent in the investigated range, the broad signals related to species B are dependent on the temperature (see Figure 7 and Figure S11 in the Supporting Information). In particular, in TCE- $d_2$ , the broad signals



**Figure 7.** Variable-temperature  $^1\text{H}$  NMR spectra of **4** in  $\text{TCE-d}_2$  ( $5.0 \times 10^{-3}$  M). The labeling of  $^1\text{H}$  NMR signals refers to species **A** (denotes by red squares, ■) and **B** (denotes by dark blue circles, ●).

**Scheme 2. Proposed Berry Pseudo-rotation Involving the  $\text{B} \rightleftharpoons \text{B}'$  Interconversion of Complex **4****



recorded at room temperature, upon going down to  $10^\circ\text{C}$ , split into two sets of signals. On the other hand, exceeding the coalescence temperature ( $18^\circ\text{C}$ ), the broad signals become sharper as the temperature increases up to  $70^\circ\text{C}$ , and then remain unchanged up to  $120^\circ\text{C}$ . This is consistent with the existence of dimers of monomeric fragments that have magnetically equivalent protons, thus ruling out the formation of mixed SP-TBP dimeric species.<sup>25</sup> Moreover, the concentration ratio **B/A** increases as the temperature decreases, in both  $\text{CDCl}_3$  and  $\text{TCE-d}_2$  solvents.

Thus, variable-temperature  $^1\text{H}$  NMR data are consistent with the existence of a nonequivalent species **B'** involved in a fluxional equilibrium with species **B**, through a Berry pseudo-rotation,<sup>23,26</sup> thus leading to two different sets of  $^1\text{H}$  NMR signals. In particular, upon switching from **B** to **B'**, the  $\text{Zn}\cdots\text{O}$  interactions change from mutually equatorial to mutually axial (see Scheme 2).

By using the Gutowski–Holm approximation,<sup>27</sup> from the coalescence temperature and  $\Delta\nu$  values, a Gibbs free energy barrier of  $14\text{ kcal mol}^{-1}$  is estimated for the  $\text{B} \rightleftharpoons \text{B}'$  interconversion. This Gibbs free energy barrier is consistent

with that found for Berry pseudo-rotations in chelate metal complexes.<sup>23b,28</sup>

## CONCLUSIONS

This contribution explores the unusual behavior of a series of amphiphilic  $\text{Zn}(\text{salen})$  aggregates in solution of noncoordinating solvents. It may be related to the nonconjugated, conformational flexible nature of the bridging diamine of the Schiff base. Actually, unlike our previous investigations on related bis(salicylaldiminato) $\text{Zn}^{\text{II}}$  derivatives having conjugated bridging diamines, in such case a reversible equilibrium between two defined dimeric species is observed, driven by the concentration of water dissolved in chloroform.

Dilute  $\text{CHCl}_3$  solutions are characterized by the presence of defined dimers, presumably in a pseudo-centrosymmetric fashion of the  $\text{Zn}(\text{salen})$  units, in which both  $\text{Zn}^{\text{II}}$  atoms mutually interact through a  $\text{Zn}\cdots\text{O}$  axial coordination, thus adopting a square-base pyramidal structure (**A**). Investigations into higher concentrations of **4** suggest the existence of a new dimeric species, **B**, that is in equilibrium with that observed at lower concentrations.

In particular, we propose that the equilibrium between these two species involves a coordination mode interconversion of an intermediate monomer presumably from a SP to a TBP structure, in which the Zn(salen) units lie orthogonal to each other. The water is likely involved in the intermediate monomeric SP species, which rapidly evolves toward the formation of the more-stable dimer (A). Variable-temperature  $^1\text{H}$  NMR studies are consistent with the existence of a nonequivalent species B' involved in a fluxional equilibrium with species B, through a Berry pseudo-rotation. Solutions of 4 in the nonpolar tetrachloromethane solvent are always characterized as species B, in agreement with its more hydrophobic nature.

This unprecedented behavior certainly deserves further investigation with regard to other bis(salicylaldiminato)Zn<sup>II</sup> derivatives.

