This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

www.rsc.org/dalton
Exploring Anagostic Interactions in 5,15-Porphodimethene Metal Complexes

M. G. Derry Holaday, a Gourav Tarafdar, b Arun Kumar, b M. L. P. Reddy, c and A. Srinivasan* b

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

By metal templating strategy, the 5,15-porphodimethene metal complexes were synthesized and confirmed by single crystal X-ray analysis. The anagostic interaction causes distortion, while hydrogen bonding interactions generate dimerisation and array formation of these complexes.

Coordination compounds have been the focus of interest from many decades due to their ability to be used as active elements in fields like catalysis, medicinal chemistry, supramolecular chemistry, etc. The ability of these compounds is not just a result of their chemical composition but also imparted to them through a deliberate consequence of noncovalent interactions between the constituent molecules. Among these, hydrogen atom assisted interactions such as hydrogen bonding, agostic and anagostic interactions are highly significant. They play major role in the structural stability, reactivity and applications like hydride extraction and elimination, which highlights the need for the study of these delicate interactions. However, compared to agostic interactions, anagostic interactions are not well explored in the literature.

Calixphyrins, which are the structural hybrids of porphyrins and calixpyrroles, provide an excellent base for exploring the anion and cation recognition properties. Among the different categories of calixphyrins, 5,15-porphodimethene is an important class with partially conjugated and non-conjugated characters in its framework. To date, many fruitful efforts have been made to design and synthesis of free-base and their metal complexes.

In general, porphodimethenes and its complexes are prepared through; (i) reductive alkylation at meso position of porphyrins; (ii) dealkylation of octaalkylcalix[4]pyrrole; and (iii) acid-catalyzed condensation of oligopyrroles and acetone or condensation of sterically hindered aldehyde and pyrrole. In the methodologies (i) and (ii), the metal complexes of porphyrins / calixpyrroles are converted into respective 5,15-porphodimethene metal complex. In the methodology (iii), the metal complexes are synthesized through stepwise strategies, which is the first step involves the synthesis of free-ligand followed by metal ion insertion. In 2000, Sessler and co-workers demonstrated the synthesis of series of calix[4]pyrroles with one, two and three sp3 hybridized meso carbons and introduced the cation complexation by using ZnCl2 in presence of Et3N. Later in 2005, Lindsey and co-workers reported the Pd complex of porphodimethene, where the 1-acyldipyrmethene afforded less than 1% of respective metal complex by metal templating strategy. However, through stepwise synthesis, the Pd complex was obtained in 22% yield. Same year, Wim Dehaen and co-workers adopted a similar strategy, where the acid-catalyzed condensation of 1-formyl-dipyromethene afforded the free-base 5,15-porphodimethene with the maximum yield of 5.5% and utilized the metal templating strategy by Ni(II) as template and obtained the respective complex in 28% yield. Recently, series of core-modified porphodimethenes such as phosphole and benzene ring incorporated derivatives were reported, which were also synthesized as free-base followed by metal complexation or used as metal ion receptors. Herein, we wish to report the synthesis of 5,15-porphodimethene metal complexes, by single step metal templating strategy. In addition to the regular spectral analyses, all the complexes were confirmed by X-ray single crystal analysis. The present contribution is focused on the study of noncovalent interactions such as hydrogen bonding and anagostic interactions using 5,15-porphodimethene metal complexes as platform. Apart from series of noncovalent interactions, the anagostic interaction explored here is hitherto unknown in porphyrin chemistry in general and calixphyrin chemistry in particular. Further, Zn(II) and its axial water coordinated complex of 5,15-porphodimethene are not known in the literature.

The syntheses of the metal complexes were carried out according to the reaction sequence outlined in Scheme 1. The synthetic methodology adopted here is basically a metal templating strategy, where stirring a methanol solution of 1-formyl-5,5-di(ethyl)dipyromethane (2) with acetates of nickel, palladium and zinc in the presence of p-toluenesulphonic acid as acid-catalyst afforded 1a and 1b in 30% and 35% yield, respectively. On the other hand, the corresponding Zn complex (1c) was obtained in 1% yield along with axial-water coordinated polymorph 1c′ in 10% yield. The identity of the complexes were examined and confirmed by electronic, 1H NMR spectral studies, ESI-MS and single crystal X-ray analyses (ESI†).

