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Structure and aggregation properties of a Schiff-base zinc(II) complex derived from *cis*-1,2-diaminocyclohexane[‡,†]

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Abstract

This contribution explores the effect of the bridging diamine upon the aggregation properties of a Zn^{II} Schiff-base complex, **1**, both in the solid state and in solution. The X-ray structure of **1,** resulted from the harvest of good quality crystals using chloroform and diethylether as solvents, shows the presence of a densely packed dimer in the solid state which pentacoordinates two Zn atoms involved in a μ-phenoxo bridge. Detailed studies in solution, through ^{1}H NMR, DOSY NMR, and optical spectroscopic investigations, indicate the typical aggregation/deaggregation behaviour on switching from non-coordinating to coordinating solvents, in relation to the Lewis acidic character of such Zn^{II} complex. Thus, while in DMSO-d_6 both ^{1}H NMR and DOSY studies suggest the existence of monomeric species, in chloroform solution experimental data support the existence of aggregates. However, unlike our previous studies, ^{1}H NMR data in chloroform solution indicate the existence of an asymmetric dimer, as observed in the X-ray crystal structure. This further evidences a very rigid backbone of the dimeric aggregate and can be related to the defined stereochemistry of the chelate *cis*-1,2-diaminocyclohexane bridge.

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[‡] *Dedicated to Emeritus Professor Paolo Finocchiaro of Università di Catania on the occasion of his 73th birthday*

[†] Electronic supplementary information (ESI) available: bond lengths, angles and relevant symmetry elements of **1**. CCDC 1055193. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/

Introduction

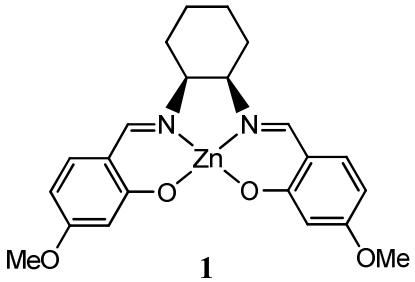
Molecular aggregation is currently a topic of wide interest[1,2] concerning various fields, ranging from sensing[3] and molecular biology,[4] to molecular electronics and optoelectronics.[5]

Recently, we have dealt with aggregation/deaggregation properties of some bis(salicylaldiminato) zinc(II) Schiff-base complexes, characterized by interesting properties.[6] In fact, by virtue of the Lewis acidic character of the Zn^{II} metal centre these complexes aggregate via intermolecular Zn···O interactions, either in solution of non-coordinating solvents[6,7] or in the solid state.[8] Thus, a variety of supramolecular structures[9] and self-assembled nanostructures[10,11] have been found. Moreover, dramatic changes of optical absorption,[6,12] second-order nonlinear optical,[13] and fluorescence emission[6,12,14] are observed upon aggregation/deaggregation of such species, useful for sensing various Lewis bases,[12,14] even in the vapour phase.[15] These complexes are also characterized by their interesting photophysical properties.[16]

Even if the leitmotif of the aggregation in such molecular species in absence of other Lewis bases is the intermolecular Zn···O interaction,[6-8] the degree and the type of aggregation in solution strongly depend upon the nature of the ligand framework. Thus, facial dimeric/oligomeric aggregates are formed in the case of π-conjugated ligands,[6b-d] while a different aggregation mode is found for complexes having a nonconjugated, conformational flexible nature of the bridging diamine of the Schiff-base.[6a]

Therefore, it is of interest to further probe the effect of the bridging diamine upon the aggregation properties of such complexes. With this idea in mind, we decided to investigate a nonconjugated bridging diamine having a defined stereochemistry around the chelate diamino bridge, for example, the Schiff-base complexes derived from the *cis*-1,2-diaminocyclohexane. Actually, neither structural studies nor aggregation properties in solution are reported for this kind of zinc(II) complexes.

In this paper, we report the X-ray structure and a detailed study in solution, through ^{1}H NMR and optical spectroscopic investigations, on the aggregation/deaggregation properties of a Zn^{II} Schiff-base complex derived from the *cis*-1,2-diaminocyclohexane (**1**).



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Results

The synthesis of **1** was accomplished by template method, involving a condensation reaction between 2-hydroxy-4-methoxybenzaldehyde and *cis*-1,2-diaminocyclohexane, followed by complexation with the Zn^{II} cation, using its perchlorate salt, in methanol solution in presence of triethylamine. Moreover, unlike our previous studies,[6] it was unnecessary to consider amphiphilic species, *i.e.*, complexes having long alkyl chains in the salicylidene rings. Actually, the presence of the cyclohexane ring ensures suitable solubility of the Zn^{II} complex **1** both in coordinating and non-coordinating solvents. Therefore, for simplicity we considered the 4-methoxy-salicylidene derivative.

Crystallographic studies

Crystals of **1** suitable for the X-ray structural determination were obtained by slow vapour diffusion of diethyl ether into a chloroform solution of **1**.

1 crystallised as an asymmetric dimer (Fig. 1a) in the monoclinic C 2/c as reported in Table 1. Although two fragments related by a two-fold axis are present in the asymmetric unit (a.u.), together with one chloroform and one diethyl ether molecule (Fig. 1b), the resulting dimer is non-centrosymmetric. The a.u. displays a four-coordinated Zn atom which is indirectly involved in a μ-phenoxo bridge[17] to give rise to this characteristic dimeric structure. At difference with the majority

of the reported structures,[8] the two Zn ions are symmetric in the N_2O_2 pocket as a result of their two-fold symmetry in the a.u.. All bond distances, angles and torsionals are within normal values[18] and are reported in the ESI.