## EXPERIMENTAL SECTION

**Materials and General Procedures.** Zinc acetate dihydrate, 2,4-dihydroxybenzaldehyde, 1-iodoethane, 1-iododecane, 1-bromohexadecane, 1-bromoicosane, and ethylenediamine (Aldrich) were used as received. Chloroform (Aldrich) stabilized with amylene was used for spectrophotometric measurements.  $\text{CDCl}_3$  (Aldrich) containing 0.5 wt % silver foil as stabilizer and TCE- $d_2$  (Aldrich) were dried over molecular sieves (3 Å).  $\text{CCl}_4$  (Aldrich) was distilled before using. Column chromatography was performed on silica gel 60 (230–400 mesh) eluting with cyclohexane and EtOAc. TLC were performed using silica gel 60 F254 plates with visualization by UV and standard staining.

**Physical Measurements.** Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. Solution NMR experiments were carried out on a Varian Unity Inova 500 (499.88 MHz for  $^1\text{H}$ ) spectrometer using an inverse-detection tunable triple-resonance pfg 5 mm  $^1\text{H}^{13}\text{C}\{\text{X}\}$  probe capable of generating field strengths of 60 G/cm. All ID  $^1\text{H}$  NMR experiments were referenced to tetramethylsilane ( $\text{Si}(\text{CH}_3)_4$ , TMS). Samples were not spinning during all the analyses. For 1D T-ROESY experiments, the  $^1\text{H}$  90° pulse was 7.300  $\mu\text{s}$ , with a relaxation delay of 3.5 s. 1D T-ROESY spectra were obtained using a spin-lock time of 250 ms.  $^1\text{H}$  DOSY experiments were carried out at 27 °C, and referenced to the residual solvent signals ( $\text{CDCl}_3$ : 7.27 ppm). The gradient strength was calibrated by using the HDO signal at 25 °C ( $D = 19.02 \times 10^{-10} \text{ m}^2/\text{s}$ ). The bipolar pulse pair stimulated echo pulse-sequence with convection compensation (Dbppste-cc in the standard Varian pulse sequence library) was used for acquiring diffusion data with a diffusion delay ( $\Delta$ ) of 35 ms, a diffusion gradient length of 2.0 ms, and 128 increments for gradient levels. Gradient strengths of 2% and 95% of maximum power were used to obtain spectral pairs with acquisition times of 2 s and recycle delays of 3.5 s. The Varian DOSY package was used for the acquisition and processing (VnmrJ version 2.2, revision C). Because this study requires an estimate of the degree of aggregation, and since the structure of present complexes in solution is far from the spherical one, thus precluding a straightforward application of the Stokes–Einstein equation,<sup>19</sup> the molecular mass in solution ( $m$ ) was simply estimated using Graham's law of diffusion:  $D = K(T/m)^{1/2}$ , where the constant  $K$  depends on geometric factors, including the area over which the diffusion is occurring. By assuming a constant temperature and that  $K$  is the same for both species in solution, the relative diffusion rate of two species  $a$  and  $b$  is given by

$$\frac{D_a}{D_b} = \left( \frac{m_b}{m_a} \right)^{1/2}$$

This allows for the calculation of an unknown molecular mass via eq 1:

$$m_b = m_a \left( \frac{D_a}{D_b} \right)^2 \quad (1)$$

Therefore, the diffusion rate values obtained by DOSY can be used to estimate the molecular mass of a species, by comparison with the actual  $D$  value of a known internal reference.<sup>2,20b</sup> Optical absorption spectra were recorded at room temperature with a Varian Cary 500 UV-vis-NIR spectrophotometer. ESI mass spectra were recorded with a Finnigan LCQ-Duo ion trap electrospray mass spectrometer (Thermo).

**General Procedure for the Synthesis of Complexes 1–3.** Syntheses of 4-ethoxy-2-hydroxybenzaldehyde, 4-decyloxy-2-hydroxybenzaldehyde, and 4-hexadecyloxy-2-hydroxybenzaldehyde have been reported previously.<sup>2</sup> The complexes were prepared using a template method.<sup>2</sup> To a solution of 4-alkoxy-2-hydroxybenzaldehyde (1.00 mmol) in ethanol (10 mL), ethylenediamine (0.500 mmol) was added under stirring. The mixture was heated at reflux with stirring for 1 h, under nitrogen atmosphere. To the solution so obtained, zinc acetate dihydrate (0.1095 g, 0.500 mmol), was added and the mixture heated at reflux with stirring for 1 h, under a nitrogen atmosphere. After cooling, the precipitated product was collected by filtration, washed with ethanol, and dried.

