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Methylresorcinarene templates uniquely 2-2-1 host-ligand-metal products with pyridine-N-oxides and copper(II), tuning coordination sphere from *cis* to *trans* and octahedral to square planar.
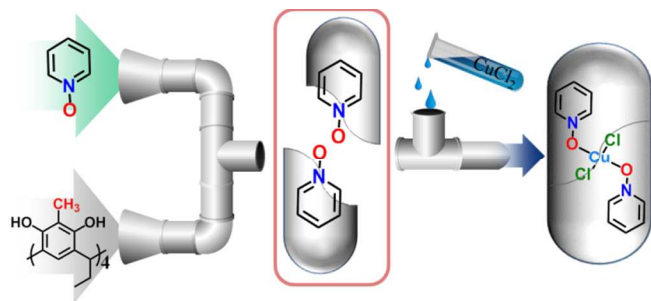
ARTICLE TYPE

Methylresorcinarene: A Reaction Vessel to Control the Coordination Geometry of Copper(II) in Pyridine *N*-oxide Copper(II) Complexes

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Pyridine and 2-picolinic acid *N*-oxides form 2:2 ligand:metal (L:M) bidentate *cis*-coordinated L_2M_2 and polymeric octahedra complexes, respectively, with copper(II) salts. The *N*-oxides also form 1:1 host-guest complexes with methylresorcinarene. In combination, the three components form a unique 2:2:1 host-ligand-metal complexes. The methylresorcinarene acts as a reaction vessel/protecting group to control the
10 coordination geometry of copper(II) from *cis*-see-saw to *trans*-square planar, and from octahedral to square planar coordination geometry. These processes were studied in solution and solid state *via* ^{1}H NMR spectroscopy and single crystal X-ray diffraction.

Introduction

The construction of supramolecular architectures utilizing a
15 variety of weak interactions has potential applications in materials science and biomimetic chemistry.[1] The challenge of constructing exotic supramolecular architectures with function from small-molecule building blocks requires understanding to design strategies.[2] Resorcinarenes are an extensively studied
20 phenolic group containing macrocyclic compounds.[3] Easy syntheses, bowl-shape and electron-rich interior cavity are strongly associated assets with resorcinarenes, making them a useful component in host-guest inclusion chemistry.[3] The size and electronic nature of the guest molecules are important in
25 determining the final structures, and morphologies of the supramolecular architectures.[3] Consequently, different guests have templated assemblies such as open inclusion complexes,[4] dimeric and hexameric capsules,[5] as well as nanotubes.[6]

The concept of metallosupramolecular chemistry is based on
30 the formation of discrete assemblies or coordination polymers through bridging organic ligands and metals.[7] Pyridine *N*-oxides are typical oxygen atom transfer reagents, routinely used in the syntheses of high-valent transition metal centers, lanthanide and actinide oxo complexes.[8] Copper plays an important role in redox
35 chemistry with applications in catalysis[9] and biology.[10] There are multiple reports of different complexes and architectures formed between copper and pyridine *N*-oxide with applications such as in catalysis,[11] as magnetic conducting materials,[12] with cytotoxic characteristics.[13]

40 The quest for potential applications of resorcinarenes is a continuous goal for researchers working in this area. There is a need to explore the bowl-shape interior cavity of electron rich resorcinarenes as an essential feature treating them as reaction vessel or protecting group tuning specific reactions. The aromatic
45 ring of pyridine *N*-oxides through $\pi\cdots\pi$ interactions, can be bound by the electron-rich resorcinarenes. There are several reports of

complexes formed between calix[4]arenes[14] and cavitands[15] with pyridine *N*-oxides. Atwood *et al*,[16] reported nano-sized spherical and helical tubular structures formed through hydrophobic and
50 numerous non-covalent interactions, such as metal-ligand coordination, $\pi\cdots\pi$ stacking, hydrogen bonding, and van der Waals forces associated with *p*-sulfonatocalix[4]arene, pyridine *N*-oxide and lanthanide nitrate.

