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Reversible Penta- and Hexacoordination Motifs in [Co(TMPP)] Resulting in Interchange of 1D and 2D Supramolecular Designs

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meso-Tetrakis(3,4,5-trimethoxyphenyl)cobalt(II) porphyrin [Co(TMPP)] (**1**) is synthesized by a new method. The X-ray structure of **1** grown in dichloromethane shows square-pyramidal coordination around the Co(II) ion, displaying a 1D polymeric network. When grown in chloroform, **1** displays an octahedral coordination around Co(II), resulting in a 2D coordination network. This solvent-dependent variation in ligation of the O-donor atom(s) of the 4-methoxy groups of the *meso*-phenyl rings in the axial position(s) of the central Co(II) is reversible, as shown by electronic spectroscopy. The magnetic and electron paramagnetic resonance (EPR) data of these two crystalline forms are dependent on the nature of the axial interaction. Increased axial coordination showed increased splitting between the e and a_1 orbitals, resulting in further separation between $^2A_1$ and ^2E. The EPR data are consistent with this result. The difference in energy levels in these two forms is in agreement with the magnetic and spectroscopic data.

Small molecules or ions such as O_2, CO, CN^-, and NO^+ are well-known for axial coordination of a metalloporphyrin in view of their biological importance.[1−3] Beyond these, functionalized porphyrins with coordinating side-arm derivatives have been used to bind axial sites to build supramolecular crystal design.[4] Readily available *meso*-tetrakis(4-pyridyl)porphyrin (H_2TPyP), *meso*-tetrakis(4-carboxylphenyl)porphyrin (H_2TCpP), *meso*-tetrakis(4-cyanophenyl)porphyrin, and other mono-, di-, and trisubstituted porphyrins have been employed to support such an extended coordination.[5−11] There are two ways a coordination network can form with metalloporphyrins.

In the first one, the peripheral coordinating group of a metalloporphyrin binds axially to the central metal atom of another molecule of the same metalloporphyrin, thus extending to a 1D, 2D, or 3D structure. Alternatively, the metalloporphyrin with peripheral coordination sites functions like a ligand to coordinate an external metal ion. In the former case, the extended arrangement may be made by repetition either of pentacoordination involving one axial ligation or of hexacoordination using biaxial ligation of each metalloporphyrin. A square-pyramidal Zn(II) with one intermolecular Zn−N(pyridyl) coordination led to a 1D network structure. However, under inclusion compounds, this led to a 3D coordination polymer involving hexacoordinate Zn(II) with ligation of two axial N(pyridyl) atoms.[12] A hexacoordinate Zn(II) porphyrin complex with two axial O donors forming a 3D polymer network has been reported.[13] Recently, a Co(II) porphyrin 1D polymer possessing both penta- and hexacoordination involving N(pyridyl) donor atom(s) has been reported.[14] Given the opportunity to opt for any such design, it will be of great interest to dictate a preferred coordination of the central metal ion over the other and the possibility of their interchange. The present Communication describes such an interchange between 1D and 2D structures governed by interchangeable penta- and hexacoordination motifs in **1**.

A new synthetic method has been developed to synthesize [Co(TMPP)] (**1**).[15] **1** crystallized differently in dichloromethane−petrol ether as **2** and in chloroform−petrol ether as **3**.[16]

The coordination geometry around the Co(II) ion in **2** is square-pyramidal and that in **3** is octahedral. As expected, for both **2** and **3**, four N-donor atoms from the four pyrrole moieties of the porphyrin ligand occupy the equatorial position along the porphyrin plane. O-donor atoms of the 4-methoxy groups of the *meso*-phenyl rings occupy the axial

