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Combined Structural and Theoretical Investigation on Differently Substituted Bispidine Ligands: Predicting the Properties of their Corresponding Coordination Polymers.

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Pyridine-based bispidine ligands L1-L7, which differ in the substituent at the N7 position of the bispidine scaffold, have been studied by single crystal X-ray diffraction and density functional theory (DFT) calculations, also including solid-state algorithms. Qualitative description of the packing interactions and quantitative data on the stability of each ligand in the solid-state have been employed to draw reasonable predictions on the ligand potential for the formation of linear 1D coordination polymers (CPs) with Mn(II)Cl₂ and on their resulting dynamic properties, in terms of adsorption and solvent exchange properties. The basic assumption lies in the fact that volume and polarizability of the ligands would similarly affect packing energies in both molecular solids and CP materials. The results here obtained confirm the data previously reported on CPs (those made from L4 are less dynamic than the ones with L1), but they also allow to predict that CPs made with L2 and L5 should be more dynamic than expected, while CPs with L6 and L7 should not form altogether. This latter prediction derived from the analysis of the steric and electronic factors of the ligand substituents on the N7 position and it is further substantiated by the obtainment of a 2:1 molecular complex, and not a CP, by crystallization of L6 with MnCl₂.

Introduction

Figure 1. Relative orientation of the 1D ribbons viewed along the main ribbon axis direction for a) 1·NB and b) 1·TCM.^{9a} Colour code: C=grey, H=white; N=blue; O=red; Cl=green; Mn=purple.

Scheme 1. a) Molecular formula of bispidine ligand L1 and b) view of the typical 1D linear ribbon-like chains in the single crystal X-ray structure of 1·NB generated by the coordination of L1 with Mn(II) ions in the solid-state. Colour code: C=grey, H=white; N=blue; O=red; Cl=green; Mn=purple.

Figure 2. Visual comparison between the relative orientation of 1D ribbons in 1·NB (left) and 4·NB (right),^{9a} (H atoms are not shown). Solvents are omitted for clarity. Substituents are in CPK. Colour code: C=grey; N=blue; O=red; Cl=green; Mn=purple.

Bispidines are bicyclic heterocyclic compounds synthesized by Carl Mannich for the first time almost a century ago.¹ Yet, they are still investigated for their several interesting catalytic and medicinal properties,² and for their usefulness in the field of metal coordination. Given their rigid structural features and the ease of their chemical functionalization, bispidine derivatives decorated with converging pyridine and / or carboxylate donor units have been used to develop efficient tetra-, penta-, hexa-, and octa-dentate ligands for metal complexation,³ totaling more than three hundred X-ray determined structures of bispidine metal complexes reported to date in the Cambridge Structural Database since the first complexes dated in the '50s of last century.⁴ Applications in catalysis, in the study of unusual isomerism, in medicinal and

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and demonstrated.⁵ In the field of materials chemistry, coordination polymers (CPs) have attracted increasing attention.⁶ Dynamic CPs, or 3rd generation compounds in Kitagawa's classification,⁷ are extremely interesting as they are capable to respond to external stimuli showing promises as selective adsorbents, sensors and catalysts.⁸ Only recently, the first CPs made with bispidine ligands were reported.⁹ This was accomplished by using novel bispidine ligands, such as **L1** (Scheme 1a), specifically designed with pyridine nitrogens at the peripheral part of the ligand pointing outwards in a divergent fashion. As determined by X-ray diffraction on single crystals (SC), the reaction of MnCl_2 with **L1** generates a one-dimensional (1D) CP, constituted of repeating $[\text{Mn}(\text{Cl})_2(\text{L1})_2]$ - non-interpenetrating ribbon-like units (Scheme 1b). $\text{Mn}(\text{II})$ ions are coordinated by two apical chloride atoms and four equatorial pyridine N atoms, from four different ligands in a slightly distorted octahedral environment. Overall, each ligand binds two different metals, one with each pyridine unit. Depending on crystallization solvents and conditions, several crystalline materials could be obtained. For example, CPs containing nitrobenzene (NB) **1·NB**, or trichloromethane (TCM) **1·TCM**, have been obtained.^{9a} They differ only by the relative orientation of the 1D ribbons and solvent content (see Figure 1a,b for **1·NB** and **1·TCM**). Interestingly, these materials could undergo structural transformations, interconverting one into another, in what can be regarded as a highly dynamic behaviour. For example, **1·NB** transforms into **1·TCM** after its exposure to TCM vapours, or by dipping its powder in liquid TCM. Both are heterogeneous solid/vapour or solid/liquid processes, in this particular case fully reversible. The stability of CPs and their propensity to structural transformation are clearly governed by inter-ribbon and solvent-ribbon interactions and hence it appears quite straightforward to envisage that ligands with different structures, once coordinatively polymerized, would lead to CPs having different dynamic solid-state properties. Several works on 1D CPs come to similar conclusions and define these systems as highly tunable and adaptable.¹⁰ Indeed, it was also demonstrated that CPs made with **L4** (benzyl vs. methyl on the N7 position of the bispidine scaffold) are quite more stable and resilient to transformation under the tested conditions.⁹ In the absence of strong specific interactions, it could be expected that the ligand accessible surface, or its volume (and the related polarizability) could constitute a simple but reliable indicator of the effectiveness of ribbons packing. In other words, by increasing the dimension of any structural elements of the ligand, an increase of the ligand accessible surface and volume, along with non-specific van der Waals and dispersion interactions

