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Construction of nonanuclear supramolecular structures from simple modular units

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Abstract—A porphyrazine based supramolecule with a nonanuclear structure has been prepared by the ready coordination of pyridine donor sites in octakis(4-pyridoxyethylthio)porphyrazinatomagnesium with vanadyl bis(acetylacetonate) and characterized by EPR spectroscopy.

Supramolecular structures with well-defined geometries have been attracting attention because of their potential use in diverse fields such as materials science, molecular electronics, and sensor development.[1] In all these instances noncovalent assemblies are of special importance while the order of the functional sites throughout the entire material is closely related to their properties. Starting with a multifunctional inner core, we are trying to develop a general route to obtain supramolecular architectures.

When symmetrical octakis functionalization of the central core is required, planar tetrapyrrole derivatives (e.g., phthalocyanines, porphyrins, or porphyrazines) with eight peripheral positions are the usual starting materials.[2] Porphyrazine systems and their metal complexes are known to exhibit tailorable physical (e.g., electronic, optical, magnetic, and redox) properties.[3]

It has been proved that functional groups fused to the peripheral positions of porphyrazines are integrated to the macrocyclic core more effectively than those of phthalocyanines.[4] For this reason, in the present work we have preferred a magnesium porphyrazine with eight hydroxyethylthio functional groups on the periphery as the central core of the supramolecular system.[5] Pyridine-4-carboxylic acid was chosen as the intermediate unit as its condensation with the –OH moieties will result in eight covalently bound pyridyl donor groups around the central core. Our choice as a 'capping' component was vanadyl bis(acetylacetonate) ($VO(acac)_2$) as this complex has a single empty coordination site and at the same time oxovanadium (VO^{2+}) ions are known to have important biological functions, for example, in the case of diabetes.[6]

Octakis(2-hydroxyethylthio)porphyrazinatomagnesium (**1**) was synthesized as previously reported.[5] Complete esterification of all the OH-groups in **1** with pyridine-4-carboxylic acid (isonicotinic acid) to give octakis(4-pyridoxyethylthio)porphyrazinato magnesium (**2**) was accomplished in pyridine in the presence of dicyclohexylcarbodiimide and 4-toluenesulfonic acid as catalysts in 7 days at ambient temperature.[7] Taking into account the ready coordination of $VO(acac)_2$ with pyridine donors,[8] the interaction of this reagent with **2** was performed in chloroform at reflux temperature for 6 h. The reaction was monitored by TLC (silica; MeOH/$CHCl_3$ 1:50). The nonanuclear dark green solid supramolecular product, $[VO(acac)_2(4\text{-pyCOOCH}_2\text{CH}_2\text{S})]_8$ MgPz (**3**) was obtained in high yield (76%).[9]

The proposed structures of the octakis(pyridyl) derivative **2** and the supramolecule **3** are consistent with their spectral characterization; the vanadium content of **3** was determined by ICP after decomposition of the product with concd HNO_3 and the result closely followed the octa coordination.[7,9] The visible absorption spectra of **2**

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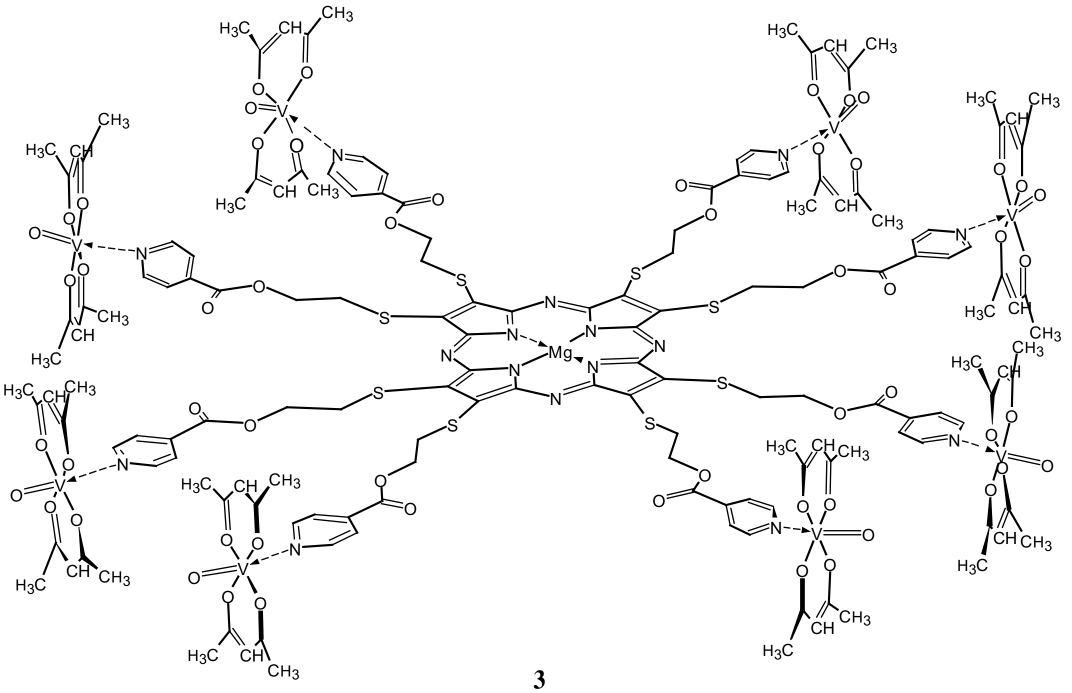