Table 1 Crystal structure data for **1**

Formula	$C_{44}H_{48}N_4O_8Zn_2$, $C_4H_{10}O$, 0.834($CHCl_3$)
Formula weight	1065.28
Crystal System	monoclinic
Space group	C2/c
a, b, c (Å)	14.1326(1) 21.8193(1) 17.6167(1)
β °	113.4603(9)
V ($Å^3$)	4983.29(6)
Z	4
F(000)	2217.4
D_{calc} (g cm^{-3})	1.420
$\mu_{(CuKa)}$ (mm^{-1})	2.893
Crystal Size (mm)	0.18 x 0.20 x 0.25
Temperature (K)	150
Wavelength (Å)	1.54180
R, wR_2	0.0348, 0.0910

Focusing our attention on the dimeric structure, the Zn atoms are involved in two identical five coordination system[19] with O2, O21, N13 and N10 (Fig. 1a). O21 is the atom that best fit the characteristics of a pivot in the so-called Berry pseudoration,[20] which however is inhibited by the quite rigid dimeric structure, where $\tau = 0.53$[21] and therefore exactly in between the two extreme forms – 0.00 for a square pyramid (SP) and 1.00 for a trigonal bipyramid (TP) – thus suggesting a hybrid geometry which does not completely fulfil neither the SP nor the TP main features. Moreover, the Zn atom lies in the middle of the pyramid popping up, in agreement with already solved structures,[22] from the N_2O_2 centroid and its average plane by 0.492 Å. The diamond shaped metallocycle Zn-O-Zn-O is planar, with a 2-fold axis passing perpendicularly to it and a glide plane through it (Fig. S1†) thus lending to the dimer its characteristic 2-fold symmetry.

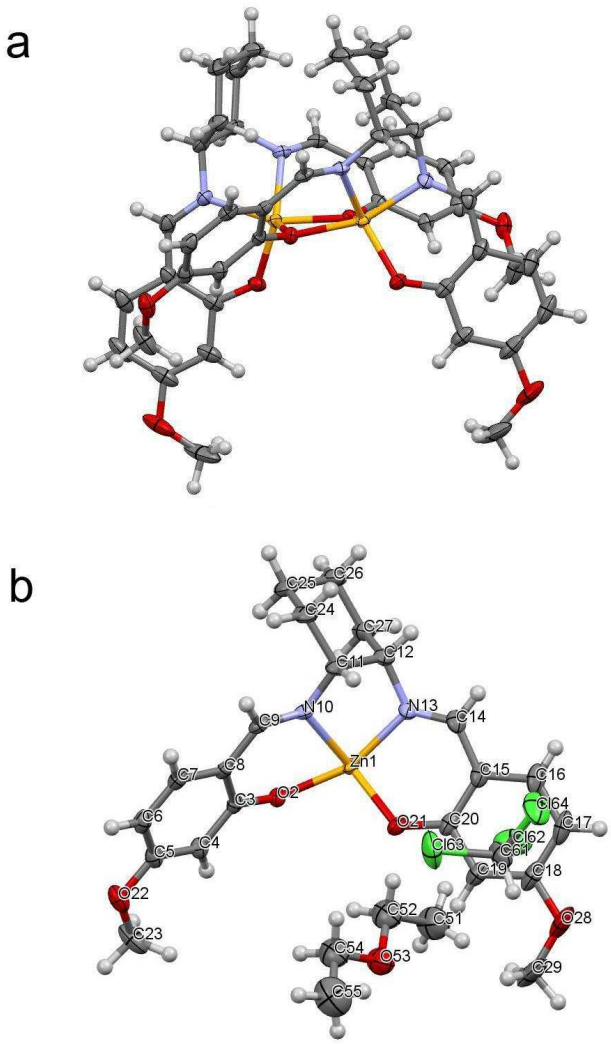

Fig. 1 The dimer backbone of **1** (a); the a.u. with the solvent molecules (b) and reported atom numbering for non-hydrogen atoms only, for the sake of clarity. Thermal displacement ellipsoids are drawn at the 40 % probability level while hydrogen atoms are represented as spheres of arbitrary radius of 0.20 Å.

A ring puckering analysis – i.e. Cremer and Pople analysis,[23] was performed on the six-membered cyclohexane ring C11 C12 C27 C26 C25 C24 (Ring 1) provided that the absolute configuration, the pivot atom and the cyclic sense agree.[24] The representation of the ring puckering can be performed by means of a single amplitude-phase pair (q2 and ϕ2) and a single puckering coordinate q3 in the case of six-membered rings, where the puckering degrees of freedom are three.

Alternatively, the same results can be obtained using spherical coordinates, Q, θ and ϕ.[25] The total puckering amplitude is 0.573(3) Å and, together with their relative standard uncertainty (s.u.), q2 = 0.028(3) Å, ϕ2 = 136(5)° and q3 = 0.572(3) Å or alternatively θ = 3.4(3)°. The resulting conformational analysis[26] quantifies the presence of a typical chair form.