are expected. A clear example is shown in Figure 2, where the two CP structures formed with ligands **L1** and **L4** and containing NB, **1·NB** and **4·NB**, are displayed; the substituents on N7 are highlighted to indicate their relative position. In the case of **4·NB**, benzyl rings of adjacent ribbons are clearly interacting with each other ($\text{CH}_2 \cdots \text{C}_{\text{centroid}} = 3.654 \text{ \AA}$), whereas methyl groups are quite far apart. One might expect that CPs made with **L4** would be more stable and less dynamic than those made with **L1**, and this is actually the case. However, things could be subtler than that, especially if smaller structural changes are implemented.

Scheme 2. Molecular formulae of ligands **L1-L7**. The R (in red) group is on the N7 position of the bispidine scaffold.

In this work, we aim at acquiring a predictive stance on the feasibility of formation and dynamic properties of this class of bispidine-based CPs by focusing only on the ligand structure. We describe the synthesis and characterization of ligands **L1-L7**, which differ in the substituent in N7 position of the bispidine scaffold (Scheme 2), and their crystal structures determined by single crystals X-ray diffraction, combined with a theoretical investigation by density functional theory (DFT) methods. This integrated approach allowed us to extract useful information on the energies involved in the packing of the ligands as determined from their solid-state structures. Lattice energy E for all ligands was estimated by the average energy required to extract a ligand molecule from the corresponding crystalline phase. In particular, E value is the result of the difference between the calculated unit cell energy and the sum between the calculated energy of the isolated ligand and the calculated energy of the rest of the crystalline cell. The correlation between ligand lattice energies E (or E^* vide infra) and their volume (and polarizability) enables the prediction of the coordination properties of CPs not yet synthesized, while confirming previous observations on the marked different dynamic behaviour between, for example, CPs made with **L1** and **L4**, being the latter the least dynamic. Furthermore, considerations about steric and electronic features of the substituent moieties, along with the isolation of a 2:1 molecular complex upon crystallization of ligand **L6** with MnCl_2 , indicate certain

Figure
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dimeric
N=blue;

Figure 7. a) View of the dimeric H-bonded pair of **L4** and b) view of the packing of **L4** in the solid state along the *a* axis; the dimeric unit is shown in CPK model. Colour code: C=grey, H=white; N=blue; O=red.

Figure 9. a) View of the dimeric H-bonded pair of **L6** and of the additional adjacent bispidine, pairing via mutual HB CH...N interactions between the nearby pyridine units; b) view of the packing of **L6** in the solid state along the *a* axis; the dimeric unit is shown in CPK model. Colour code: C=grey, H=white; N=blue; O=red.

restrictions about which ligand may or may not form CPs.

Results and discussion

Figure 3. Molecular structures of ligands **L1-L7**, as determined by X-ray diffraction on single crystals. Colour code: C=grey, H=white; N=blue; O=red; F=yellow-green.

