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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 and 2 : 1 ligand : metal (L : M) discrete L_2M_2 and polymeric complexes with $CuCl_2$ and $Cu(NO_3)_2$, 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 complex. The methylresorcinarene acts as a reaction vessel/protecting group to control the coordination 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 in the solid state *via* ^{1}H NMR spectroscopy and single crystal X-ray diffraction.

Introduction

The construction of supramolecular architectures utilizing a 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 a better understanding to design strategies.[2] Resorcinarenes are an extensively studied phenolic group containing macrocyclic compounds.[3] Easy syntheses, bowl-shape and electron-rich interior cavity are assets strongly associated with resorcinarenes, making them a useful component in host–guest inclusion chemistry.[3] The size and the electronic nature of the guest molecules are important for 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 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 chemistry with application 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] and with cytotoxic characteristics.[13]

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-shaped interior cavity of electron rich resorcinarenes as an essential feature, treating them as a reaction vessel or a protecting group tuning specific reactions. The aromatic ring of pyridine *N*-oxides through π···π 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 numerous non-covalent interactions, such as metal–ligand coordination, π···π 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 interior cavity of methylresorcinarene **1** (Fig. 1) as a host for pyridine *N*-oxides **2–3** to form unique 2 : 1 ligand–metal

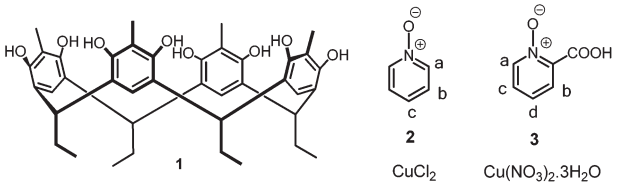

Fig. 1 Methylresorcinarene **1**, pyridine *N*-oxide **2**, 2-picolinic acid *N*-oxide **3**, $CuCl_2$ and $Cu(NO_3)_2$.

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N-oxide Cu^{II} square planar products. In the process, methylresorcinarene acts as a protecting group creating steric hindrance for *N*-oxide coordination, thus changing its coordination mode and the 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.

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 methyl groups increase the electron density of the aromatic rings and thus increase 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 they 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 a π-electron deficient system to exhibit π···π interactions. Also, the presence of hydroxyl groups in methylresorcinarene and oxygen in pyridine *N*-oxide makes it a suitable composite for hydrogen bond interactions between the host and the guest. With this prior knowledge of their behaviour towards metal coordination, we started to investigate the host–guest chemistry systematically, starting with solution based studies to inspect 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 $\log K = 1.8157 \pm 0.0171$.[17] A 1 : 1 mixture of methylresorcinarene **1** and pyridine *N*-oxide **2** in CD_3OD at 303 K showed significant upfield 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 the carboxylic acid group at the *ortho*- position of pyridine *N*-oxide and its electron withdrawing nature render 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 with the pyridine *N*-oxide **2**. Chemical shift 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 $P\bar{1}$ with a 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 interactions[19] with one of the host aromatic rings at a centroid-to-centroid distance 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 a bidentate hydrogen bond acceptor for two out-of-cavity water molecules at $(N–O)_{guest}\cdots O–H$ distances of 2.638 Å [$\angle(N–O)_{guest}\cdots O–H$, 135.66°] and 2.635 Å [$\angle(N–O)_{guest}\cdots O–H$, 163.69°]. The hydrogen bonding between the water molecules and the N–O group of pyridine *N*-oxide plays an important role in bringing two 1 : 1 host–guest assemblies closer. As a result, the oxygens of N–O groups are at a distance of *ca.* 6.032 Å, which provided us an insight to glue the N–O groups of the guests with metals (Fig. S3a†).