In the study described herein, we explore the electron-rich
55 interior cavity of methylresorcinarene **1** (Fig. 1) as a host for pyridine *N*-oxides **2-3** to form a unique 2:1 ligand-metal *N*-oxide Cu[II] square planar products. In the process, methylresorcinarene act as a protecting group creating steric hindrance for *N*-oxide coordination, thus changing its coordination mode and
60 coordination environment of Cu[II] products. These processes were studied in solution and in the solid state *via* ^{1}H NMR spectroscopy and single crystal X-ray diffraction analyses.
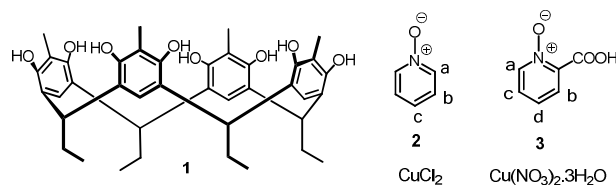

Fig. 1 Methylresorcinarene **1**, pyridine *N*-oxide **2**, 2-picolinic acid
65 *N*-oxide **3**, $CuCl_2$ and $Cu(NO_3)_2$.

Results and Discussion

Resorcinarenes possess an electron rich interior cavity suitable for the recognition of positively charged and electron deficient guest molecules.[3-6] In methylresorcinarenes, the electron donating
70 methyl groups increases the electron density of the aromatic rings, and thus increases their affinity towards electron deficient guest compounds. The electron push and electron pull nature of the negatively charged oxygen towards the aromatic ring in pyridine *N*-oxides makes these compounds a unique class of

guest molecules; and act as either electron rich or poor guest molecules with respect to the approaching reagents. Herein, for a π-electron rich receptor, pyridine *N*-oxide adopts π-electron deficient system to exhibit π⋯π interactions. Also, the presence of hydroxyl groups in methylresorcinarene and oxygen in pyridine *N*-oxide makes a suitable composite for hydrogen bond interactions between the host and the guest. With this prior knowledge and their behaviour towards metal coordination, we started to investigate the host-guest chemistry systematically starting with solution based studies to inspect for such evidence.

Host-Guest Complexation

We recently reported the ^{1}H NMR complexation studies of pyridine *N*-oxide **2** and methylresorcinarene **1** with an association constant of log$K$=1.8157±0.0171.[17] A 1:1 mixture of methyresorcinarene **1** and pyridine *N*-oxide **2** in CD$_3$OD at 303 K showed significant up field shifts of the pyridine *N*-oxide **2** aromatic protons. The most intense shift of 0.62 ppm was observed for the *para-* protons thus confirming its location deep in the cavity of the host.[17] The generally large shifts of the guest signals highlight the shielding effects of the aromatic rings of the host **1**.[18]

The use of carboxylic acid group at the *ortho-* position of 2-picolinic acid *N*-oxide **3**, and its electron withdrawing nature renders the aromatic ring further electron deficient. This fact is highlighted by the larger shifts of the 2-picolinic acid *N*-oxide protons upon complexation with methylresorcinarene **1** (Fig. 2) as compared to the pyridine *N*-oxide **2**. Chemical shifts changes greater than 1 ppm are observed for the *para-* (1.22 ppm) and *meta-* (1.10 ppm) protons. Again, the large shift of the *para-* protons also suggests the guest located deep in the cavity of the host.