Single Crystal X-ray structures.

Good quality single crystals of all ligands (Scheme 2) were obtained by slow evaporation of chloroform or methanol solutions and analysed by X-ray diffraction.¹¹ A view of **L1-L7** molecular structures is represented in Figure 3. In the solid state, **L1** (*P*-1) adopts a classic chair-chair conformation with the two ester groups arranged in *anti* geometry (Figure 4a). Two main packing interactions are observed: adjacent bispidines interacted *via* a mutual double H-bond (HB) established between one of the esteric carbonyl and the two CH units of the bispidine core (distances: $d_{C=O\cdots H-C} = 2.451(2)$ Å and $d_{C=O\cdots H-C} = 2.467(3)$ Å), and by the central carbonyl which shows a close $CH_{arom}-O=C$ contact with a pyridine ring edge (with a $d_{C=O\cdots H-C} = 2.699(3)$ Å) (Figure 4a). Finally, lateral esteric carbonyl arms, belonging to two molecules, match their local dipole and mutually point their methoxy groups towards the aromatic rings ($CH\cdots pyr_{centroid}$

Figure 5. a) View of the dimeric H-bonded pair of **L2** and b) view of the packing of **L2** in the solid state, along the *a* axis; one dimeric unit is shown in CPK model. Colour code: C=grey, H=white; N=blue; O=red.

$2.894(4)$ Å). In the overall packing, the molecules are parallel and antiparallel oriented to each other (Figure 4b).

Ligand **L2** (Figure 3) maintains the previously described molecular interaction pattern of **L1** (Figure 5a). Again, two adjacent bispidines interacted *via* a mutual double HB established between one of the esteric carbonyl and the two CH methyne units of the bispidine core (distances: $d_{C=O\cdots H-C} = 2.500(2)$ Å and $d_{C=O\cdots H-C} = 2.514(3)$ Å), and by the central carbonyl, which shows a weak contact with one CH methyne unit of the rigid core (distance: $d_{C=O\cdots H-C} = 2.964(2)$ Å.) and a close $CH_{arom}-O=C$ contact with a pyridine ring edge (with a $d_{C=O\cdots H-C} = 2.649(5)$ Å). In this case, however, the molecules are oriented at 60 deg relatively to each other and again in parallel and antiparallel fashion. This leads to a change in the space group (*P* 2₁/*c* for **L2** versus *P*-1 for **L1**) and on the overall packing (Figure 5b).

Ligand **L3** (Figure 3) crystallizes in the monoclinic *P* 2₁ space group and, due to the presence of the cyclohexyl moiety, it presents a quite different packing compared to the previous two cases. The only specific interaction worth mentioning is the HB established by the central carbonyl with the CH_{arom} of the pyridine ($d_{C=O\cdots H-C_{arom}} = 2.519(3)$ Å).

Figure 8. a) View of the dimeric H-bonded pair of **L5** and of the additional adjacent bispidine, pairing via mutual HB CH...N interactions between the nearby pyridine units; b) view of the packing of **L5** in the solid state along the *a* axis; the dimeric unit is shown in CPK model. Colour code: C=grey, H=white; N=blue; O=red.

However, in the crystal packing, it is evident the predominant role of the cyclohexyl moiety in terms of occupation volume (Figure 6). Another important feature is related to the two ester groups, which are each other *syn*

different packing interactions. Pyridine rings belonging to adjacent bispidine interact with each pairing with $d_{C=N\cdots H} = 2.641(2) \text{ \AA}$, but also act as HB acceptors for one aromatic CH of the trifluoromethyl substituted ring ($d_{C=N\cdots H} = 2.643(2) \text{ \AA}$). This

Figure 10. a) View of the dimeric H-bonded pair of L7; b) view of the packing of L7 in the solid state along the *a* axis; the dimeric unit is shown in CPK model. Colour code: C=grey, H=white; N=blue; O=red.

oriented. It is important to note this structural detail, because it exerts a non-negligible impact on the whole molecular dipole, which in turn influences the overall crystal packing (vide infra).