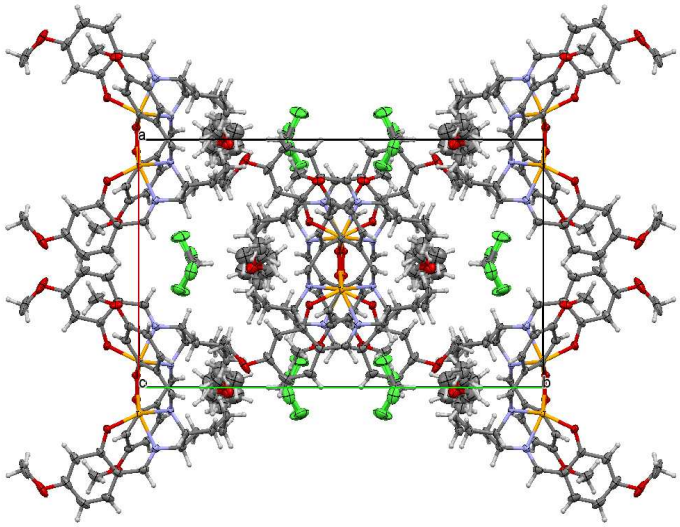

Fig. 2 Packing diagram viewed down the c axis. Ellipsoids setting is as in Figure 1.

Structure stabilization is strongly increased by the presence of two disordered crystallization solvent molecules – one chloroform and one diethyl ether – as reported in Fig. 2. Chloroform is involved in some relevant interactions with **1** as commented in details soon after in this section.

No packing index[27] was calculated as a result of the above mentioned solvent disorder present in this densely packed structure. Moreover, no additional solvent accessible voids were found.

A linear[28] although weak[29] intermolecular hydrogen bond is found between C(11)--H(111) and O(22) along the crystallographic direction *1-x,1-y,1-z* with a distance between donor and acceptor of 3.524(2) Å and an angle of 173°.

Three different π-stacking interactions are present. They are reported in Table 2 together with T-shaped interactions and halogen–π interactions. They all contribute almost equally to the overall structure stabilization.[30] T-shaped interactions are in fact not only present between the methyl group

at C23 and its terminal hydrogen H23 which points towards the centre of gravity (Cg) of the six membered ring defined by C15, C16, C17, C18, C19 and C20 (Ring 2), but also by all the chloroform's chlorine atoms.[31] This last finding emphasizes the role of the solvent in the final layout and stabilization of the molecule architecture.

Table 2 π-stacking and T-shaped non covalent interactions. s.u. is reported in parentheses where its calculation is meaningful. Ring 1: C11 C12 C27 C26 C25 C24; Ring 2: C15 C16 C17 C18 C19 C20; Ring 3: C3 C4 C5 C6 C7 C8.

π-stacking interactions

Ring - Ring	Distance (Å)	Angle between planes (°)	Slippage (Å)	Crystallographic directions
CgR3 – CgR3	4.5450(12)	0.03(9)	2.974	*1-x,1-y,1-z*
CgR2 – CgR3	5.6415(12)	53.09(9)	0	*x,1-y,1/2+z*
CgR2 – CgR3	5.8810(13)	59.72(9)	0	*1-x,y,1/2-z*

T-shaped and halogen–π interactions[a]

Atoms - Ring	Distance (Å)	Angle of the bond with π plane (°)	Crystallographic directions
C23 – H233 – CgR2	2.97	71	*1-x,y,1/2-z*
C61 – Cl62 – CgR2	3.4501(18)	81.62	*x,y,z*
C61 – Cl63 – CgR3	3.809(6)	26.98	*1-x,1-y,1-z*
C61 – Cl64 – CgR3	3.661(4)	64.53	*1+x,1-y,1/2+z*

[a] The reported distances measured in Å are relative to the most protruding H or Cl atom and the centroid of the most adjacent ring.

^{1}H NMR studies

The ^{1}H NMR spectrum of **1** in solution of DMSO-d_6 (≈1 × 10^{-2} M) indicates the presence of sharp signals with the expected multiplicity and chemical shifts,[6] according to its molecular structure and consistent with the existence of monomeric species, presumably as **1**·DMSO adducts (Fig. 3).