**[*N,N*-Bis(4-ethoxy-2-hydroxybenzylidene)-1,2-ethylenediaminato]Zn<sup>II</sup> (1).** White powder (0.178 g, 85%).  $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_4\text{Zn}$  (419.80): Calcd C, 57.22; H, 5.28; N, 6.67; Found C, 57.19; H, 5.29; N, 6.69. ESI-MS:  $m/z = 841 [(M)_2+H]^+$ .  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , TMS):  $\delta = 1.31$  (t,  $^3J_{\text{HH}} = 7.0$  Hz, 6 H;  $\text{CH}_3$ ), 3.63 (s, 4 H;  $\text{NCH}_2\text{CH}_2\text{N}$ ), 3.96 (q,  $^3J_{\text{HH}} = 7.0$  Hz, 4 H;  $\text{OCH}_2$ ), 6.03 (dd,  $^3J_{\text{HH}} = 8.5$  Hz,  $^4J_{\text{HH}} = 2.5$  Hz, 2 H; ArH), 6.08 (d,  $^4J_{\text{HH}} = 2.5$  Hz, 2 H; ArH), 7.01 (d,  $^3J_{\text{HH}} = 8.5$  Hz, 2 H; ArH), 8.28 (s, 2 H;  $\text{CH}=\text{N}$ ).

**[*N,N*-Bis(4-decyloxy-2-hydroxybenzylidene)-1,2-ethylenediaminato]Zn<sup>II</sup> (2).** White powder (0.290 g, 90%).  $\text{C}_{36}\text{H}_{54}\text{N}_2\text{O}_4\text{Zn}$  (644.24): Calcd C, 67.12; H, 8.45; N, 4.35; Found C, 67.22; H, 8.47; N, 4.38. ESI-MS:  $m/z = 1289 [(M)_2+H]^+$ .  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , TMS):  $\delta = 0.86$  (t,  $^3J_{\text{HH}} = 6.5$  Hz, 6 H;  $\text{CH}_3$ ), 1.22–1.45 (m, 28 H;  $\text{CH}_2$ ), 1.68 (m, 4 H;  $\text{CH}_2$ ), 3.63 (s, 4 H;  $\text{NCH}_2\text{CH}_2\text{N}$ ), 3.90 (t,  $^3J_{\text{HH}} = 6.5$  Hz, 4 H;  $\text{OCH}_2$ ), 6.02 (dd,  $^3J_{\text{HH}} = 8.5$  Hz,  $^4J_{\text{HH}} = 2.5$  Hz, 2 H; ArH), 6.08 (d,  $^4J_{\text{HH}} = 2.5$  Hz, 2 H; ArH), 7.00 (d,  $^3J_{\text{HH}} = 8.5$  Hz, 2 H; ArH), 8.28 (s, 2 H;  $\text{CH}=\text{N}$ ).

**[*N,N*-Bis(4-hexadecyloxy-2-hydroxybenzylidene)-1,2-ethylenediaminato]Zn<sup>II</sup> (3).** White powder (0.385 g, 95%).  $\text{C}_{48}\text{H}_{78}\text{N}_2\text{O}_4\text{Zn}$  (812.56): Calcd C, 70.95; H, 9.68; N, 3.45; Found C, 71.03; H, 9.69; N, 3.47. ESI-MS:  $m/z = 1625 [(M)_2+H]^+$ .  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , TMS):  $\delta = 0.85$  (t,  $^3J_{\text{HH}} = 6.5$  Hz, 6 H;  $\text{CH}_3$ ), 1.19–1.45 (m, 52 H;  $\text{CH}_2$ ), 1.67 (m, 4 H;  $\text{CH}_2$ ), 3.62 (s, 4 H;  $\text{NCH}_2\text{CH}_2\text{N}$ ), 3.89 (t,  $^3J_{\text{HH}} = 6.5$  Hz, 4 H;  $\text{OCH}_2$ ), 6.02 (d,  $^3J_{\text{HH}} = 8.5$  Hz, 2 H; ArH), 6.08 (s, 2 H; ArH), 7.00 (d,  $^3J_{\text{HH}} = 8.5$  Hz, 2 H; ArH), 8.28 (s, 2 H;  $\text{CH}=\text{N}$ ).