To further study these systems in the solid state, single crystals suitable for X-ray analysis were obtained by mixing the respective methanol solutions of **1**, **2** and **1**, **3** to give 1:1 complexes of host **1**+pyridine N-oxide (**I**) and host **1**+2-picolinic acid N-oxide (**II**), respectively, as shown in Fig. 3. Complex **I** crystallizes in the triclinic space group *P*-1 with 1:1 host-guest ratio, together with three water molecules in the asymmetric unit. Pyridine N-oxide **2** sits inside the cavity at a height of *ca.* 3.09 Å from the centroid of the lower rim carbon atoms, and stabilizes by π⋯π interaction[19] with one of the host aromatic rings at centroid-to-centroid distances of 3.643 Å. In addition, the *meta-* and *para-* hydrogens of pyridine N-oxide **2** are stabilized with C-H⋯π(centroid) interactions at distances of 2.684 Å and 3.040 Å, respectively, as shown in Fig. 3a. The N-O group is bidentate hydrogen bond acceptor for two out-of-cavity water molecules at (N-O)$_{guest}$⋯O-H distances of 2.638 Å [∠N-O)$_{guest}$⋯O-H, 135.66°] and 2.635 Å [∠N-O)$_{guest}$⋯O-H, 163.69°]. The hydrogen bonding between the water molecules and N-O group of pyridine N-oxide play an important role in bringing two 1:1 host-guest assemblies closer. As a result, the oxygens of N-O group are at distances of *ca.* 6.032 Å, which provided us an insight to glue the N-O groups of the guests with metals (Fig. S3a).

The crystal structure of **II** was solved in the triclinic space group *P*-1, asymmetric unit contains 1:1 host-guest complex

ratio. 2-Picolinic acid *N*-oxide **3** sits deeper inside the cavity than pyridine *N*-oxide **2** at a depth of *ca.* 2.58 Å, stabilized by π⋯π interaction with one of the host aromatic rings at centroid-to-centroid distances of 3.704 Å. As shown in Fig. 3c, two of the aromatic protons of the guest **3** are stabilized by C-H⋯π interactions at distances of 2.578 Å and 2.658 Å. The N-O group forms an intramolecular hydrogen bond with -COOH group at (N-O)$_{guest}$⋯O-H distances of 2.443(2) Å [∠N-O)$_{guest}$⋯O-H, 152(3)°]. However, the intermolecular hydrogen bond with the hydroxyl group of host **1** [(O⋯H-O), 2.748(2) Å; ∠O⋯H-O, 146(3)°] brings two 1:1 host-guest complexes together with oxygens of N-O group at distances of *ca.* 3.335 Å (Fig. S3b).
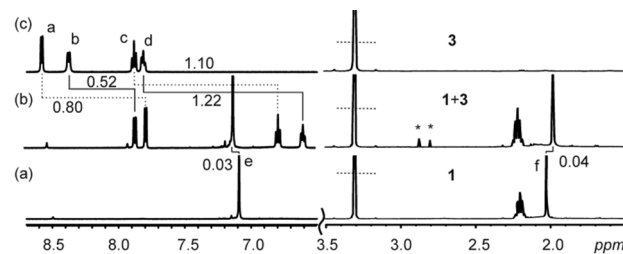
**Fig. 2**. ^{1}H NMR spectra (CD$_3$OD, 303 K) of a 30 mM solution of (a) **1**, (b) 1:1 mixture of **1** and **3**, (c) **3**. The chemical shifts changes are in ppm. Stars represent water molecules present in the complex (see Fig 3).

As shown in Fig.3a and 3b, the C-H⋯π interactions significantly contribute and support the ^{1}H NMR shift changes. The short C-H⋯π distances in **II** than in **I** explains the delocalization of shared π-electrons with the electron withdrawing –COOH group, followed by the formation of stable six-membered ring by intramolecular hydrogen bonding. The large shifts of *c-* and *d-* protons of the guest **3** also explains the presence of *para-* electron withdrawing –COOH and N-O groups, and their shielding by π-rich cavity after complexation. Besides π⋯π and C-H⋯π interactions, the cavity displays remarkable breathing properties (Fig. S4) and offers hydrogen bonding with the oxygen atoms of the pyridine *N*-oxides as well as the solvent molecules. The effect and the strength of shielding on C-H protons by π-rich cavity also depend upon the height (Fig. S5) of the guest located in the cavity of the host. With such host breathing properties, guest **3** (2.583 Å) was accessed deeper in the cavity than **2** (3.099 Å), supporting the enhanced shielding observed in solution.