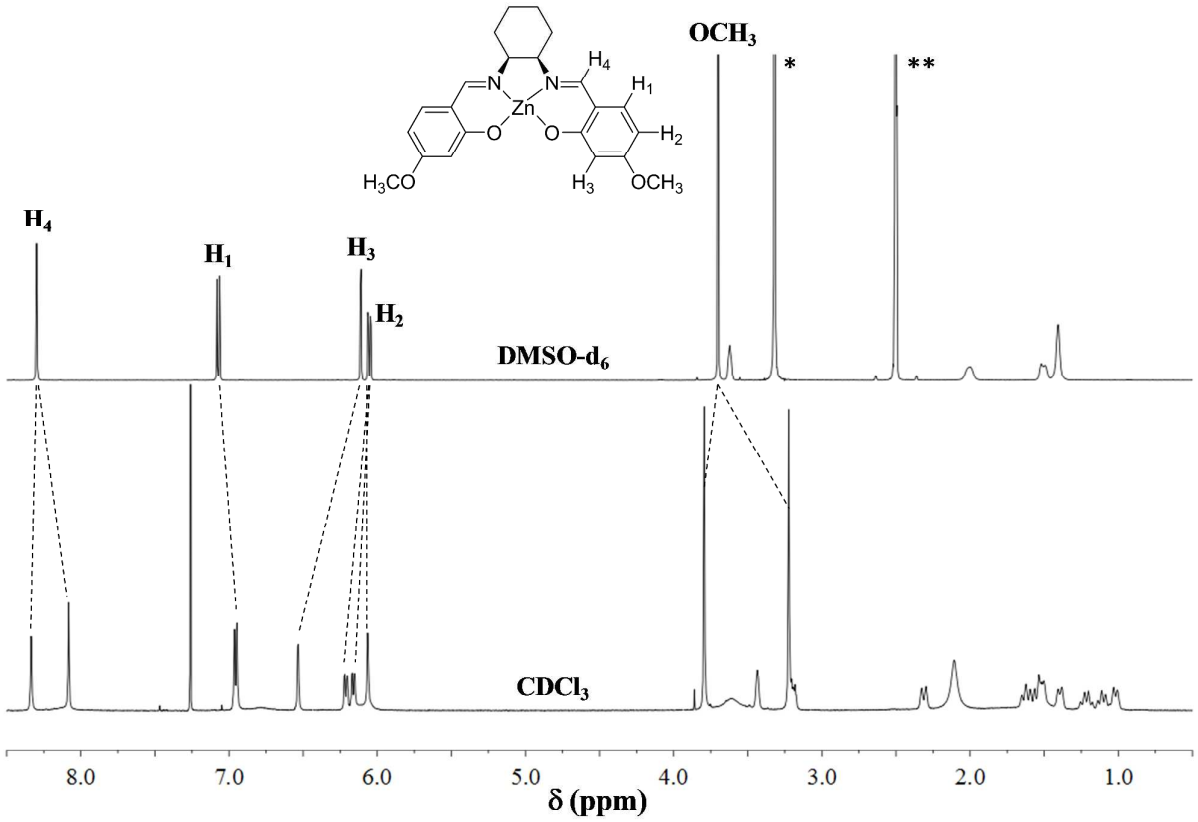

Fig. 3 Comparison of ^{1}H NMR spectra of **1** in DMSO-d_6 and $CDCl_3$ solutions (≈1 × 10^{-2} M). Single and double asterisked peaks refer to water and residual DMSO solvent signals, respectively.

On switching to the non-coordinating $CDCl_3$ solvent (≈1 × 10^{-2} M), a considerable change of the ^{1}H NMR spectrum is observed (Fig. 3). In particular, H_4, H_3, and -OCH_3 signals are split into two new signals, having almost the same intensity, consistent with the existence of either two different species in solution, or the presence of a single species (*e.g.*, dimeric) having an asymmetric structure. In particular, from the comparison of the chemical shifts in the two involved solvents, we note that on switching from DMSO-d_6 to $CDCl_3$, of the two H_4 signals one remains almost unaltered whereas the other is ca. 0.2 ppm upfield shifted, while in the case of H_3 signals one is ca. 0.4 ppm downfield and the other is roughly unchanged. Analogously, -OCH_3 signals are ca. 0.1 ppm downfield and ca. 0.5 ppm upfield shifted with respect to that recorded in DMSO. Finally, the 1-2.4 ppm region related to cyclohexane hydrogens, in contrast with the broad signals observed

in DMSO-d_6, is much more complex in the $CDCl_3$ solvent by the presence of many multiplet signals, indicating greater stereochemical rigidity on the NMR timescale[32] of the cyclohexane rings.

Dilution studies in both DMSO and $CDCl_3$ solvents indicate that solutions of **1** do not show concentration dependence in the investigated (10^{-2} – 5×10^{-4} M) range.

Diffusion ordered NMR spectroscopy (DOSY) has been used as an independent method to estimate the degree of aggregation and the molecular mass of species in solution, through the measurement of the diffusion coefficient, *D*. This technique plays an important role in the identification of supramolecular species in solution owing to the straightforward two-dimensional (2D) representation of the components of the system. Moreover, molecular masses from DOSY measurements were estimated by using a known internal reference species by their relative diffusion coefficient.[6]

The ^{1}H NMR DOSY spectrum of **1** in DMSO-d_6 ($\approx 1 \times 10^{-2}$ M) shows a single component in the diffusion dimension ($D = 2.7 \times 10^{-10}$ m^2 s^{-1}), whose estimated molecular mass (582 Da) is indicative of a monomeric species, as **1**·DMSO-d_6 adducts (530.0 Da) with the DMSO axially coordinated. Analogously, the ^{1}H NMR DOSY spectrum of **1** in $CDCl_3$ (1.0×10^{-2} M) shows a single component in the diffusion dimension ($D = 5.8 \times 10^{-10}$ m^2 s^{-1}), whose estimated molecular mass (816 Da) is, however, consistent with the existence of a dimeric species (891.7 Da).

^{1}H NMR studies of **1** in mixtures of non-coordinating/coordinating ($CDCl_3$/DMSO-d_6) solvents further support the existence of an aggregate species in the former solvent. Actually, the addition of defined amounts of DMSO-d_6 to a $CDCl_3$ solution of **1** leads to substantial ^{1}H NMR spectral changes. In particular, an appreciable variation of the ^{1}H NMR spectrum is observed upon the addition of ca. 5-fold mole excess of DMSO-d_6, involving a decrease of the intensity of proton signals of the aggregate **1** and the appearance of a new set of signals, consistent with the formation of the **1**·DMSO adduct. The progressive addition of DMSO leads to the regular decrease of the intensity of proton signals of **1** and the parallel appearance of a new set of signals of the **1**·DMSO adduct. Upon the addition of ca. 100-fold mole excess of DMSO-d_6 an almost complete

disappearance of species **1** is observed, and the ^{1}H NMR spectrum is comparable to that recorded for solutions of **1** in DMSO-d_6 (Fig. 4).