**4-Icosyloxy-2-hydroxybenzaldehyde.** To a solution of 2,4-dihydroxybenzaldehyde (0.690 g, 5.00 mmol) in acetone (20 mL), potassium carbonate (0.691 g, 5.00 mmol), 18-crown-6 (0.0661 g, 0.250 mmol), and 1-bromoicosane (1.807 g, 5.00 mmol) were added. The resulting mixture was heated at reflux with stirring for 48 h, under a nitrogen atmosphere. After evaporating the solvent, the residue was portioned between 30 mL of diethyl ether and 20 mL of 1.0 M hydrochloric acid. The organic phase, was washed with brine (2 × 10 mL), dried over anhydrous sodium sulfate, and evaporated under vacuum. The brown solid was purified by column chromatography (silica gel, eluent: cyclohexane/ethyl acetate, 98:2 v/v) to afford a colorless oil which solidified upon standing (1.13 g, yield 54%).  $\text{C}_{27}\text{H}_{46}\text{O}_3$  (418.66): Calcd C, 77.46; H, 11.07; Found C, 77.32; H, 11.02.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS):  $\delta = 0.88$  (t,  $^3J_{\text{HH}} = 6.5$  Hz, 3 H;  $\text{CH}_3$ ), 1.20–1.40 (m, 32 H;  $\text{CH}_2$ ), 1.44 (m, 2 H;  $\text{CH}_2$ ), 1.79 (m, 2 H;  $\text{CH}_2$ ), 4.00 (t,  $^3J_{\text{HH}} = 6.5$  Hz, 2 H;  $\text{OCH}_2$ ), 6.41 (d,  $^3J_{\text{HH}} = 2.5$  Hz, 1 H; ArH), 6.52 (dd,  $^3J_{\text{HH}} = 9.0$  Hz,  $^4J_{\text{HH}} = 2.5$  Hz, 1 H; ArH), 7.41 (d,  $^3J_{\text{HH}} = 9.0$  Hz, 1 H; ArH), 9.70 (s, 1 H;  $\text{CH}=\text{O}$ ), 11.47 (s, 1 H; OH).

***N,N*-Bis(4-icosyloxy-2-hydroxybenzylidene)-1,2-ethylenediamine (4a).** To a solution of 4-icosyloxy-2-hydroxybenzaldehyde (0.209 g, 0.500 mmol) in hot ethanol (25 mL), ethylenediamine (17  $\mu\text{L}$ , 0.250 mmol) was added under stirring. The mixture heated at reflux with stirring for 1 h, under a nitrogen atmosphere. After cooling, the precipitated product was collected by filtration, washed with



ethanol, and dried. The white solid product was purified by crystallization from ethanol/cyclohexane (0.118 g, 55%).  $C_{56}H_{94}N_2O_4$  (861.39): Calcd C, 78.08; H, 11.23; N, 3.25; Found C, 78.14; H, 11.25; N, 3.21. ESI-MS:  $m/z = 861$   $[M+H]^+$ .  $^1H$  NMR (500 MHz,  $CDCl_3$ , TMS):  $\delta = 0.89$  (t,  $^3J_{HH} = 7.0$  Hz, 6 H;  $CH_3$ ), 1.23–1.38 (m, 64 H;  $CH_2$ ), 1.43 (m, 4 H;  $CH_2$ ), 1.77 (m, 4 H;  $CH_2$ ), 3.85 (s, 4 H,  $NCH_2CH_2N$ ), 3.95 (t,  $^3J_{HH} = 7.0$  Hz, 4 H;  $OCH_2$ ), 6.38 (dd,  $^3J_{HH} = 9.0$  Hz,  $^4J_{HH} = 2.5$  Hz, 2 H; ArH), 6.41 (d,  $^4J_{HH} = 2.5$  Hz, 2 H; ArH), 7.07 (d,  $^3J_{HH} = 8.5$  Hz, 2 H; ArH), 8.20 (s, 2 H;  $CH=N$ ), 13.67 (s, 2 H; OH).

