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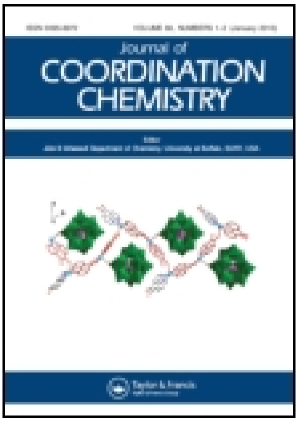

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Synthesis and EPR studies of soluble vanadyl octakis (4-*tert*-butylbenzylthio) porphyrazine

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Magnesium porphyrazinate substituted with eight 4-*tert*-butylphenylthio-groups on peripheral positions has been synthesized by cyclotetramerization of 1,2-bis(4-*t*-butylphenylthio)maleonitrile in the presence of magnesium butanolate. The metal-free derivative was obtained by treatment with trifluoroacetic acid and further reaction of this product with vanadyl(IV) sulfate led to the vanadyl porphyrazinate. These new compounds have been characterized by elemental analysis, together with FTIR, and UV–vis spectral data. The magnetic properties of the complex have been investigated by electron paramagnetic resonance spectroscopy.

Keywords: Porphyrazine; Vanadyl(IV) sulfate; EPR

1. Introduction

Porphyrazines (Pz) belong to a broad class of macroheterocyclic tetrapyrrolic systems, constitutionally tetraaza analogs of porphyrins in which *meso* nitrogens replace the methine groups and phthalocyanines (Pc) which contain benzenoid rings fused to the macrocyclic periphery. Porphyrazines have dominant blue and blue-green pigments due to their intense absorption at long wavelengths in the visible spectrum, excellent durability, and unique electronic and optical properties [1–3]. Strong correlation between the nature of the substituent and the presence of soft S-donors in affecting solid-state interactions of the macrocyclic ring system, coupled with relative ease of synthesis, has led to a large series of derivatives with physical and chemical properties of the porphyrazines comparable to those of phthalocyanines [4, 5]. In comparison to other family members, porphyrazines maintain a unique class due to much increased solubility in organic solvents compared with their phthalocyanine analogs and interactions with alkali or transition metal ions incorporated into the macrocycle core provides candidates for a series of applications [6–13]. Although porphyrazines possess numerous potential applications in technology including chemical sensors, molecular electronics, organic solar cells, photodynamic therapy, organic field effect transistors, biological agents, and metal-insulator-semiconductor-based devices, the

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*Corresponding author. Emails: bahadirkeskin@gmail.com; bkeskin@yildiz.edu.tr electronic and paramagnetic properties of porphyrazine have not been widely studied [14–19].

Vanadyl phthalocyanine (VOPc), a non-planar metallo-phthalocyanine [20, 21] with hydrophilic V=O core, high-valence vanadium ions (denoted as V(IV)), like the parent Pc and many of its metal derivatives, exhibits photoconductive and semiconductive properties [22]. The V–O axis in VOPc is located perpendicular to the plane of the molecule [23], leading the vanadyl oxygen to "stick out" of the overall molecular plane [24]. VOPc is known to be a dye with high thermal and chemical stabilities, large third-order nonlinear optical susceptibility [25], ultra-fast optical response, and good stability against visible light irradiation [26]. The coordination chemistry of vanadium originates from its relevance in several biological systems, with applications of its complexes in medicinal chemistry, organic synthesis, and catalysis [27]. They are promising candidates for realizing optical and electronic functional devices; transparent organic thin-film transistors [28]; hole transport layers with increased carrier density and conductivity [29]; and important biological functions in the case of diabetes with oxovanadium (VO^{2+}) ions [30]. Therefore, electronic and magnetic properties of these compounds should be sensitive to the nature of substituent ions and peripheral complexes [15, 31].