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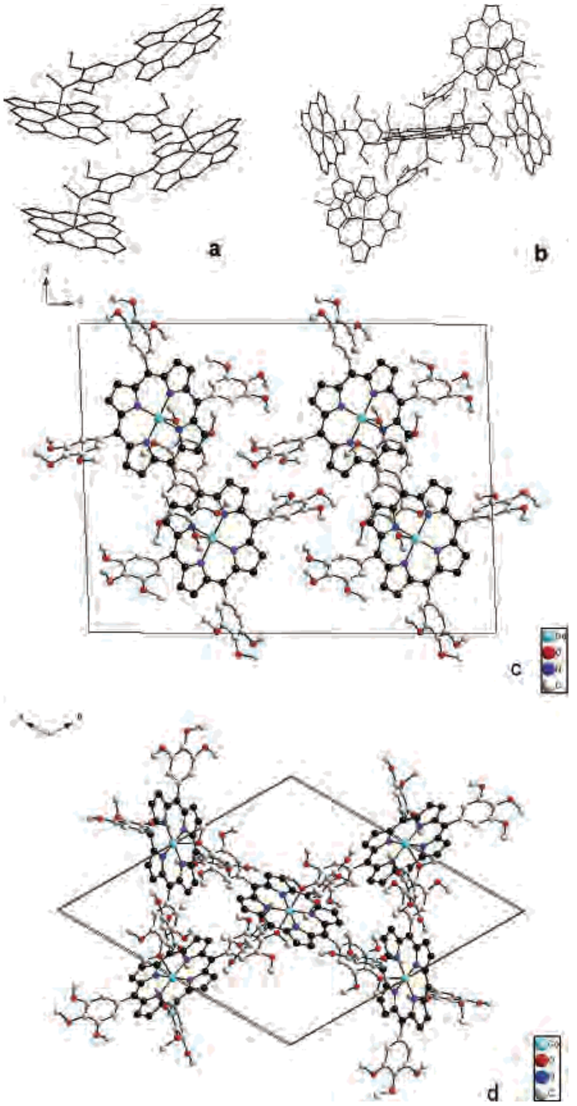

Figure 1. Basic building blocks for the two structures: (a) structure **2**; (b) structure **3**. Only the coordination around the metal ion is shown for clarity. Arrangement of structural motifs: (c) structure **2** viewed parallel to the *b* axis; (d) structure **3** viewed parallel to the *c* axis. The carbon atoms of the porphyrin ring are colored dark for a better representation.

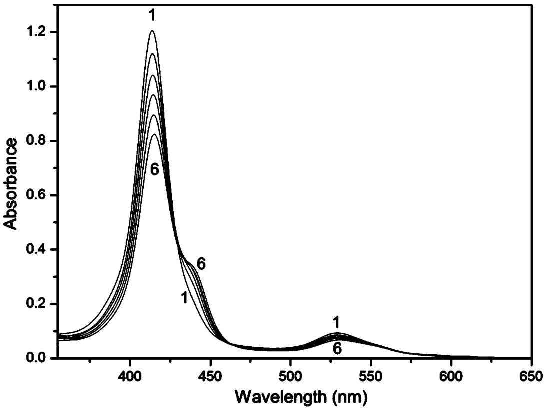

Figure 2. Typical electronic spectra of **1** (5×10^{-6} M) in dichloromethane (run 1) with changing solvent composition: 20, 30, 50, 70, and 100% chloroform (runs 2−6).

positions. Thus, **2** consists of zigzag-shaped polymeric aggregates involving ligation of only one methoxy substituent of the TMPP molecule to the metal center of another metalloporphyrin framework. In **3**, every porphyrin monomer is strongly linked to four neighboring porphyrin units. A sheet structure is formed, utilizing two trans-related trimethoxyphenyl substituents coordinating metal centers of two adjacent porphyrins along one axis, while the Co atom binds through two methoxy groups of other monomeric units along up and down faces of the porphyrin plane (Figure 1). The average Co−N distances are 1.970 Å for **2** and 1.977 Å for **3**, and Co−O distances are 2.331 Å for **2** and 2.479 Å for **3**. The angles between Co−O−C(phenyl ring) are 119.26° for **2** and 123.69° for **3**, and the angles between the neighboring porphyrin planes are 59.40° for **2** and 86.30° for **3**. Structure **2** is a 1D coordination polymer with weak van der Waals type C−H···O interaction bridging the 1D framework motif, while structure **3** is a 2D coordination polymer. The crystal structures of cobalt complexes of *meso*-tetrakis(4-methoxyphenyl)porphyrin[17] and *meso*-tetrakis(3,4-dimethoxyphenyl)porphyrin showed no such type of axial ligation,[18] revealing unique tuning of the electron density over the oxygen atom of the 4-methoxy group in *meso*-tetrakis(3,4,5-trimethoxyphenyl)porphyrin.