**[N,N-Bis(4-icosyloxy-2-hydroxybenzylidene)-1,2-ethylene-diaminato]Zn<sup>II</sup> (4)**. A suspension of **4a** (0.152 g, 0.18 mmol) in refluxing ethanol (50 mL) was dissolved by addition of the minimum amount of cyclohexane. To the solution obtained, an ethanolic solution of zinc acetate dihydrate (0.040 g, 0.18 mmol) was added. The mixture was heated at reflux with stirring for 2 h, under nitrogen atmosphere. The precipitated product was collected by filtration, washed with ethanol, and dried to give a white powder (0.166 g, 95%).  $C_{56}H_{94}N_2O_4Zn$  (924.77): Calcd C, 72.73; H, 10.25; N, 3.03; Found C, 72.68; H, 10.23; N, 3.00. ESI-MS:  $m/z = 1850$   $[(M)_2+H]^+$ .  $^1H$  NMR (500 MHz,  $5 \times 10^{-4}$  M,  $CDCl_3/DMSO-d_6$  83:17 v/v, TMS):  $\delta = 0.79$  (t,  $^3J_{HH} = 7.0$  Hz, 6 H;  $CH_3$ ), 1.10–1.30 (m, 64 H;  $CH_2$ ), 1.33 (m, 4 H;  $CH_2$ ), 1.66 (m, 4 H;  $CH_2$ ), 3.61 (s, 4 H,  $NCH_2CH_2N$ ), 3.82 (t,  $^3J_{HH} = 6.5$  Hz, 4 H;  $OCH_2$ ), 6.00 (dd,  $^3J_{HH} = 9.0$  Hz,  $^4J_{HH} = 3.0$  Hz, 2 H; ArH), 6.29 (d,  $^4J_{HH} = 3.0$  Hz, 2 H; ArH), 6.86 (d,  $^3J_{HH} = 9.0$  Hz, 2 H; ArH), 8.12 (s, 2 H;  $CH=N$ ).

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Additional  $^1H$  NMR data; ESI-MS spectrum of complex **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) (a) Cano, M.; Rodríguez, L.; Lima, J. C.; Pina, F.; Dalla Cort, A.; Pasquini, C.; Schiaffino, L. *Inorg. Chem.* **2009**, *48*, 6229–6235. (b) Germain, M. E.; Vargo, T. R.; Khalifah, G. P.; Knapp, M. J. *Inorg. Chem.* **2007**, *46*, 4422–4429. (c) Dalla Cort, A.; Mandolini, L.; Pasquini, C.; Rissanen, K.; Russo, L.; Schiaffino, L. *New J. Chem.* **2007**, *31*, 1633–1638. (d) Ma, C. T. L.; MacLachlan, M. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 4178–4182.
- (2) (a) Consiglio, G.; Failla, S.; Finocchiaro, P.; Oliveri, I. P.; Di Bella, S. *Dalton Trans.* **2012**, *41*, 387–395. (b) Consiglio, G.; Failla, S.; Finocchiaro, P.; Oliveri, I. P.; Purrello, R.; Di Bella, S. *Inorg. Chem.* **2010**, *49*, 5134–5142. (c) Consiglio, G.; Failla, S.; Oliveri, I. P.; Purrello, R.; Di Bella, S. *Dalton Trans.* **2009**, 10426–10428.
- (3) (a) Martínez Belmonte, M.; Wezenberg, S. J.; Haak, R. M.; Anselmo, D.; Escudero-Adán, E. C.; Benet-Buchholz, J.; Kleij, A. W. *Dalton Trans.* **2010**, 39, 4541–4550. (b) Escudero-Adán, E. C.; Benet-Buchholz, J.; Kleij, A. W. *Inorg. Chem.* **2008**, *47*, 4256–4263. (c) Gallant, A. J.; Chong, J. H.; MacLachlan, M. J. *Inorg. Chem.* **2006**, *45*, 5248–5250. (d) Odoko, M.; Tsuchida, N.; Okabe, N. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2006**, *E62*, m708–m709. (e) Kleij, A. W.; Kuil, M.; Lutz, M.; Tooke, D. M.; Spek, A. L.; Kamer, P. C. K.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *Inorg. Chim. Acta*

**2006**, *359*, 1807–1814. (f) Matalobos, J. S.; García-Deibe, A. M.; Fondo, D. N.; Bermejo, M. R. *Inorg. Chem. Commun.* **2004**, *7*, 311–314. (g) Reglinski, J.; Morris, S.; Stevenson, D. E. *Polyhedron* **2002**, *21*, 2175–2182.

(4) (a) Bhattacharjee, C. R.; Das, G.; Mondal, P.; Prasad, S. K.; Rao, D. S. S. *Eur. J. Inorg. Chem.* **2011**, 1418–1424. (b) Wezenberg, S. J.; Escudero-Adán, E. C.; Benet-Buchholz, J.; Kleij, A. J. *Chem.—Eur. J.* **2009**, *15*, 5695–5700. (c) Di Bella, S.; Consiglio, G.; Sortino, S.; Giancane, G.; Valli, L. *Eur. J. Inorg. Chem.* **2008**, 5228–5234. (d) Leung, A. C. W.; MacLachlan, M. J. *J. Mater. Chem.* **2007**, *17*, 1923–1932. (e) Kleij, A. W.; Kuil, M.; Tooke, D. M.; Lutz, M.; Spek, A. L.; Reek, J. N. H. *Chem.—Eur. J.* **2005**, *11*, 4743–4750.