The limited solubility of the parent VOPc molecule causes difficulties in purification and interconversion among the morphological forms. This has been resolved by the addition of solubilizing groups such as *tert*-butyl on the periphery [31, 32]. The *tert*-butyl substituted phthalocyanine and analogues provide high solubility in organic solvents [32] and extends the potential applications of these macromolecules, such as good volatility in vacuum and they were shown to be good candidates for the preparation of thin films by vacuum thermal evaporation [33]. Thus, in the present article, we report a porphyrazine core with eight 4-*tert*-butylbenzyl units attached to the peripheral positions through methylthio bridges and vanadyl (VO^{2+}) insertion into the inner core resulting in soluble octakis(4-*tert*-butylbenzylthio)porphyrazinato vanadyl complex (VOPz). We also reported an electron paramagnetic resonance (EPR) investigation of the paramagnetic properties of the compound.

2. Experimental

2.1. *Materials and methods*

The 1,2-bis-(4-*t*-butylbenzylthio)maleonitrile (TBBTMNT), octakis(4-*tert*-butylbenzylthio) porphyrazinato magnesium(II) (MgPz), and metal-free octakis(4-*tert*-butylbenzylthio) $^{21}H,^{23}H$ porphyrazine (H_2Pz) were prepared according to previously reported procedures with minor changes and characterized by comparing their spectral data to those reported earlier [13]. Mg(II) complex and metal-free porphyrazine were stable at room temperature and they were non-hygroscopic and insoluble in water but soluble in many common organic solvents. Reagents: chemicals employed were of the highest grade available. Unless specified otherwise, reagent grade reactants and solvents were used as received from chemical suppliers.

FTIR spectra were recorded from 4000 to 400 cm^{-1} on a Perkin-Elmer Spectrum One spectrometer using KBr pellets. The electronic spectra and absorbance measurements were recorded on an Agile 8453 UV–visible spectroscopic system. Proton NMR spectra were recorded on Bruker 250 and 500 MHz Varian Inova spectrometers. Elemental analyses were recorded on Thermo Flashea 1112 series equipment. The EPR powder spectrum was recorded with a Bruker EMX X-band spectrometer (9.512 GHz) with about 100.8 mW microwave power and 100 kHz magnetic field modulation.

2.2. *Synthesis of H_2Pz*

MgPz complex (985 mg, 0.559 mM) was dissolved in minimum CF_3COOH and stirred for 6 h at room temperature. The reaction mixture was added into ammonia solution (25%, 7 mL) to neutralize and then cooled at 0 °C. It was treated with chloroform and then the organic phase was washed first with water, then with a solution of 10% Na_2CO_3, and then with water again. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated in vacuum. The oily product was treated with a small amount of diethyl ether by cooling in an ice-bath to enhance precipitation and was filtered cold. Finally, pure violet-colored metal-free porphyrazine was obtained after it was dried in vacuum. Product **2** was soluble in chloroform, dichloromethane, dimethylformamide (DMF) and THF. Yield: 0.341 g (%35). IR (KBr), ν_{max}/cm^{-1}: 3289w (m, N–H), 3024w (m, H–Ar), 2956 m (C–H in C–$(CH_3)_3$), 1513, 1461, 1201, 834, 741, 703. ^1H NMR ($CDCl_3$ 250 MHz): $d = 7.33$–7.17 (m, 4H, Ar–H), 5.18 (s, 2H, CH_2–S), 1.17 (s, 9H, (CH_3)–C), −1.55 (br, m, 2H, N–H). UV–vis (in $CHCl_3$) λ_{max} (nm) (log ε): 336 (3.95) 652 (3.74) 711 (3.87).