Metal Complexation

NMR spectroscopy is a useful tool in studying structural and magnetic properties of Cu[II] coordination compounds.[20] The slow electronic relaxation of Cu[II] ions mostly results in large line widths and poor resolution, making the interpretation of spectra of Cu[II] complexes almost impossible. This paramagnetic effect is stronger for protons in close proximity to the copper ions.[20]

The ^{1}H NMR of a 1:1 mixture of pyridine *N*-oxide **2** and CuCl$_2$, show only one broad signal around 9.2 ppm within the 0-100 ppm window (Fig. 4c). From X-ray crystal structures (Fig. 3), the guest is tilted towards a phenyl ring of the host **1** to maximize π⋯π interactions. This orientation of the pyridine *N*-oxide creates steric hindrance for bidentate coordination, which will tune the coordination geometry of the Cu[II].
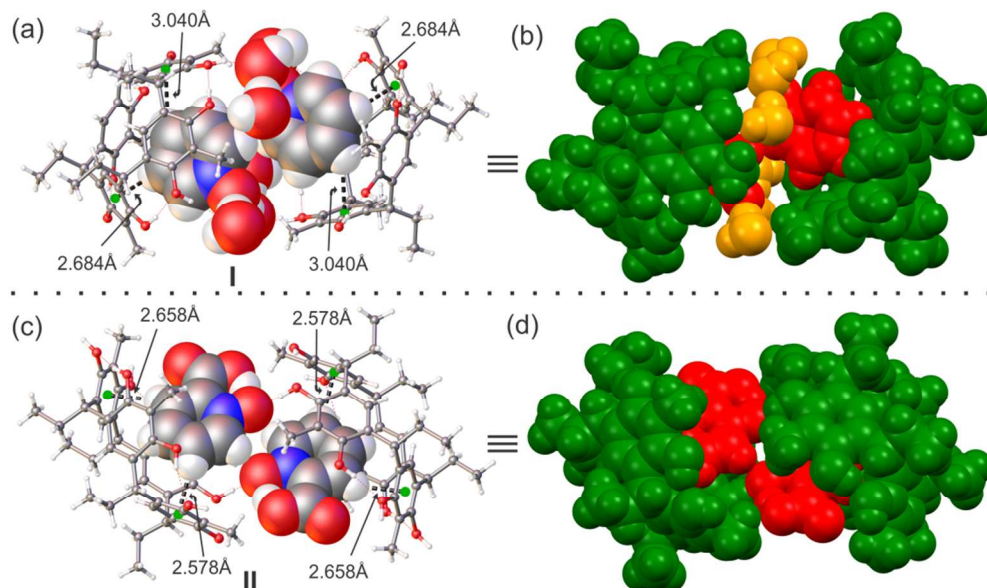
Fig. 3. (a) Representation of two 1:1 host-guest complexes of host **1**+pyridine *N*-oxide (**I**), and (b) colour coded CPK model of complex **I**. (c) Representation of two 1:1 host-guest complexes of host **1**+2-picolinic acid *N*-oxide (**II**), and (d) colour coded CPK model of complex **II**. The C-H···π interactions are shown by black broken lines from hydrogens of aromatic rings of N-oxide to the centroid of host aromatic rings.

A series of ^{1}H NMR experiments were done to test this hypothesis. In the experiment, several samples were prepared consisting of the host **1**, the *N*-oxides **2-3**, CuCl$_2$ and Cu(NO$_3$)·3H$_2$O salts. The ^{1}H NMR of the mixture containing **1**, **2** and CuCl$_2$ shows a substantial increase of 0.84 ppm of the broad pyridine *N*-oxide signals at 8.3 ppm (Fig. 4b). This up field shift is either consistent with shielding of the guest signals by the phenyl rings of the host **1** or the formation of a different product. The pyridine *N*-oxide **2** signals are broadened as a result of the slow relaxation of the Cu[II] ions, while all the methylresorcinarene **1** signals are observed. The up field shift changes of the methylresorcinarene **1** signals support the formation of a host-guest complex with the Cu[II] coordinated pyridine *N*-oxides (Fig. 4).