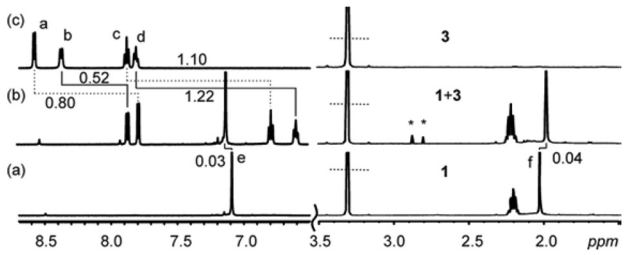

Fig. 2 ^{1}H NMR spectra (CD_3OD, 303 K) of a 30 mM solution of (a) **1**, (b) a 1 : 1 mixture of **1** and **3**, and (c) **3**. The chemical shift changes are in ppm. Stars represent water molecules present in the complex (see Fig. 3).

The crystal structure of **II** was solved in the triclinic space group $P\bar{1}$, and the asymmetric unit contains a 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 interactions with one of the host aromatic rings at a centroid-to-centroid distance 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 the –COOH group at a $(N–O)_{guest}\cdots O–H$ distance of 2.443(2) Å [$\angle(N–O)_{guest}\cdots O–H$, 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 groups at a distance of *ca.* 3.335 Å (Fig. S3b†).

As shown in Fig.3a and b, 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 a stable six-membered ring by intramolecular hydrogen bonding. The large shifts of c- and d-protons of the guest **3** also explains the pres-

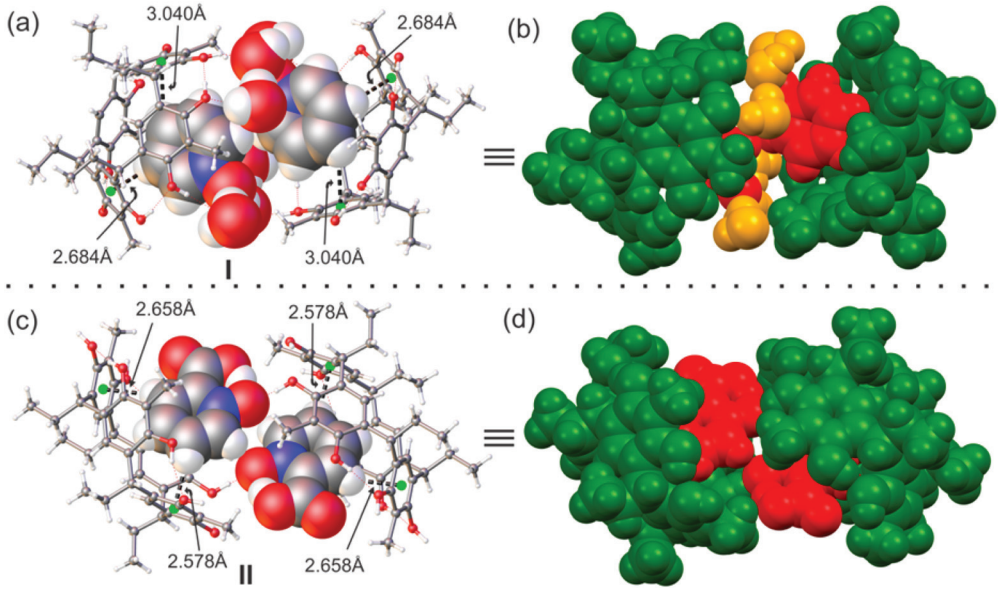

Fig. 3 (a) Representation of two 1 : 1 host–guest complexes of host **1** + pyridine *N*-oxide (**I**), and (b) a colour coded CPK model of complex **I**. (c) Representation of two 1 : 1 host–guest complexes of host **1** + 2-picolinic acid *N*-oxide (**II**), and (d) a colour coded CPK model of complex **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.

ence of *para*- electron withdrawing –COOH and N–O groups, and their shielding by the 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 the π-rich cavity also depends 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.