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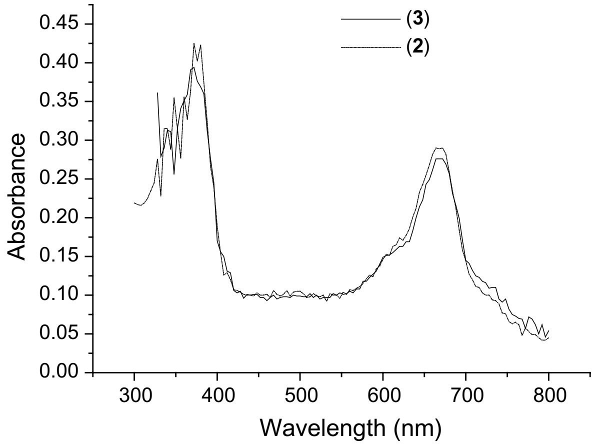

Figure 1. Electronic absorption spectra of **2** and **3** in chloroform.

and **3** in chloroform are similar (Fig. 1). Since VO(acac)$_2$ complexes are not expected to have intense absorptions comparable with the B and Q bands of porphyrazines, this result is meaningful. Although the Q bands are known to be extremely sensitive to aggregation of the tetrapyrrole cores, complexation of pyridine units on the periphery has negligible effect in this sense.

Coordination of the VO(acac)$_2$ groups to the pyridine donors on the periphery of diamagnetic **2** resulted in the paramagnetic supramolecular structure **3**. This phenomenon has been followed by the EPR technique.[10] The EPR spectra of **3** in powder form or as a chloroform solution clearly indicated the presence of paramagnetic centers (Fig. 2). When compared with the EPR spectrum of the VO(acac)$_2$ precursor, typical hyperfine splitting of the X-band EPR spectrum in **3** is evident.

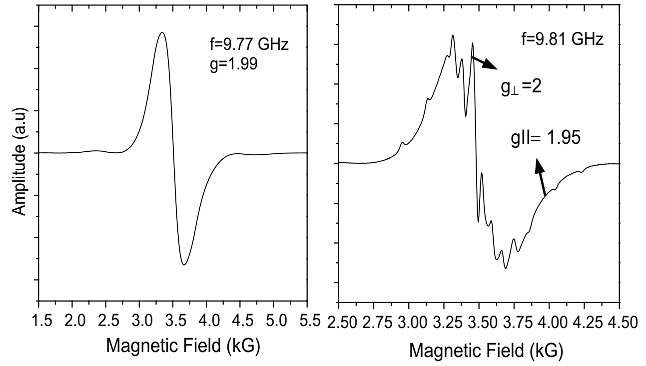

Figure 2. X-band EPR spectra of (a) VO(acac)$_2$ and (b) **3** in powder form at 300 K.

The signal recorded in the case of the supramolecular structure **3** has a characteristic and anisotropic curve that specifies a uniaxial symmetry for the compound with $g_\perp$ slightly greater than $g_\parallel$. Here, $g_\perp$ and $g_\parallel$ denote the effective g values when the external DC field is perpendicular and parallel, respectively, to the symmetry axis of the crystal field around the paramagnetic center. Both the parallel and perpendicular part of the spectrum contain hyperfine peaks. At the perpendicular part of the spectrum, seven hyperfine peaks are well separated due to their location at the central region. For the parallel part, six hyperfine peaks are clearly observed at both sides of the perpendicular region. However, eight hyperfine peaks are expected due to the interaction between the electronic spin of the magnetic electrons and the nuclear spin of the V^{4+} ($I = 7/2$) ion for both the parallel and perpendicular parts of this porphyrazine compound. The reason for the appearance of fewer peaks is probably due to superimposition and line broadening in the spectrum.

In summary, the new procedure described here for the synthesis of supramolecular product **3** may be a versatile approach to multinuclear compounds. Further studies on **3** and closely related molecules are currently in progress.

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