(5) (a) Hui, J. K.-H.; MacLachlan, M. J. *Dalton Trans.* **2010**, 39, 7310–7319. (b) Elemans, J. A. A. W.; Wezenberg, S. J.; Coenen, M. J. J.; Escudero-Adán, E. C.; Benet-Buchholz, J.; den Boer, D.; Speller, S.; Kleij, A. J.; De Feyter, S. *Chem. Commun.* **2010**, 46, 2548–2550. (c) Hui, J. K.-H.; Yu, Z.; Mirfakhrai, T.; MacLachlan, M. J. *Chem.—Eur. J.* **2009**, *15*, 13456–13465. (d) Jung, S.; Oh, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 2049–2051. (e) Hui, J. K.-H.; Yu, Z.; MacLachlan, M. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 7980–7983.

(6) Oliveri, I. P.; Failla, S.; Malandrino, G.; Di Bella, S. *New J. Chem.* **2011**, *35*, 2826–2831.

(7) (a) Dalla Cort, A.; De Bernardin, P.; Forte, G.; Yafteh Miha, F. *Chem. Soc. Rev.* **2010**, *39*, 3863–3874. (b) Khatua, S.; Choi, S. H.; Lee, J.; Kim, K.; Do, Y.; Churchill, D. G. *Inorg. Chem.* **2009**, *48*, 2993–2999. (c) Germain, M. E.; Knapp, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 5422–5423. (d) Wezenberg, S. J.; Escudero-Adán, E. C.; Benet-Buchholz, J.; Kleij, A. W. *Org. Lett.* **2008**, *10*, 3311–3314. (e) Kaletas, B. K.; Williams, R. M.; König, B.; De Cola, L. *Chem. Commun.* **2002**, 776–777.

(8) (a) Oliveri, I. P.; Di Bella, S. *Tetrahedron* **2011**, *67*, 9446–9449. (b) Oliveri, I. P.; Di Bella, S. *J. Phys. Chem. A* **2011**, *115*, 14325–14330.

(9) Di Bella, S.; Oliveri, I. P.; Colombo, A.; Dragonetti, C.; Righetto, S.; Roberto, D. *Dalton Trans.* **2012**, *41*, 7013–7016.

(10) Oliveri, I. P.; Maccarrone, G.; Di Bella, S. *J. Org. Chem.* **2011**, *76*, 8879–8884.

(11) In the case of complex **4**, because of its insolubility in DMSO, the spectrum in DMSO- $d_6$  was extrapolated from that in  $CDCl_3$  upon the addition of a 5000-fold mole excess of DMSO- $d_6$  (see *infra*).

(12) See, for example: (a) Zhang, F.; Bai, S.; Yap, G. P. A.; Tarwade, V.; Fox, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 10590–10599. (b) Barnard, P. J.; Vagg, R. S. *J. Inorg. Biochem.* **2005**, *99*, 1009–1017. (c) Gunter, M. J.; Farquhar, S. M. *Org. Biomol. Chem.* **2003**, *1*, 3450–3457. (d) Chen, M. J.; Rathke, J. W. *J. Porphyrins Phthalocyanines* **2001**, *5*, 528–536.

(13) (a) The lacking of conjugation between the salicylidene moieties, leads to a J-type coupling between the salicylidene groups of each unit in the dimer and, hence, a red shift of the optical absorption bands on switching from the monomer to the dimer. See, for example: (b) Beletskaya, I.; Tyurin, V. S.; Tsivadze, A. Y.; Guillard, R.; Stern, C. *Chem. Rev.* **2009**, *109*, 1659–1713. (c) Di Bella, S.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 5842–5849.

(14) Vladimirova, K. G.; Freidzon, A. Y.; Kotova, O. V.; Vaschenko, A. A.; Lepnev, L. S.; Bagatur'yants, A. A.; Vitukhnovskiy, A. G.; Stepanov, N. F.; Alfimov, M. V. *Inorg. Chem.* **2009**, *48*, 11123–11130.