The classical pairing of two bispidines is again found in the solid-state structure of L4 (Figure 7). The molecules centrosymmetrically interact through the HB between the ester carbonyls and the core bispidine CH ($d_{C=O\cdots H-C} = 2.491(3) \text{ \AA}$). On one side of this dimeric unit, those adjacent are arranged tilting by approximately 120 degrees, positioning the lateral carbonyl arm in close contact with the methyl of the methoxy group ($d_{C=O\cdots H-C} = 2.565(2) \text{ \AA}$ ($C\cdots C$ 3.122(3) \AA). In addition, one pyridine weakly hydrogen bonds the aromatic CH of an adjacent bispidine framework. As to the benzylic group, the conformation of the molecule is characterized by a weak intramolecular T-shaped π - π stacking, with the closest centroid-centroid distance of 3.581(2) \AA .

In the next series L5-L7, all ligands have a benzylic substituent differently functionalized in its *para* position; therefore, they can be directly compared with L4 and among themselves. Weakly H-bonded dimers are also observed for L5 (ester $C=O\cdots$ core CH distances $d_{C=O\cdots H-C} = 2.541$ and 2.689(4) \AA , Figure 8); however, in this case, a more conspicuous role of the substituent is noticed, as the central carbonyl interacts with the benzylic methylene group ($C=O\cdots H-C$ a $d_{C=O\cdots H-C} = 2.672(4) \text{ \AA}$), while the *para* methoxy group interacts with a lateral ester chain ($d_{C=O\cdots H-C} = 2.638(3) \text{ \AA}$). Moreover, pyridine rings of adjacent bispidines form pairs via a double mutual HB involving $CH_{arom}\cdots N_{pyr}$ at a distance $d_{C=N\cdots H} = 2.640(4) \text{ \AA}$. Again, the conformation of the benzylic substituent allows a weak intramolecular T-shaped π - π stacking, with the closest C to C distance of 3.739(2) \AA .

Ligand L6 (Figure 3) presents the strong electron-withdrawing *para* trifluoromethyl group, which could lead to

different packing interactions. Pyridine rings belonging to adjacent bispidine interact with each pairing with $d_{C=N\cdots H} = 2.641(2) \text{ \AA}$, but also act as HB acceptors for one aromatic CH of the trifluoromethyl substituted ring ($d_{C=N\cdots H} = 2.643(2) \text{ \AA}$). This

Table 1. Summary of the lattice energy, E values, their break down into electrostatic, E_{vdw} , and dispersion, E_{electr} , terms. E values: calculated dipole (D) and polarizability α (Bohr³) values.

Ligand	E_{vdw}	E_{electr}	E_{total}	Dipole (D)	Polarizability α (Bohr ³)
L1	-79.48	-49.72	-129.20	1.480	290.61
L2	-79.48	-49.72	-129.20	1.480	290.61
L3	-79.48	-49.72	-129.20	1.480	290.61
L4	-86.15	-54.24	-140.39	1.517	311.7
L5	-83.08	-53.06	-136.14	1.428	287.93
L6	-87.11	-56.49	-143.60	1.581	311.7
L7	-87.11	-56.49	-143.60	1.581	311.7

generates a different packing arrangement compared to L5 (Figure 9). On the other hand, as usual, the lateral carbonyl arm interacts with a hydrogen of the bispidine core through $C=O\cdots H-C$ with $d_{C=O\cdots H-C} = 2.561(2) \text{ \AA}$ and 2.646(2) \AA ; moreover, the central carbonyl group contacts the benzylic methylene group through $C=O\cdots H-C$ with $d_{C=O\cdots H-C} = 2.633(2) \text{ \AA}$. The conformation of the benzyl substituent is similar to that found in L4 or L5, but π - π stacking is longer ($d > 4 \text{ \AA}$). Finally, L6 and L7 (Figure 3), functionalized with a *para* trifluoromethoxy-benzyl group, presents a wider range of intermolecular interactions, which are evident by examining the crystal packing at short contact distances (Figure 10): (i) the contacts between the central carbonyl and the benzylic CH_2 are at $d_{C=O\cdots H-C} = 2.585(3) \text{ \AA}$, (ii) the methoxy group of the carbonyl arm interacts with a CH_2 from an adjacent molecule with $d_{C-O\cdots H-C} = 2.984(3) \text{ \AA}$ and 3.179(3) \AA and with the carbonyl group of an adjacent molecule with a $d_{C=O\cdots H-C} = 2.831(3) \text{ \AA}$ and (iii) is also present a $C-H\cdots N$ contact involving an adjacent pyridine ring, with $d_{CH\cdots C_{pyr}} = 2.795(3) \text{ \AA}$. In addition, (iv) two pyridine rings from neighbouring molecules are bridged through $N_{pyr}\cdots H_{C_{arom}}$ interactions, with $d_{CH\cdots N} = 3.478(3) \text{ \AA}$. As previously found in the other crystal structures, the bispidine core interacts with the lateral carbonyl arm, displaying $d_{C=O\cdots H-C} = 2.581(3) \text{ \AA}$ and $d_{C=O\cdots H-C} = 2.553(3) \text{ \AA}$. A minor contribution to the overall packing stability is also given by the $CF_3\cdots CH_3O$ interactions ($d_{C-F\cdots H-C} = 2.596(3) \text{ \AA}$ and 2.577(3) \AA). Intramolecularly, a