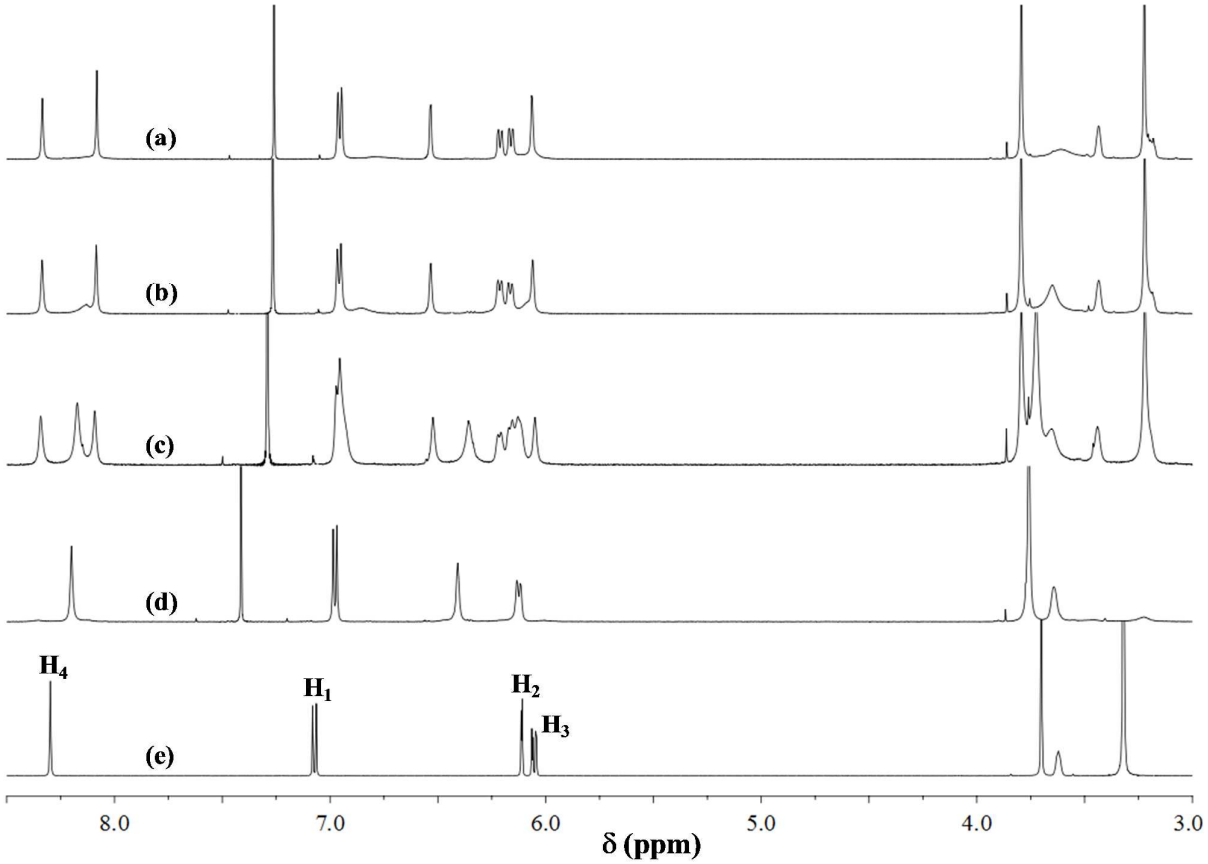

Fig. 4 ^{1}H NMR spectra of **1** in $CDCl_3$ (1.0×10^{-2} M; 6.0×10^{-6} mol) (**a**), and with addition of 2.8×10^{-5} mol (**b**), 1.4×10^{-4} mol (**c**), 7.0×10^{-4} mol (**d**) of DMSO-d_6. The ^{1}H NMR spectrum of **1** in DMSO-d_6 is reported for comparison (**e**).

Optical absorption Spectroscopy Studies

The UV/vis absorption spectrum of complex **1** in DMSO consists of two defined bands, at 283 nm and 344 nm, independent from the concentration in the range (1.0×10^{-3} M – 1.0×10^{-5} M) considered. On switching to the $CHCl_3$ non-coordinating solvent, the UV/vis absorption spectrum of **1** is analogous to that recorded in DMSO, except for a blue-shift, ca. 10 nm, and a decrease of the intensity of the band at 334 nm (Figs. 5 and S2). This is a common feature, previously observed for other Zn^{II} Schiff-base complexes,[6b-d,12] indicative of the presence of aggregate species in non-

coordinating solvents. Moreover, analogously to the absorption spectrum recorded in DMSO it is independent from the concentration in the range (1.0×10^{-3} M - 1.0×10^{-5} M) considered.

Steady-state fluorescence studies of **1** in solution of $CHCl_3$ and DMSO solvents indicate the presence of an unstructured band, with a maximum at 423 nm in CHCl3 and 430 nm in DMSO, independent of the excitation wavelength (Fig. S2), having a comparable intensity.

The addition of defined amounts of DMSO to a 1.0×10^{-3} M $CHCl_3$ solution of **1** leads to optical changes analogous to those observed on switching to solutions of **1** in DMSO. In particular, a progressive red-shift of the band at 334 nm with the presence of an isobestic point at 338 nm, are observed. The saturation point is reached after addition of ca. 500-fold mole excess of DMSO (Fig. 5).