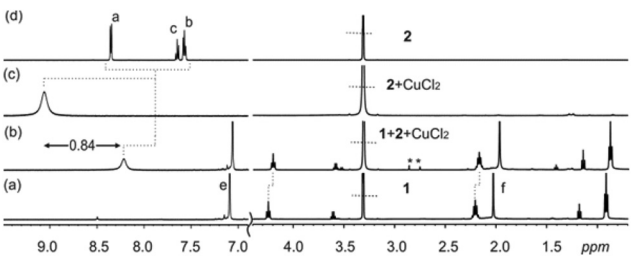

Fig. 4 ^{1}H NMR spectra (CD_3OD, 303 K) of a 30 mM solution of (a) **1**, (b) a 2 : 2 : 1 mixture of **1**, **2** and $CuCl_2$, (c) a 1 : 1 mixture of **2** and $CuCl_2$, and (d) **2**. The shift changes are highlighted by the dotted lines. Stars represent water molecules present in the complex (see Fig. 5).

Metal complexation

NMR spectroscopy is a useful tool for studying the 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 spectra 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}.

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 $Cu(NO_3)_2{\cdot}3H_2O$ salts. The ^{1}H NMR spectrum 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 upfield 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 upfield shifts 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 spectrum of a 1 : 1 mixture of 2-picolinic acid *N*-oxide **3** and $Cu(NO_3)_2{\cdot}3H_2O$ 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 $Cu(NO_3)_2{\cdot}3H_2O$, also suggesting

shielding or the formation of a different product. However, upfield changes of the methylresorcinarene **1** signals are analogous to those observed with the pyridine *N*-oxide **2**, hinting at a similar host–guest product (Fig. S6†).

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 $Cu(NO_3)_2{\cdot}3H_2O$ 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 a 1 : 1 ligand to metal ratio. The μ_2-*O*,*O* pyridine *N*-oxide **2** bridges Cu1 and Cu1a, with Cu^{II} in the Cl_2O_2 coordination sphere, and have adopted *cis*-see-saw **III**[21] ($\tau_4 = 0.34$)[22] geometry.

On the other hand, complex **V** is a 1D polymeric structure (Fig. 5d and S9†) with octahedral Cu^{II} in the O_4 coordination sphere. Complex **V** crystallized in the monoclinic space group $P2_1/c$, the asymmetric unit contains one 2-picolinic acid *N*-oxide **3** chelating half a copper in a 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 under different conditions.

Single crystal X-ray structure from the combination of the host **1**, the *N*-oxides **2–3** and the Cu^{II} salts $CuCl_2$ and $Cu(NO_3)_2{\cdot}3H_2O$ gave the 2 : 2 : 1 host–ligand–metal products of $(\mathbf{1})_2$ + $(\mathbf{2})_2$ + $CuCl_2$, **IV** (Fig. 5b and c) and $(\mathbf{1})_2$ + $([\mathbf{3}{-}2H]^{-2})_2$ + Cu^{2+}, **VI**, respectively (Fig. 5e and f). Interestingly, the coordination geometry of the Cu^{II} is different from the products obtained without host **1**. The reaction of **2** + $CuCl_2$ and **3** + $Cu(NO_3)_2{\cdot}3H_2O$ with methylresorcinarene **1** retains the characteristic π···π interactions (**IV**; 3.956 Å and **VI**; 3.869 Å) as shown in Fig. 5b and e. 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 cavity of the host **1** compared with 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 deprotonated –COOH functionality (Fig. 5c). The self-assembly of the *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 a similar *trans*-coordination mode (Refcodes: CEGGOK, 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 a commonly observed phenomenon (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 the resorci-