weak T-shaped π - π stacking, with the closest C to C distance of 3.796(3) Å is observed between the benzylic and pyridine rings.

Solid State and gas phase DFT calculations

From these structural data, it is quite evident that all ligands maintain a preferential mode of interaction in the solid state, because in each case a dimeric unit built upon a recurrent set of HBs is detected. However, the substituent surely modulates the overall packing geometry and efficiency. As these aspects cannot be easily determined only by pointing out specific interactions from a metric analysis of X-ray data, we embarked in a detailed gas phase (isolated molecules) and solid-state (crystalline architectures) DFT calculations, in order to get more quantitative data on the stability of the packing in each system. The relative stability of the crystalline phases was estimated with solid-state DFT calculations (PBE/DNP level, see ESI), with explicit van der Waals contribution, according to the approach proposed by Grimme,¹² which we have successfully adopted in several cases for a variety of different systems.¹³ Table 1 reports

lattice energy E , van der Waals contribution E_{vdw} and, by difference, an estimate of the electrostatic component of the interaction, E_{electr} . Experimental densities of the crystalline phases, volume, surface, dipole and polarizability of isolated molecules, calculated at the B3LYP/6-31G** level (ESI) in the experimentally determined conformation, are also shown. Referring to the more general E term, the data showed a marked progressive increase of the overall stability of the packing from L1 to L3 and to L4-L7. Notably, L4 seems to be slightly more stable than L5 and L6, among the benzylic substituents, while the L7 is the most stable derivative. Dispersion forces mainly contributed to the overall stability (E_{vdw}), in line with the high density of these crystalline phases (between ca. 1.26 and 1.42 mg/cm³). Molecular dipoles evaluated at the B3LYP/6-31G** level showed no direct correlation with the overall stability and probably the local charge distributions mostly influenced the resulting packing arrangement. The surprisingly higher molecular dipole of L3 (if compared to L1 and L2) is due to the *syn* orientation of the esteric groups, which is observed only in this derivative. A plot correlating the E values with ligand molecular volume (V) and polarizability (α) in a quadratic form is shown in Figure 11a.¹⁴ Although it could be considered a rough comparison, based on that, L2, L6 and L5 especially, give rise to lattices which are slightly less stable than expected, and relatively to L1. This can be visually recognized by the position of these ligands' data points placed on the upper part of the plot relatively to the correlation best fit (black and orange lines). On the other hand, L4 and L7 show increased stability, and conversely, these ligands' data points reside on the lower part of the plot, below the fit lines. In the cases of L3, L4 and L6, the difference between their V and α values are more significant due to the difference in polarizability between aromatic and aliphatic rings with respect to their volumes. Translating this information to the CP systems originated by these ligands, we could predict that L4 and L7 will give rise to less dynamic CPs, while the contrary is expected for L2, L5 and L6. Considering that specific interactions within the dimeric units may be less relevant in the corresponding CPs, we also calculated the lattice energy for dimeric species, E_{dimer} (Table S1 ESI).