Either **2** or **3** in dichloromethane displayed a band at 414 nm in the Soret region. With the gradual increase of the chloroform concentration in a mixed dichloromethane−chloroform solvent, a new band at 440 nm appears with the gradual decrease in the intensity of the 414-nm band (Figure 2).

In pure chloroform, both **2** and **3** showed identical spectra with the appearance of 414- and 440-nm bands. The α peak in dichloromethane at 530 nm also broadened with the appearance of a shoulder around 555 nm in the chloroform solution. We assign these solvent-dependent spectral changes due to the formation of hexacoordinate species in the chloroform medium. The existence of penta- and hexacoordination, like LCo^{II} porphyrin + L $\leftrightarrow$ L_2Co^{II} porphyrin in equilibrium under the addition of an external donor molecule (L), is well documented.[19,20]

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(15) An equimolar amount of substituted benzaldehyde and pyrrole with cobalt chloride under reflux in DMF containing a catalytic amount of concentrated HCl led to the formation of a cobalt-containing porphyrin. For detailed synthesis and characterization, see the Supporting Information.

(16) Crystal data for **2** [$(C_{56}H_{52}CoN_4O_{12})\cdot(C_2H_2Cl_2)$]: formula weight 1116.87, monoclinic, space group $P2_1/c$, $a = 22.276(5)$ Å, $b = 8.075(5)$ Å, $c = 29.333(5)$ Å, $\beta = 92.09(0)°$, $V = 5272.88$ Å^3, $Z = 4$, $T = 100$ K, $D_{calc} = 1.409$ g cm^{-3}. Of a total of 34 032 reflections collected, 12 971 were independent ($R_{int} = 0.080$). The structure was solved by direct methods and refined by full-matrix least squares on F^2. Final R1 [$I > 2\sigma(I)$] = 0.087 and wR2 = 0.231 (all data); GOF = 1.044. Crystal data for **3** [$(C_{56}H_{52}CoN_4O_{12})$: formula weight 1031.95, trigonal, space group $R\bar{3}$, $a = 21.255(5)$ Å, $c = 28.310(5)$ Å, $V = 11076.25$ Å^3, $Z = 9$, $T = 100$ K, $D_{calc} = 1.392$ g cm^{-3}. Of a total of 19 658 reflections collected, 5488 were independent ($R_{int} = 0.066$). The structure was solved by direct methods and refined by full-matrix least squares on F^2. Final R1 [$I > 2\sigma(I)$] = 0.050 and wR2 = 0.109 (all data); GOF = 0.875. Data were collected on a Bruker-AXS Smart APEX CCD diffractometer.

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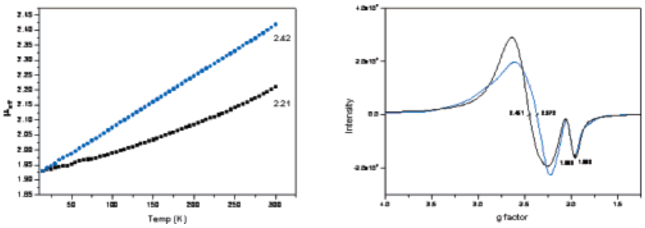

Figure 3. Variation of μ_{eff} with temperature (left) and EPR spectra at 120 K in solid form (right): **2**, blue; **3**, black.