(15) Under these conditions, a white suspension in the NMR sample, is observed. An insoluble white precipitate then was isolated and characterized as  $Zn(OH)_2$  by IR analysis. Analogous results are obtained from water-saturated  $CDCl_3$  solutions after standing for several days.

(16) Actually, hexacoordinated  $Zn^{II}$  complexes are common for tridentate Schiff-base ligands. See, for example: (a) Samanta, B.; Chakraborty, J.; Shit, S.; Batten, S. R.; Jensen, P.; Masuda, J. D.; Mitra, S. *Inorg. Chim. Acta* **2007**, *360*, 2471–2484. (b) Basak, S.; Sen, S.; Banerjee, S.; Mitra, S.; Rosair, G.; Garland Rodriguez, M. T. *Polyhedron* **2007**, *26*, 5104–5112. (c) Correia, V. R.; Bortoluzzi, A. J.; Neves, A.; Joussef, A. C.; Vieira, M. G. M.; Batista, S. C. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2003**, *E59*, m464–m466.

- (17) Hall, D.; Moore, F. H. *J. Chem. Soc. A* **1966**, 1822–1824.
- (18) (a) Johnson, C. S., Jr. *Prog. Nucl. Magn. Reson.* **1999**, *34*, 203–256. (b) Morris, K. F.; Johnson, C. S., Jr. *J. Am. Chem. Soc.* **1992**, *114*, 3139–3141.
- (19) (a) Macchioni, A.; Ciancaleoni, G.; Zuccaccia, C.; Zuccaccia, D. In *From Supramolecular Chemistry: From Molecules to Nanomaterials*; Steed, J. W.; Gale, P. A., Eds.; Wiley: New York, 2012; Vol. 2, pp 319–330. (b) Macchioni, A.; Ciancaleoni, G.; Zuccaccia, C.; Zuccaccia, D. *Chem. Soc. Rev.* **2008**, *37*, 479–489. (c) Pregosin, P. S. *Prog. Nucl. Magn. Reson. Spectrosc.* **2006**, *49*, 261–288. (d) Song, F.; Lancaster, S. J.; Cannon, R. D.; Schormann, M.; Humphrey, S. M.; Zuccaccia, C.; Macchioni, A.; Bochmann, M. *Organometallics* **2005**, *24*, 1315–1328.
- (20) See, for example: (a) Kagan, G.; Li, W.; Hopson, R.; Williard, P. G. *J. Am. Chem. Soc.* **2011**, *133*, 6596–6602. (b) Fielden, J.; Long, D.; Slawin, A. M. Z.; Kolgerler, P.; Cronin, L. *Inorg. Chem.* **2007**, *46*, 9090–9097.
- (21) Holmes, R. R. *Prog. Inorg. Chem.* **1984**, *32*, 119–235.
- (22) See, for example: (a) Blagg, R. J.; Adams, C. J.; Charmant, J. P. H.; Connelly, N. G.; Haddow, M. F.; Hamilton, A.; Knight, J.; Orpen, A. G.; Ridgway, B. M. *Dalton Trans.* **2009**, 8724–8736. (b) Casares, J. A.; Espinet, P. *Inorg. Chem.* **1997**, *36*, 5428–5431.
- (23) For recent, general accounts on pseudo-rotation see, for example: (a) Moberg, C. *Angew. Chem., Int. Ed.* **2011**, *50*, 10290–10292. (b) Couzijn, E. P. A.; Slootweg, J. C.; Ehlers, A. W.; Lammertsma, K. *J. Am. Chem. Soc.* **2010**, *132*, 18127–18140.
- (24) Geometry optimization by semiempirical (MP3) calculations on the Zn(salen)-H<sub>2</sub>O monomeric adduct in a SP or TBP structure indicates a more-stable structure in the former case.
- (25) Actually, the presence of mixed SP-TBP dimers would lead to a more-complex <sup>1</sup>H NMR spectrum, including signals related to the TBP-TBP dimer.
- (26) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933–938.
- (27) Gutowsky, S. H.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228–1234.
- (28) See, for example: (a) Zhang, J.; Pattaccini, R.; Braunstein, P. *Inorg. Chem.* **2009**, *48*, 11954–11962. (b) Nakazawa, H.; Kawamura, K.; Kubo, K.; Miyoshi, K. *Organometallics* **1999**, *18*, 2961–2969.

#### ■ NOTE ADDED AFTER ASAP PUBLICATION

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