Figure 11. a) Plot of the correlation between E (kcal/mol) and Volume (black circle) and polarizability α (orange circles) for ligands L1-L7; b) Plot of the correlation between E^* (kcal/mol) and Volume (black circle) and polarizability α (orange circles) for ligands L1, L2, L4 and L6. Lines represents best quadratic fitting.

Figure 12. Electrostatic potential maps for ligands L4-L7 calculated at B3LYP 6-31G level of theory, for conformations as found in the X-ray data; a) L4, b) L5, c) L6 and d) L7.

In particular, E_{dimer} value is the results of the difference between the calculated unit cell energy and the sum between the calculated energy of the a given ligand dimeric unit and the calculated energy of the rest of the crystalline cell. It is important to add that ligands also possess quite different dipole moments, calculated in the 1.23 - 4.68 D range, and this could make the comparison a little harder, all the more so due to the fact that ligands in the CP ribbons adopt a centrosymmetric arrangement and their molecular dipoles are antiparallel. To make the dipolar term less relevant in our calculations, we noticed that, in some cases, it was possible to choose the dimeric units in a way to generate an overall null dipole moment (L1, L2, L4 and L6). In these cases, the E_{dimer} energies are smaller than those calculated when the above condition does not apply (Table S1 ESI). This can be easily explained: additional energy is required to extract a unit with a non-zero dipole moment with respect to an analogous overall apolar one. Unfortunately, not all the potential dimeric assemblies of first shell molecules did resulted in a null dipole moment, and the same theoretical approach translated to tetramers, or higher aggregates, became quite cumbersome and it was not pursued further. Nevertheless, it was possible to get refined lattice energy values, E^* , for L1, L2, L4 and L6 (calculated as the half of the E_{dimer} values for the apolar dimeric assemblies, see Table S1 in ESI). A correlation plot of these E^* values with V and α is shown in Figure 11b. On the basis of this limited data set, it is quite striking the difference between L1, L2 and L6 with the overall higher intrinsic stability of L4. This is in agreement with the previously reported data showing a less dynamic behaviour of CPs made with L4 with respect to those of L1,⁹ thus confirming the validity of our approach.

Substitution effect over polymerization

The final point of this structural comparison is related to the steric hindrance and electronic properties of the N7

Figure 13. Partial view of 4•NB CP (ball&stick) which highlights the vicinity and orientation of the benzylic substituent towards the MnCl₂ moiety (in CPK); b) superimposition of the CP structure in a) with the structure of ligand L4 (in orange). Colour code: C=grey, H=white; N=blue; O=red, Cl=green, Mn=purple.

substituents, which increase their size from L1 to L5-L7, also featuring different electronic distributions. It is evident that the R=Me substituent (L1) is less sterically demanding than the isopropyl (L2) or cyclohexyl (L3) and benzylic ones (L4-L7). Regarding the electronic properties, the influence of the *p*-substituents on the ring can be detected in the electrostatic potential maps (EPM) of the ligands L4-L7 showed in Figure 12, where the electron withdrawing (CF₃ and CF₃O) or electron donating (CH₃O) groups were analysed. This is important because, as pointed out by the structural comparison shown in Figure 13a, the substituent in the benzylic groups in the CP made with L4 (4•NB) leans towards the MnCl₂ moiety. In particular, it orients towards the partially negatively charged Mn-bound chloride. The structural comparison between the bispindines belonging to the two structures is reliable since the conformation of the ligand crystallized alone and that of the complexed ligand in the CP are almost superimposable (Figure 13b). This means that should the ligand conformation be maintained in all cases, the substituent on the benzylic ring would become too bulky to allow the polymerization to happen. We envisaged that this could be especially important for the CF₃ and OCF₃ derivatives (L6 and L7). Indeed, the electron rich, less polarizable nature of their substituent, and partial negative charge on the extremities of the benzyl moiety (Figure 12 c-d) is expected to result in repulsive, rather than stabilizing interactions, when approaching the Mn-bound chloride.