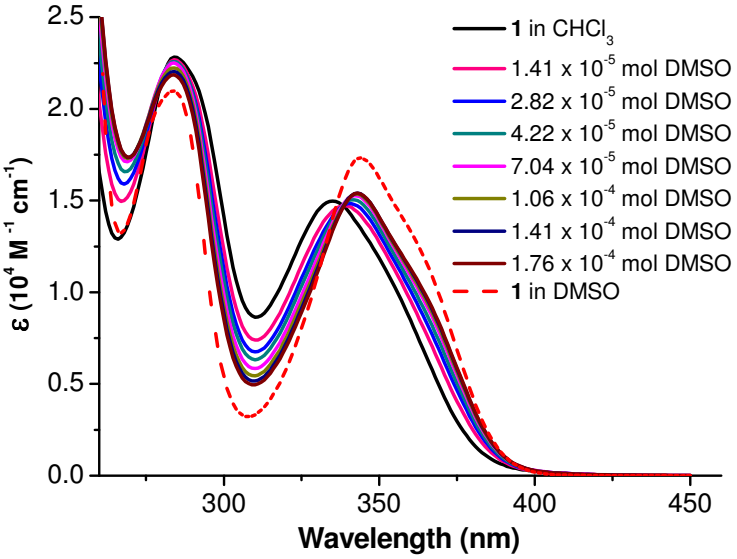

Fig. 5 UV/vis absorption spectra of **1** (1.0×10^{-3} M; 2.5×10^{-7} mol) in $CHCl_3$, and with the addition of DMSO. The absorption spectrum of **1** in DMSO (dotted line) is reported for comparison.

Discussion

The solid state dimeric structure of **1**, inferred by means of the single crystal X-ray diffraction, evidences a very rigid backbone. Its stiffness results not only from the presence of the diamond shaped metallocycle which forbids any possible different metal coordination, but also by the

cyclohexane ring in its energetically favoured chair conformation. This latter feature suggests a key role of the cyclohexane ring in determining the final molecular packing: having found its most stable conformation it hinders R2 and R3 rearrangement around the Zn atom (Fig. 1a) preventing the formation of a symmetric arrangement. The crystallization solvents present in the unit cell contribute to the final structure outcome. Surprisingly, there is evidence of the preservation of this layout even in solution, as commented and interpreted below. It seems relevant to comment that at difference with the vast majority of similar structures, but in analogy with the work by Sanmartín Matalobos et al.,[17] the structure of **1** is non-centrosymmetric being the two building blocks constituting the dimer related "only" by a two-fold axis.

Present ^{1}H NMR and UV/vis spectroscopic studies on switching from coordinating to non-coordinating solvents allowed establishing the nature of species in solution. While in DMSO-d_6 both ^{1}H NMR and DOSY studies suggest the existence of monomeric species, in chloroform solution experimental data support the existence of aggregate species. Although ^{1}H NMR data in chloroform solution would be consistent either with the existence of two different species, or with a single species having an asymmetric structure, further experimental evidences unambiguously support the presence of a single asymmetric dimer in solution. In fact, DOSY NMR data, ^{1}H NMR and optical absorption studies of **1** in mixtures of non-coordinating/coordinating solvents indicate the existence of an aggregate dimeric species, as observed in the X-ray crystal structure. Actually, ^{1}H NMR chemical shifts of **1** in chloroform solution are fully consistent with its X-ray crystal structure. In fact, the observed split of the two magnetically non-equivalent H_4 and -OCH_3 signals is in agreement with an asymmetric dimeric structure in which one of the H_4 and -OCH_3 hydrogens of a unit lie under the shielding zone of the π electrons of the aromatic ring of the other unit, while the others hydrogens are not affected by the other molecular unit (Fig. 6). Analogously, the deshielding effect of the aromatic ring current upon one of the two non-equivalent H_3 hydrogens of a unit leads to the splitting of the H_3 signals (Fig. 6). The finding that the intensity ratio of the H_4, H_3, and -

OCH_3 signals remains unaltered upon the progressive addition of DMSO-d_6, further confirms the existence of an asymmetric, dimeric species in solution.

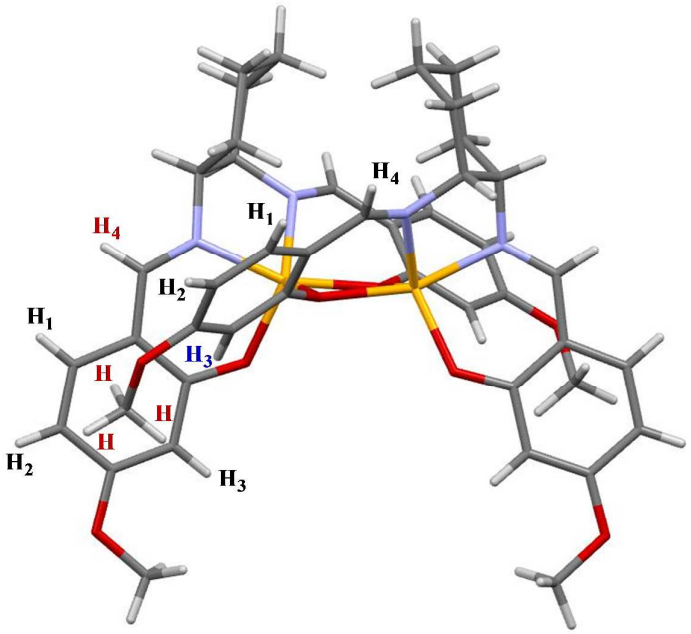

Fig. 6 Schematic sketch of the X-ray structure of **1**. Shielded (red) and deshielded hydrogens (blue) are highlighted.