2.3. *Synthesis of VOPz*

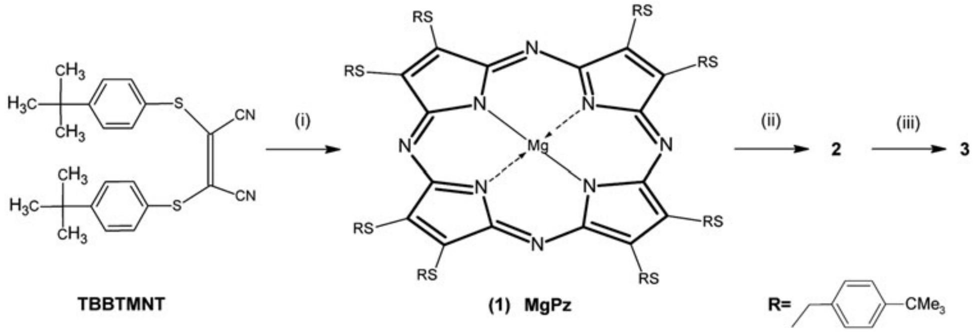
A mixture of H_2Pz (0.12 g, 0.07 mM) and $VOSO_4 \cdot 5H_2O$ (0.107 g, 0.8 mM) was refluxed for 18 h in 15 mL of DMF. After cooling to room temperature, the vanadyl derivative of porphyrazine was precipitated by the addition of methanol and the solid compound was isolated by centrifugation. The complex was filtered, washed with methanol, and dried to get constant weight under vacuum (0.05 g, yield ca. 61%). Product **3** was very soluble in chloroform and THF. IR (KBr), ν_{max}/cm^{-1}: 3048w (m, H–Ar), 2957 m (C–H in C–$(CH_3)_3$), 1631, 1446, 990 m (V=O). UV–vis (in $CHCl_3$) λ_{max} (nm) (log ε): 354 (3.82), 692 (3.51). Calculated for $C_{104}H_{120}N_8OS_8V$: C 69.18%, H 6.70%, N 6.21%, S 14.21%. Anal. Calcd Found: C 68.23%, H 6.52%, N 5.86%, S 12.34%.

3. Results and discussion

3.1. *Synthesis*

The starting point of this new VOPz structure with eight (4-*tert*-butylbenzylthio) groups bound to the periphery is 1,2-bis-(4-*t*-butylbenzylthio)maleonitrile (TBBTMnt), which was synthesized as a solid product in relatively high yield according to the previously reported procedure (scheme 1) [13]. The presence of electron-donating sulfur is expected to shift the absorption range of the porphyrazine Q-band to higher wavelength and *tert*-butyl groups to enhance solubility [6, 12, 13, 34].

The cyclotetramerization process of dinitrile derivative (TBBTMnt) by the template effect of magnesium butanolate in butanol resulted in blue-green octakis(4-*tert*-butyl-benzylthio)porphyrazinato magnesium **1** in very good yield (figure 1). The metal-free derivatives of **2** were obtained in a reasonable yield of 30–40% by treatment of **2** with trifluoroacetic acid at room temperature for 6 h. Change of color from dark blue-green to



Scheme 1. Synthesis of VOPz; (i) Mg turnings, I_2, n-BuOH; (ii) CF_3CO_2H; (iii) $VOSO_4{\cdot}5H_2O$, reflux.

Figure 1. Schematic representation of porphyrazines.

purplish blue and lower solubility are differences between magnesium and metal-free derivatives. Porphyrazines having eight 4-*tert*-butyl-benzylthio groups, VOPz, are similar to phthalocyanine macrocycles in terms of structure and other important properties like low solubility, high stability, and characteristic Soret and Q-band absorptions [30]. Insertion of vanadyl into **2** with vanadyl(IV) sulfate was performed in DMF at reflux for 18 h affording **3** in good yield. Elemental analyses follow the values calculated for **3**. Octakis (4-*tert*-butyl-benzylthio)porphyrazines and t-Bu_8VOPz are very poorly soluble in some organic solvents, such as hydrocarbons, ethanol, and methanol, but have higher solubility in chloroform and donor solvents (DMSO, DMF) [33, 35, 36].

3.2. *Spectroscopic properties*

Spectroscopic investigations on the newly synthesized intermediates and porphyrazines are in accord with the proposed structures. In the FTIR spectrum of TBBTMNT, the stretch of C≡N is observed at 2213 cm^{-1}, *t*-butyl peak at 2978 cm^{-1}, S–CH_2 peak at 680 cm^{-1}, and aromatic C–H peaks at 3028 cm^{-1}. These values comply with those reported in the literature for similar compounds and with the previous report for TBBTMNT [13]. The sharp C≡N vibration at 2213 cm^{-1} disappeared after the formation of porphyrazine **1**. The N–H stretch of the inner core of metal-free porphyrazine **2** was observed at 3289 cm^{-1} by demetalation [13, 37]. The FTIR spectrum of VOPz (**3**) showed a stretch of the *t*-butyl peak at 2863–2956 cm^{-1} and aromatic C–H peaks at 3028 cm^{-1}, which are very similar with the literature (M = Cu, Co, Zn) as expected [12, 13]. The absence of N–H peaks and the presence of a V=O peak at 990 cm^{-1} are evidences for the formation of VOPz [31].