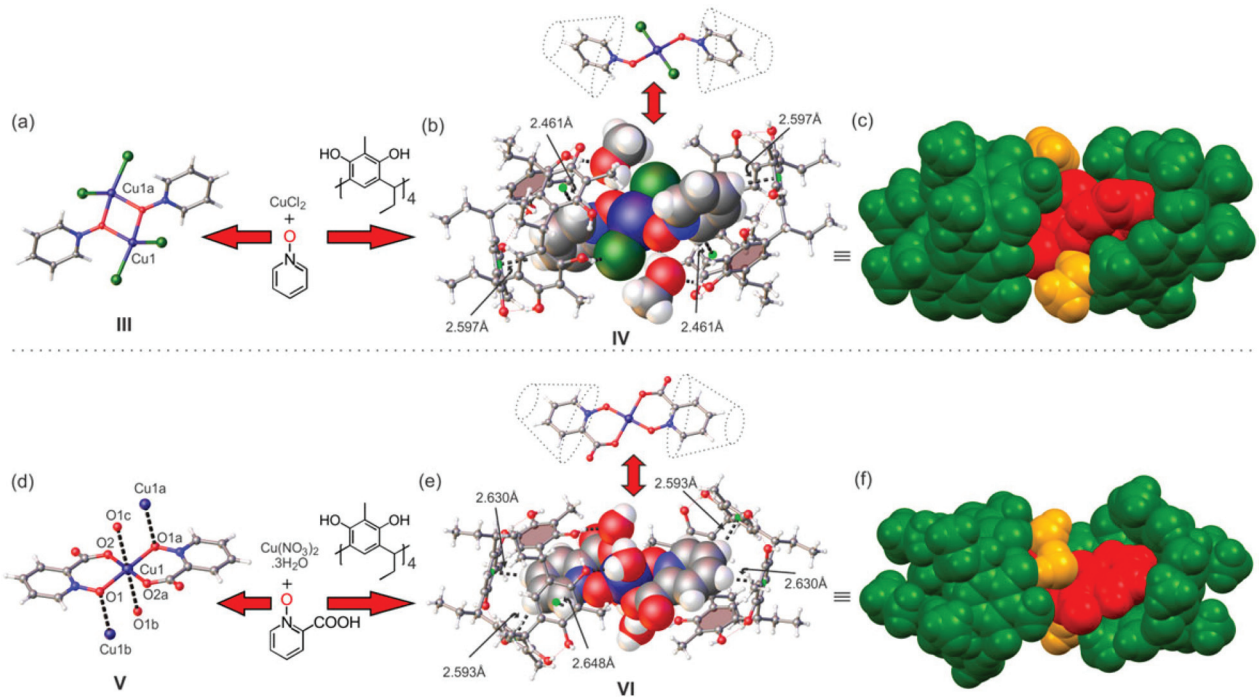

Fig. 5 (a) Ball and stick representation of complex **III**. (b) 2 : 2 : 1 Host–guest metal complex of **IV**. (c) Colour coded CPK model of complex **IV**. (d) Ball and stick representation of complex **V**. (e) 2 : 2 : 1 Host–guest metal complex of **VI**. (f) Colour coded CPK model of complex **VI**.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

narene host is rare, and a CSD search for similar four coordinate systems revealed one hit (Refcode: EBUPIC).[26] Besides different coordination spheres of Cu^{II} and their stabilization by hydrogen bond interactions, *N*-oxides **2–3** and methylresorcinarene components prefer to exchange the π-electrons by π···π and C–H···π interactions.

The π···π and C–H···π interactions 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 the 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, ∠O–H···O 138.57°) and –OH···Cl (3.127 Å, ∠O–H···Cl 163.33°) interactions (Fig. S7b†). Interestingly, the *N*-oxide in **IV** preserves its bidenticity through hydrogen bonding with a methanol molecule (Fig. S7b†). The Cu^{II} in **VI** is apically stabilized by water molecules at a Cu···O distance of 2.740 Å. Square planar geometries, especially Cu^{II} ions, compete with aqua ligands for binding and such a 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) complex 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 as a passive spectator. Despite the paramagnetic nature of Cu^{II}, the host signals could be monitored to confirm the complexation in solution *via* ^1H 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 a reaction vessel for pyridine *N*-oxide copper complexes in tuning specific Cu^{II} coordination sphere products governed by several weak interactions.

Acknowledgements

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