Deaggregation of **1** in chloroform solution by addition of defined amounts of DMSO results in a decrease of the intensity of proton signals of the aggregate **1** and the appearance of a new set of signals, consistent with the formation of the **1**·DMSO adduct. This is a new feature for this family of compounds, as generally the formation of the **1**·DMSO adducts in non-coordinating solvents leads to a fast equilibrium in the NMR timescale between the two involved, dimer and adduct, species in solution, and hence, the observation of a single set of signals progressively drifted toward those of the adducts. [6,9e,14h]

Present UV/vis data upon deaggregation of **1** in chloroform solution with DMSO, in comparison to our previous data achieved on other Zn^{II} Schiff-base complexes,[6] allows establishing a stronger Lewis acidic character of **1** than that of the analogous Zn(salen) (salen = ethylendiamine bridge)

complexes, more comparable to the Lewis acidity deduced for Zn^{II} complexes having a conjugated diamine bridge. This suggests a lower stability of the asymmetric dimer of **1** in solution of non-coordinating solvents by the presence of the stereochemically defined cyclohexane rings, which probably helps in preventing the formation of a pseudo centrosymmetric structure, as in the case of Zn(salen).[6a,22]

Experimental

Materials and General Procedures

Zinc perchlorate hexahydrate, 2-hydroxy-4-methoxybenzaldehyde, *cis*-1,2-diaminocyclohexane and triethylamine (NEt_3) (Aldrich) were used as received. Chloroform (Aldrich) stabilized with amylene was used for spectrophotometric measurements. $CDCl_3$ (Aldrich) was dried over 3A molecular sieves.

Physical Measurements

Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. ESI mass spectra were recorded with a Finnigan LCQ-Duo ion trap electrospray mass spectrometer (Thermo). Optical absorption spectra were recorded at room temperature using a UV/vis V650 Jasco spectrophotometer. Fluorescence spectra were recorded at room temperature with a Fluorolog-3 (Jobin Yvon Horiba) spectrofluorimeter. Solution NMR experiments were carried out on a Varian Unity S 500 (499.88 MHz for ^1H) spectrometer using an inverse-detection tunable triple-resonance pfg 5 mm $^1H^{13}C\{X\}$ probe capable of generating field strengths of 60 G/cm. All 1D ^1H NMR experiments were referenced to tetramethylsilane ($Si(CH_3)_4$, TMS). Samples were not spinning during all the analyses. ^1H DOSY experiments were carried out at 27 °C, and referenced to the residual solvent signals ($CDCl_3$ = 7.27 ppm). The gradient strength was calibrated by using the HDO signal at 25 °C ($D = 19.02 \times 10^{-10}$ m^2 s^{-1}). 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 (Δ) of 50 ms ($CDCl_3$) or 80 ms

(DMSO-d_6), a diffusion gradient length of 2.0 ms, and 128 increments for gradient levels. Gradient strengths of 10% and 90% of maximum power were used to obtain spectral pairs with acquisition times of 3 s and recycle delays of 5.0 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, the molecular mass in solution was simply estimated using an internal reference species, by means of their relative diffusion rate, as previously described.[6] In particular, in the case of measurements in DMSO-d_6 solution the diffusion coefficient of the solvent ($D = 7.10 \times 10^{-10}$ m^2 s^{-1}) was used to estimate the molecular mass, while for DOSY measurements in chloroform solution, the diffusion coefficient of the **1**·DMSO-d_6 adduct ($D = 7.20 \times 10^{-10}$ m^2 s^{-1}), upon addition of 5-fold mole excess of DMSO-d_6 to a 1.0×10^{-2} M of **1** in $CDCl_3$, was more consistently used.

Synthesis of [*N*,*N*-bis(4-methoxy-2-hydroxybenzylidene)-*cis*-1,2-diaminocyclohexanediamina-to]Zn^{II} (1)

To a solution of 2-hydroxy-4-methoxybenzaldehyde (0.304 g, 2.00 mmol) in methanol (20.0 mL) *cis*-1,2-diaminocyclohexane (0.114 g, 1.00 mmol) was added under stirring. The mixture was heated at reflux with stirring for 2 h, under nitrogen atmosphere. To the solution so obtained, zinc perchlorate hexahydrate (0.372 g, 1.00 mmol) and neat NEt_3 (1.00 mL) were added and the mixture was heated at reflux with stirring for 24 h under a nitrogen atmosphere. After cooling, the precipitated product was collected by filtration, washed with methanol and dried under vacuum at 120 °C using sulfuric acid as a desiccant agent. White powder (0.378 g, 85%). $C_{22}H_{24}N_2O_4Zn$ (445.85): Calcd. C, 59.27; H, 5.43; N, 6.28; Found C, 59.11; H, 5.39; N, 6.32. ESI-MS: *m/z* = 893 $[(M)_2 + H]^+$. ^1H NMR (500 MHz, DMSO-d_6): δ = 1.40 (br, 2H, cyclohexyl-*H*), 1.49 (br, 4H, cyclohexyl-*H*), 1.99 (br, 2H, cyclohexyl-*H*), 3.62 (br, 2H, -C*H*-N=CH), 3.70 (s, 6H; OCH_3), 6.05 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.5 Hz, 2H; Ar*H*), 6.10 (d, $^4J_{HH}$ = 2.5 Hz, 2H; Ar*H*), 7.07 (d, $^3J_{HH}$ = 8.5 Hz, 2H; Ar*H*), 8.29 (s, 2H; C*H*=N). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 21.69, 27.47, 55.14, 62.68, 102.12, 104.92, 114.62, 136.68, 163.98, 165.83, 173.32. Suitable crystals of **1** were obtained by slow vapor diffusion of diethyl ether into a chloroform solution of **1**.