In ^{1}H NMR spectra of **1** and **2,** chemical shifts corresponding to *tert*-butyl protons are the expected singlet at 1.3 ppm in TBBTMNT, 1.14 ppm in **1**, and 1.33 ppm in **3**. The inner core N–H protons of the metal-free porphyrazine **2** were also identified in the ^{1}H NMR spectra with a broad peak at −1.55 ppm presenting the typical shielding of inner core protons, common in ^{1}H NMR spectra of metal-free porphyrazines [3, 13, 37].

To identify the structure of **1–3**, electronic spectra are especially useful. The electronic absorption spectra of metallo-porphyrazines **1** and **3** exhibit a strong absorption between 675 and 692 nm, which is due to a $\pi \rightarrow \pi^*$ transition from HOMO–LUMO energy levels having D_{4h} molecular symmetry and is commonly referred to as the Q-band. A second intense and broad $\pi \rightarrow \pi^*$ transition in the near UV region (336–378 nm), called the soret or B-band, is also a characteristic of tetrapyrrole derivatives [3, 12, 13]. UV–vis spectra of metallo-porphyrazines **1** and **3** (4×10^{-5} M solutions in chloroform) prepared in the present work exhibited intense single Q-band absorption of the $\pi \rightarrow \pi^*$ transition at 675 and 692 nm and B-bands at 378 and 352 nm, respectively (figure 2). The Q-band absorption of VOPz in chloroform is a broad single peak which indicates axial ligation of chloroform at the vacant site of vanadium with similar symmetry to the Mg(II) complex [31]. The change of symmetry of porphyrazine core from D_{4h} for metallo-species to D_{2h} in metal-free **2** shows a split Q-band at 652 and 711 nm, as expected [4, 13, 38]. UV–vis spectra were measured at different concentrations to assess whether or not **3** reveals aggregation.

3.3. *EPR spectroscopy of VOPz*

The powder EPR spectrum of VOPz recorded at room temperature is given in figure 3, with its computer simulation by using SimFonia program with the experimental values as input data. Low and high intensity lines with hyperfine splitting have been seen in this

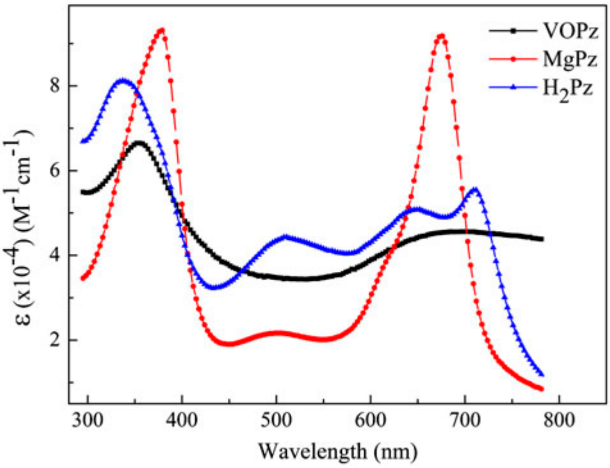


Figure 2. Electronic spectra of octakis(4-*tert*-butylbenzylthio) substituted porphyrazines **1**, **2**, and **3** as solutions in $CHCl_3$.