The ^{1}H NMR of a 1:1 mixture of 2-picolinic acid *N*-oxide **3** and Cu(NO$_3$)$_2$·3H$_2$O was analogous to the pyridine *N*-oxide **2**, with a single broad signal around 10.5 ppm within the 0-100 ppm window (Fig. S6). This larger downfield shift is as a result of the more electron-deficient product. The single broad signal of the 2-picolinic acid *N*-oxide **3** disappears in the combination of **1**, **3** and Cu(NO$_3$)$_2$·3H$_2$O also suggesting shielding or the formation of a different product. However, up field changes of the methylresorcinarene **1** signals are analogous to those observed with the pyridine *N*-oxide **2** hinting to a similar host-guest product (Fig. S6).
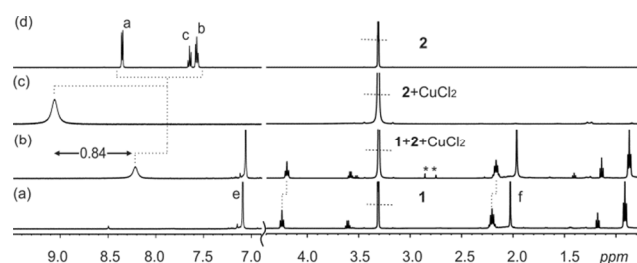

Fig. 4. ^{1}H NMR spectra (CD$_3$OD, 303 K) of a 30 mM solution of (a) **1**, (b) 2:2:1 mixture of **1**, **2** and CuCl$_2$, (c) 1:1 mixture of **2** and CuCl$_2$, (d) **2**. The shift changes are highlighted by the dotted lines. Stars represent water molecules present in the complex (see Fig 5).

To unambiguously confirm the structures of the host-ligand-metal complexes, solid state analyses *via* single crystal X-ray diffraction were done. Reactions of pyridine N-oxide **2** and CuCl$_2$, and between 2-picolinic acid *N*-oxide **3** and Cu(NO$_3$)·3H$_2$O resulted in a discrete structure **III** (Fig. 5a) and 1D polymeric self-assembly **V** (Fig. 5d), respectively. Complex **III** crystallized in the monoclinic space group P2$_1$/*c* with 1:1 ligand to metal ratio. The μ_2-*O,O* pyridine N-oxide **2** bridges Cu1 and Cu1a, with Cu[II] in Cl$_2$O$_2$ coordination sphere, and have adopted *cis*-see-saw **III**[21] (τ_4 = 0.34)[22] geometry.