Despite several attempts, crystallization tests with ligand L7 and MnCl₂, following the published conditions,⁹ did not yield any CP material suitable for X-ray experiments, either as SC or microcrystalline materials. In agreement with our assumption, ligand L6 crystallized with MnCl₂ forming a 2:1 dimeric complex [(L6)₂-MnCl₂] and its X-ray crystal structure is shown in Figure 14. In this case, the coordination at the Mn(II) center is maintained as octahedral, however,

Figure 15. a) Schematic view of the molecular motion related to the rotation of the pyridyl arms for ligands L1-L7; b) VT-NMR spectra of L1 in DMSO-*d*₆ (T= 305-340 K) and c) corresponding Eyring plot.

two water molecules fill the position that in CPs are typically occupied by the ligands. In the CP, the ligand conformation is very similar to that observed in the structure of the ligand alone, and the steric hindrance exerted by the CF₃-benzyl group near one of the two pyridine arms is quite evident (Figure 14). An additional water molecule interacted via HB to the uncoordinated pyridine nitrogen, and further stabilized by the CF₃ unit ($d_{\text{CF}\cdots\text{O}} = 3.012(3) \text{ \AA}$; $d_{\text{N}\cdots\text{OH}} = 2.829(3) \text{ \AA}$). This finding, although not conclusive, suggests the possibility to control the polymerization by introducing small changes in the steric and electronic feature of the N7 substituent, and strengthens our attempt to correlate the properties of the ligands to those of the CPs.

Finally, it is interesting to note two characteristic features of L1-L7, which are not present in the more common bispidine ligands with convergent pyridine nitrogens. The first was previously commented by us,^{9a} and it is related to the steric hindrance of the aromatic CH of the pyridine ring, which prevents the metal coordination for the inner aliphatic nitrogens.¹⁵ A similar conclusion could have been reached also by considering DFT and structural studies on the preorganization of the more classic bispidines having convergent pyridine metal coordination sites.^{3,5} The second effect of the different substitution pattern in the pyridine moiety does not directly influence the ligand solid-state behaviour. By looking at ¹H-NMR spectra of L1-L7, the pyridine rings display four signals at 305 K (Figure 15b). This observation points to a sterically hindered rotation of the bond connecting the pyridine ring to the aliphatic bicyclic core. VT-NMR experiment in the 305-340 K range measured for L1 in DMSO-*d*₆ (Figure 15c) provides means to evaluate a rotational enthalpy barrier ΔH^\ddagger of ca. 3.7 kcal/mol (ΔS^\ddagger ca. 1 cal/molK).

Conclusions

Bispidine-based 1D CPs with Mn(II) have shown interesting dynamic properties in terms of solvent adsorption and exchange processes.⁹ This work is an attempt to correlate their dynamic behaviour to simple essential characteristics of the ligand used. Dynamic properties of 1D CPs are related to the presence of weak inter-ribbon interactions among robust coordinatively polymerized ribbon-like arrays. Given the lack of strong specific inter ribbon interactions, as confirmed by the analysis of the X-ray structures of CPs made with L1 and L4, we speculated that ligand modification on position N7 could have a direct impact on the CP material properties, by altering the ligand volume and polarizability, and thus its aptitude to interact with the surroundings. Therefore, we have synthesized ligands L1-L7 and studied their solid-state assemblies by X-ray diffraction on SC and by DFT calculations, identifying the common packing modes and interactions and extracting quantitative information. The results of this approach confirm the higher tendency to respond and adapt to external stimuli observed for CP made with L1 with respect to CPs of L4, and predict that CPs with L2, L5 and L6 should share a similar (or even enhanced) dynamic behaviour than those made with L1; at the same time, L7 should afford less responsive CPs. Ongoing

work is aimed at the production of the relevant CPs and at performing further test to support our prediction. Furthermore, on the basis of the tendency of all ligands to maintain a very rigid conformation, by considering the steric and electronic factors of the various substituents, ligands L6 and L7 are not expected to give rise to CP materials altogether. This is partially confirmed by the crystallization of a 2:1 molecular complex, instead of a CP, by reacting L6 and MnCl₂ under the same experimental crystallization conditions. The change of the position of the nitrogen atoms on the pyridine rings of these ligands, in comparison to the more classic pyridine-based bispidines, also affects the ligands conformational freedom as detected and analysed by VT-NMR. This work contributes to the general effort aimed at disclosing new ways to efficiently design ligands, in order to obtain novel functional materials with tunable adsorption properties.

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