In the present case, less polar chloroform favored the formation of hexacoordinated species isolated in the solid form **3**. However, in solution both of the forms remain in equilibrium, suggesting that the energy difference between these two forms is small under ambient conditions. Thus, **2** when recrystallized in chloroform, changed to **3**, and **3** upon recrystallization in dichloromethane changed to **2**.[21]

The solid-state magnetic moment by SQUID measurement showed $\mu_{eff} = 2.21\ \mu_B$ for **2** and $2.42\ \mu_B$ for **3** at 300 K, and both of the values dropped to show identical $\mu_{eff} = 1.9\ \mu_B$ at 10 K (Figure 3). The higher spin-only magnetic moment value for a single unpaired electron for Co(II) is attributed to the coupling of the s and p_z orbitals of the axial oxygen (of the methoxy group) with the Co d_{z^2} orbital containing the unpaired electron.[22] A larger contribution from two oxygen's in **3** is responsible for a higher μ_{eff} value than that observed in **2**. Thus, the nature of axial interaction would affect primarily the energy of the d_{z^2} orbital. In **3**, the increase in coordination along the axial *z* direction would increase the splitting between the e and a_1 d orbitals, resulting in further separation between $^2A_1$ (ground state) and ^2E (first excited state).

The EPR data (Figure 3) are consistent with this because the increase in the $^2A_1$–^2E splitting resulted in a decrease in the magnetic anisotropy value ($g_\perp$) in the case of **3** (2.372) compared to that in **2** (2.451). Expectedly, because $^4A_2$ (second excited state) is least affected by axial coordination, the observed $g_\parallel$ values remained almost unchanged ($g_\parallel$ for **2** is 1.960 and that for **3** is 1.963).[23]

This solvent-dependent penta- and hexacoordination in **1** thus mediates the interconversion between 1D and 2D structures. DFT calculation[24] using the *Gaussian 03* program[25] showed the spacing in the d orbital in **2** and **3** (Figure 4). The relative difference in energy (63.27 kJ) of the highest occupied molecular orbitals in penta- and hexacoordination supports ready structural interconversion under ambient conditions, as was observed in the electronic spectral study.

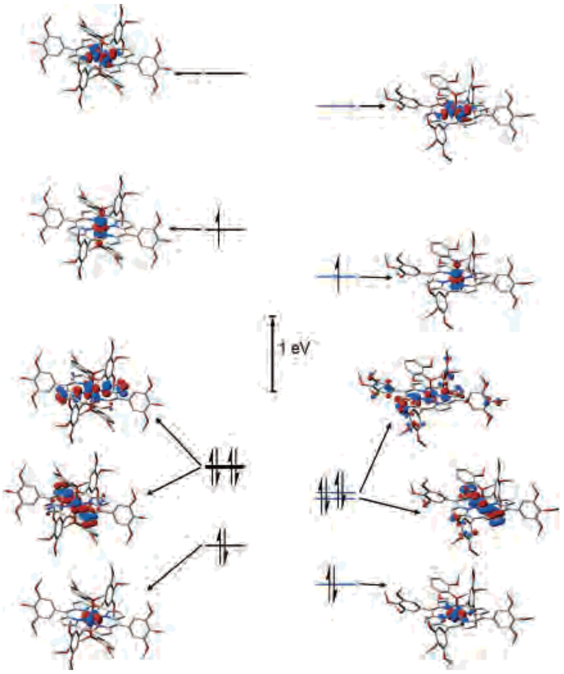

Figure 4. Metal d-type orbitals and their relative energy plots: (right) pentacoordinated (**2**); (left) hexacoordinated (**3**).

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Supporting Information Available: ORTEP plots, XRD spectra, χ_M vs *T* plot, table for *XYZ* coordinates for pentacoordinated and hexacoordinated species, and X-ray crystallographic files in CIF format for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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