---

Scheme 1 Synthesis of metal complexes 1a – 1c′

The mass
spectral analysis of complexes 1a-1c' shows the isotopically resolved signals at m/z 481.1964 (Calcd for \([\text{C}_2\text{H}_8\text{N}_3\text{Ni}]^+\) = 480.1824), 529.1683 (Calcd for \([\text{C}_2\text{H}_8\text{N}_3\text{Pd}]^+\) = 528.1505), 486.1914 (Calcd for \([\text{C}_2\text{H}_8\text{N}_3\text{Zn}]^+\) = 486.1762) and 487.5171 (Calcd for \([\text{C}_2\text{H}_8\text{N}_3\text{OZn}]^+\) = 504.1868) respectively. The single crystals of 1a-1c' were grown at room temperature by vapour diffusion method in CHCl₃/hexane solvent combination. Crystallographic data is listed in Table S2 (ESI†).

The ¹H NMR spectra of 1a, 1b and 1c' were recorded in CDCl₃ at room temperature and shown in Fig. 1a. In general, the meso-CH protons are resonated as a sharp singlet in the range of 6.71 – 6.94 ppm. The doublets are centered at 6.44 to 6.78 ppm correspond to pyrrolic β-CH protons. The ethyl protons are observed as quartet / broad singlet around 2.05 – 2.50 ppm and triplet around 0.66 to 0.84 ppm, respectively. Furthermore, as compared to 1-formyl-5,5-di(ethyl) dipyrromethane 2, the disappearance of the signals corresponding to pyrrolic α-CH and NH protons along with upfield shift of the 1-formyl-CH signals suggests the formation of the macrocycle with metal ion insertion. For example, the ¹H NMR spectrum of 1b shows the meso-CH protons as singlet at 6.94 ppm, the pyrrolic β-CH protons resonate at 6.93 and 6.40 ppm, while the ethyl protons are at 2.05 and 0.82 ppm, respectively.

In addition to the regular pattern as that of 1b, where the methylene protons in the meso-ethyl unit appears as a quartet, the respective protons in 1a resonate as a broad peak at 2.46 ppm, which is 0.41 ppm downfield shifted as compared to 1b. This was further investigated by the temperature dependent NMR measurements (Fig. 1b). Upon increasing the temperature from 298 to 323 K, the broad peak at 2.46 ppm (H₆ – H₇) converts into quartet. On the other side, upon lowering the temperature from 298 to 223 K, all the proton signals become broad, however, the methylene protons further split into three sets with the intensity ratio of 4:2:2 (Fig. 1b inset). Out of eight methylene protons, four are shifted to upfield and resonate at 2.07 ppm (H₉), which is 0.41 ppm downfield shifted as compared to 1b. The remaining four protons are shifted to downfield and resonate between 2.50 to 3.60 ppm (H₈ – H₁₂) suggests that these protons are in closer proximity to the metal center and have an interaction with it. The low yield of 1e hampers the NMR characterization, however, 1c' shows the regular pattern as that of 1b and the axial water protons are resonated as a broad singlet at 2.01 ppm, which is further confirmed by D₂O exchange experiment.

While excavating the structural features of all the complexes, we found that 1a is embedded with multiple type of noncovalent interactions involving the hydrogen atoms. The single crystal X-ray structure of 1a is shown in Fig. 2a and 2b where one of the meso-ethyl units (C1-H1A) shows an unusual electrostatic interaction with the Ni centre. The distance and angle of C1-H1A…Ni is 2.72 Å and 130°, respectively. As evident from the literature, these interactions in which a hydrogen atom is held close to a metal centre are termed as anagostic or pre-agostic interactions. Such interactions are characterized by M–H distance ranging from 2.3 to 2.9 Å and M–H–C bond angle of 110° to 170° with a NMR downfield shift for the M–H–C proton. The observed results are well within the limit of anagostic interactions and the downfield shift of the methylene protons from the NMR spectral analysis further confirm such interactions. It is pertinent to point out here that such an interaction is hitherto unknown in 5,15-porphodimethene metal complexes. In addition to such interaction, 1a shows intermolecular hydrogen bonding interactions, where meso-CH of one unit (C18-H18) interacts with Ni of another unit to generate the self-assembled dimer and also generates the 1-D array, where one unit of pyrrolic β-CH (C12-H12) interacts with next unit pyrrolic π cloud. The distances and angles of self-assembled dimer (C10-H10…Ni and 1-D array (C18-H18…Py(π)) are 2.84 Å, 105° and 2.67 Å, 163°, respectively (Fig. S13†). Overall, the β-anagostic interaction between the ethyl group and the nickel centre leads to the lowering of symmetry and distortion of the molecule as evident from the NMR and crystal analysis of 1a. The hydrogen bonding interaction leads to self-assembled dimerisation as well as 1-D array formation.