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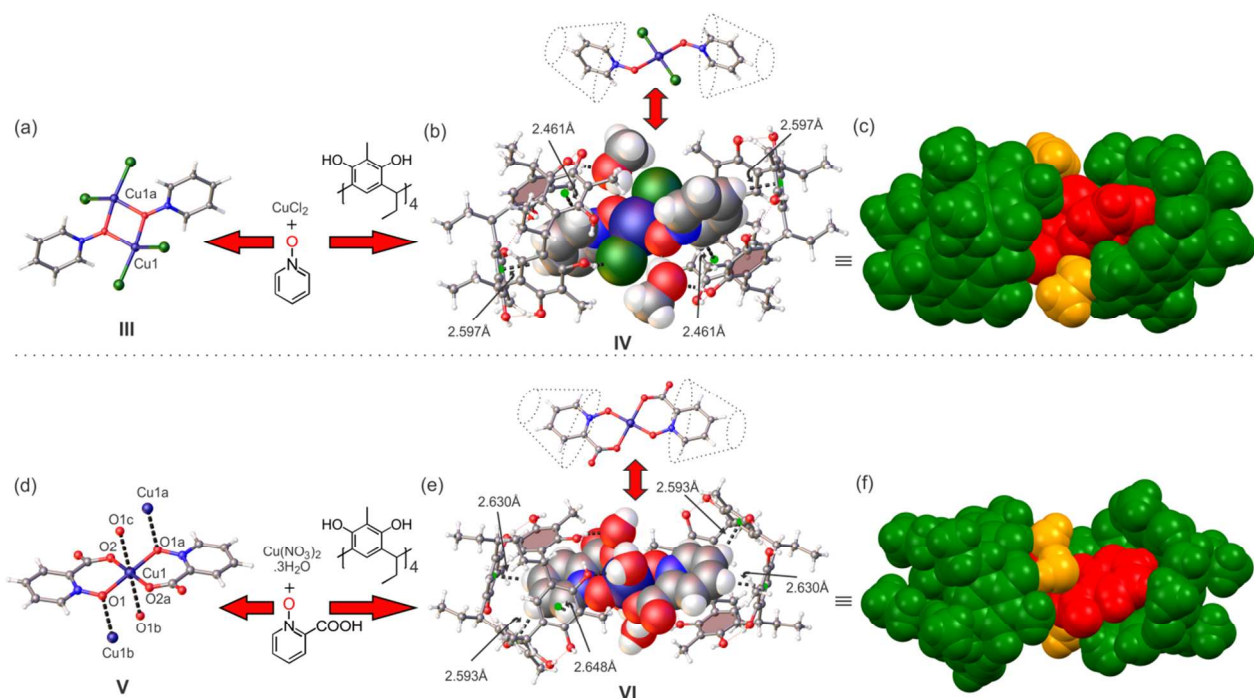
Fig. 5. (a) Ball and stick representation of complex **III**. (b) 2:2:1 Host-guest metal complex of **IV**(c) Colour coded CPK model of complex **IV**. (d) Ball and stick representation of complex **V**. (e) 2:2:1 Host-guest metal complex of **VI**. (f) Colour coded CPK model of complex **VI**. The insets of the *N*-oxide-copper complexes inside the hosts are shown for clarity. The C-H⋯π interactions are shown in black broken line from hydrogens of aromatic *N*-oxide
5 guest molecules to the centroid of the host aromatic rings.

On the other hand, complex **V** is 1D polymeric structure (Fig. 5d and S9) with octahedral Cu^{II} in O_4 coordination sphere. Complex **V** crystallized in the monoclinic space group $P2_1/c$, asymmetric unit contains one 2-picolinic acid *N*-oxide **3** chelating half a
10 copper in 2:1 ligand to metal ratio. A CCDC search related to **III** (CSD Refcodes: CUCPYO, CUCPYO11 and CUCPYO12)[21] and **V** (CSD Refcode: SIJRIN)[23] revealed three and one hits, respectively, which are synthesized from different conditions.

Single crystal X-ray structure from the combination of the
15 host **1**, the *N*-oxides **2-3** and the Cu^{II} salts $CuCl_2$ and $Cu(NO_3)\cdot 3H_2O$ gave the 2:2:1 host-ligand-metal products of $(1)_2+(2)_2+CuCl_2$, **IV** (Fig. 5b and 5c) and $(1)_2+([3-2H]^{-2})_2+Cu^{2+}$, **VI** respectively (Fig. 5e and 5f). Interestingly, coordination geometry of the Cu^{II} is different from the products obtained
20 without host **1**. The reactions of $2+CuCl_2$, and $3+Cu(NO_3)\cdot 3H_2O$ with methylresorcinarene **1**, retains the characteristic π⋯π (**IV**; 3.956 Å and **VI**; 3.869 Å) as shown in Fig. 5b and 5e. Although both structures **IV** and **VI** show similar interactions, the 2-picolinic acid *N*-oxide **3** in **VI** is located deeper (2.643 Å) in the
25 cavity of the host **1** compared to pyridine *N*-oxide **2** in **IV** (3.099 Å), thus displaying shorter C-H⋯π interactions. In complex **IV**, the Cu^{II} is *trans*-coordinated by two chloride anions and pyridine *N*-oxide **2** molecules (Fig 5b); while in complex **VI**, 2-picolinic