X-ray crystallography

Single crystal diffraction data were collected using an Oxford Diffraction (Agilent Technologies) SuperNova A diffractometer using a micro-focus sealed tube with multilayer X-ray optics. A representative single crystal was selected and mounted on a hair using perfluoro-polyether oil. The crystal was then rapidly cooled to 150 K using an Oxford CryoSystems CryoStream 600.[33] Raw frame data were collected using the copper source (λ = 1.54180 Å) and reduced using CrysAlisPro including unit cell parameter refinement, interframe scaling, corrections for the Lorentz effect and absorption. The crystal structure was solved using SuperFlip[34] within the CRYSTALS structure refinement suite[35] to give the atomic positions for the non-hydrogen atoms. Initial refinement yielded prolate displacement ellipsoids which severely failed the Hirshfeld condition, affecting one of the diethyl ether and chloroform solvent molecules suggesting the presence of disorder. Both molecules were disordered around a two-fold axis with the oxygen atom of the diethyl ether constrained by its location on the special position. Thus, both were modelled as occupying a position spit over two sites with 50% occupancy and the symmetry generating the second component. Restraints were required to maintain a sensible geometry and displacement ellipsoids in both cases. Despite the disorder, the hydrogen atoms were visible in the difference Fourier map and were refined with restraints prior to inclusion in the final refinement with a riding model.[36] The final structure was refined using full matrix least-squares to give R1 = 0.0363, wR2 = 0.0910 (from the 5189 reflections used in the refinement where $I > -3.0\sigma(I)$) and ρmin,max = 0.45,0.64 e $Å^{-3}$.

Full structural data are included in the Electronic Supplementary Information and have been submitted to the CCDC 1055193. These data can also be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Conclusions

This study deals with the effect of the bridging diamine upon the aggregation properties of a Zn^{II} Schiff-base complex, **1**, derived from the *cis*-1,2-diaminocyclohexane. The X-ray crystal structure of **1** indicates the existence of an asymmetric dimer, with a very rigid backbone. This stiffness results not only from the presence of the diamond shaped metallocycle, which forbids any possible different metal coordination, but also by the *cis*-cyclohexane ring because of the energetically favoured chair conformation, thus preventing the formation of a symmetric arrangement. Surprisingly, there is evidence of the preservation of this asymmetric structure even in solution, as inferred from ^{1}H NMR studies of **1** in chloroform solution. The observation of an asymmetric dimeric structure in solution is rather unusual for this family of Zn^{II} Schiff base complexes since in all other cases so far studied, ^{1}H NMR studies in solution of non-coordinating solvents indicated the presence of a single set of signals even if associated with a dimeric or oligomeric species.[6,7b] These peculiarities evidence the crucial role of the defined stereochemistry around the chelate *cis*-1,2-diaminocyclohexane bridge in determining the aggregation properties of such Lewis acidic species.

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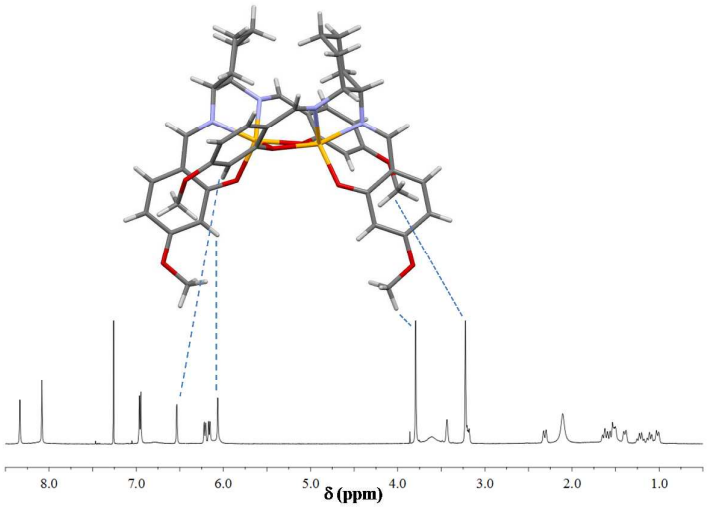

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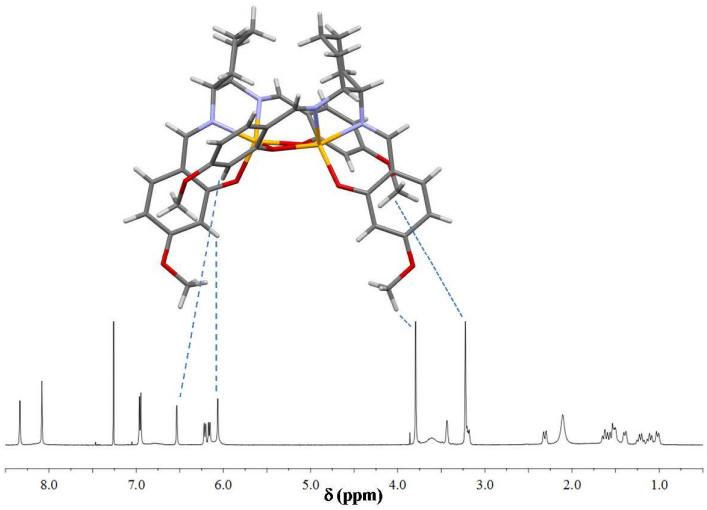

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