The crystal analysis of 1b reveals that two units of metal complexes are present in the unit cell, where both the units are perpendicular to each other and are connected through strong intermolecular hydrogen bonding interactions. The meso-CH (C5-H5) and the pyrrolic β-CH (C7-H7) of one unit interact with
The single crystal X-ray structure of 1c is shown in Fig. 2d. As observed in 1b, the unit cell of 1c also contains two units of respective metal complexes, which are perpendicular to each other. The distance between two Zn in 1c is 8.30 Å. These two units are connected through intermolecular hydrogen bonding interaction, where meso-hydrogen (H9A) of the second unit interacts with pyrrolic π cloud of the first unit and generates the dimeric complex. In addition, there is an intramolecular hydrogen interaction, where hydrogen atoms (H101) in the H2O molecule with Zinc metal center.

The single crystal X-ray structure of 1c is shown in Fig. 2d. As predicted from the NMR spectral analysis, Zn1 in 1c is further coordinated to the H2O molecule to generate 1c′. One of the hydrogens (H101) in the H2O molecule is in intramolecular hydrogen bonding with Zn1 with a distance of 2.71 Å (Fig. 2f). Unlike 1c, the coordinated H2O molecule pushes the Zn1 to the center of the cavity and generates a planar structure which is unprecedented in the calixpyrrole coordination chemistry. The Zn1 is 0.23 Å above the mean plane of the macrocyclic ring. The crystal analysis of 1c′ generates two 1-D intermolecular hydrogen bonding interactions, which are between; (i) one of the hydrogen atoms (H101) in the coordinated H2O molecule with one of the pyrrolic-π [Py1(π)] clouds, and (ii) one of the meso-CHs (C18-H18) with another pyrrolic-π (Py2(π)) cloud. The distances and angles of O1-H101…Py1(π) and C18-H18…Py2(π)1 are 2.81, 2.88 Å and 161°, 171° respectively (Fig. S17†). Combining these two 1-D arrays, 1c′ generates 2-D supramolecular assembly in the solid state (Fig. 2g). As evident from the NMR and crystal structure, 1c′ lacks anagostic interactions due to the stronger interaction of the apical water molecule with Zinc metal center.

The electronic spectral analysis of the complexes 1a-1c′ in CHCl3 consists of two broad bands around 386 to 518 nm with considerable difference in intensity. The bands centered around 500 nm are assigned to π-π* transition.13 1a shows absorption maxima at 423 nm with shoulder around 518 nm; on the other hand, 1b shows a broad band at 386 nm with an intense band at 472 nm (Fig. 3). The molar extinction coefficient values of the complexes are summarized in Table S1 and suggests that the intense bands are around 2.5 fold higher than the broad ones. All the metal complexes have practically no emission.
Fig. 3 Normalised absorption spectra of 1a - 1e′ in CHCl₃.

Conclusion

In summary, noncovalent interactions like hydrogen bonding and anagostic interactions play a decisive role in structure, geometry, and properties of the metal complexes. We have successfully explored the role of noncovalent interactions governing the structure and stability of the metal incorporated 5,15-porphodimethene synthesized via metal templated methodology. Investigation of the crystal structure revealed that 1a and 1e were found to show a rare case of M···H–C anagostic interactions in addition to the normal hydrogen bond interactions. The anagostic interaction explored here demonstrated the structural features in 5,15-porphodimethene metal complexes for the first time. The extra coordinated water molecule in 1e′ converts the roof like conformer to planar form which is hitherto unknown in the calixphyrin metal complexes. Overall, the anagostic type interaction leads to structural distortions while the hydrogen bond interaction leads to *dimerisations* and *array formations*. The role of these interactions in H-activation, catalytic application and receptor properties of these complexes are currently going on in our group.

Acknowledgments

A. S. thanks the Director, NISER for financial support. M. G. D. H. thanks UGC for research fellowship. We thank Dr. Babu Varghese, SAIF, IIT-Chennai for solving the crystal structure of 1b. We greatly acknowledge Mr. Deepak, Mr. Parthasarathi and Mr. Subba Reddy Marri, NISER for recording the single crystal XRD of 1a, 1c and 1e′. We thank Mr. Sanjay, Mr. Amit Sankar and Mr. Rajkumar, NISER for recording NMR and ESI-MS spectra.

Notes and references

*Photoacuences and Photonics Section, †Inorganic Chemistry Section, Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology (NIIST), Trivandrum 695 019, Kerala, India.


By using 5,15-porphodimethene metal complexes, the weak noncovalent anagaostic interaction is explored by variable temperature NMR studies and further confirmed by single crystal X-ray analysis.
By using 5,15-porphodimethene metal complexes, the weak noncovalent anagaostic interaction is explored by variable temperature NMR studies and further confirmed by single crystal X-ray analysis.