acid *N*-oxide **3** alone chelates in *trans*-mode with the help of
30 deprotonated –COOH functionality (Fig. 5c). The self-assembly of *trans*- coordination mode between pyridine N-oxide and $CuCl_2$ in complex **IV** has not been previously reported. A CSD survey revealed 10 crystal structures with other N-oxides and $CuCl_2$ having similar *trans*- coordination mode (Refcodes: CEGGOK,
35 CMPOCU, CMPOCU01, DETFAK, IVVUYUU, PIJDUH, QQQBVY, QQQBWA, TANSUW and TANSUW10).[24] On the other hand, the four coordinated *trans*- chelation mode between deprotonated 2-picolinic acid N-oxide and metals of $M(NO_3)_2$ stabilized with solvent molecules apically is commonly observed
40 phenomena (for example see Refcodes: BIVWIM, BIVWOS, BIVWUY, BIVXAF, IDULOJ, TENKAA, XISBOR, TOTTED, TOZMEC, TOZMEC01).[25] The four coordinated and *trans*-chelated complex inside the complex **VI** stabilized by resorcinarene host is rare, and a CSD search for similar four
45 coordinate systems revealed one hit (Refcode: EBUPIC).[26] Besides different coordination sphere of Cu^{II} and their stabilization by hydrogen bond interactions, *N*-oxides **2-3** and methylresorcinarene components prefers to exchange the π-electrons by π⋯π and C-H⋯π interactions.
50 The π⋯π and C-H⋯π interaction between the host **1** and the guest molecules **2**, **3** engendered a steric effect thus causing a

dramatic change in the coordination sphere around Cu^{II}; which is different from complexes **III** and **V**.[20,22] As a consequence, the bidentate pyridine *N*-oxide **2** in L_2M_2 host free complex now adopts a monodentate coordination mode with *trans*- L_2M geometry in **IV** (Fig. 5). The coordination sphere of the Cu^{II} changes from *cis*-see-saw in **III** to *trans*-square planar geometry in **IV**. The coordination sphere of square planar Cu^{II} in **IV** is tightly held and stabilized by -OH···O (2.803 Å, ⌀-H···O 138.57°) and -OH···Cl (3.127 Å, ⌀-H···Cl 163.33°) interactions (Fig. S7b). Interestingly, the *N*-oxide in **IV** preserves its bidenticity through hydrogen bonding with methanol molecule (Fig. S7b). The Cu^{II} in **VI** is apically stabilized by water molecules at Cu···O distances of 2.740 Å.. Square planar geometries, especially Cu^{II} ions compete with aqua ligands for binding and such preference often leads to ligand field stabilization either by strong coordination[24] or by weak interactions (Fig. S8b).

Conclusions

In summary, the interior cavity of methylresorcinarene **1** through π···π, CH···π and hydrogen bond interactions templates the formation of a unique 2:2:1 (Host-Ligand-Metal) complexes with *N*-oxides **2-3** and Cu^{II} salts $CuCl_2$ and $Cu(NO_3)_2 \cdot 3H_2O$. The coordination geometry of the Cu^{II} changes from *cis*-see-saw (**III**) to *trans* square planar (**IV**), and from octahedral (**V**) to square planar (**VI**) products. With pyridine *N*-oxide **2**, the anion (Cl⁻) completes the coordination geometry. Introducing a chelating carboxylic acid functional group in the *ortho*- position of the pyridine *N*-oxide **3**, led to a similar coordination compound. Though the Cu^{II} ion retains the same geometry, the carboxylic acid group completes the coordination geometry with the nitrate anion a passive spectator. Despite the paramagnetic nature of Cu^{II}, the host signals could be monitored to confirm the complexation in solution *via* ^{1}H NMR spectroscopy. Single crystal X-ray diffraction studies unambiguously confirmed the formed products and their specific coordination geometries. This work highlights the usefulness of the resorcinarene framework as reaction vessel for pyridine N-oxide copper complexes in tuning specific Cu^{II} coordination sphere products governed by several weak interactions.

Notes and references

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