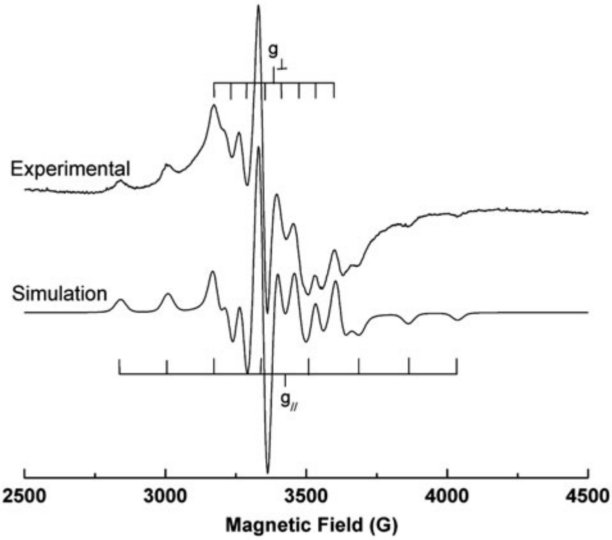


Figure 3. The EPR powder spectrum of VOPz at room temperature and its computer simulation.

spectrum. The group with low intensity is the parallel component, because in this case the external dc field is parallel to the symmetry axis of the crystal field around the paramagnetic center. The group with high intensity represents a perpendicular component owing to external dc field, perpendicular to the symmetry axis around the paramagnetic center. These groups are denoted as $g_{//}$ and $g_{\perp}$ in terms of spin-Hamiltonian parameters in figure 3. Each set of eight hyperfine lines can be explained in terms of an unpaired electron ($S = 1/2$) interacting with ^{51}V having a nuclear spin $I = 7/2$. The VO^{2+} ion consists of a V^{4+} in $3d^1$ configuration. The intensities of the two sets of lines are a measure of population of VO^{2+} ions in the parallel and perpendicular orientations.

The spin-Hamiltonian parameters obtained from the spectra are $g_{//} = 1.975$ and $g_{\perp} = 1.994$ with $g_{av} = 1.987$, where $g_{av} = 1/3(g_{//} + 2g_{\perp})$; $A_{//} = 171$ G and $A_{\perp} = 61$ G with $A_{av} = 98$ G, where $A_{av} = 1/3(A_{//} + 2A_{\perp})$. The g values suggest that local symmetry of the paramagnetic center is axial. The order of $g_e > g_{\perp} > g_{//}$ (free electron g value, $g_e = 2.0023$) reveals a VO^{2+} in a tetragonally compressed octahedron and the b_2 (d_{xy}) level is lowest [39]. Small variations in the value of g and A indicate sensitivity of VO^{2+} in different ligand field environments. Thus, the EPR spectrum of this ion is strongly dependent on the donors bound to the metal, different for nitrogen and oxygen donors. With more covalent bonding, the g values are higher and hyperfine splitting lowers [40].

VO^{2+} has very large $A_{//}$ principal value of the ^{51}V hyperfine splitting constant; $A_{\perp}$ principal value (= A_{xx}, A_{yy}) is normally about three times smaller. This originates from a strong tendency to form a very short V–O bond. Because of this, $A_{//}$ (= A_{zz}) is approximately aligned along the V–O bond direction which defines the oxygen involved in the V–O bond.

EPR data can be interpreted in terms of molecular orbitals by using g and A parameters. The values of $A_{//}$ and $A_{\perp}$ for VO^{2+} can be written as [40]:

$$A_{//} = -PK - \tfrac{4}{7}\beta_2^2 P - (g_e - g_{//})P - \tfrac{3}{7}(g_e - g_{\perp})P \qquad (1)$$

$$A_{\perp} = -PK + \tfrac{2}{7}\beta_2^2 P - \tfrac{11}{14}(g_e - g_{\perp})P \tag{2}$$

where P is the direct dipole–dipole interaction constant of the magnetic moment of the electron with the magnetic moment of vanadium (taken as 13.6 mT) [41], K is the Fermi contact term and indicates the d-orbital population for unpaired electron, and β_2 is in plane π-bonding coefficient of VO^{2+} with the ligands. Using the $A_{//}$, $A_{\perp}$ (taking as negative) and $g_{//}$, $g_{\perp}$ values given for VO^{2+}, we obtain $K = 0.703$ and $\beta_2^2 = 0.915$.

The largest value of β_2^2 is 1 and deviation from this value is a measure of the bonding of the d_{xy} orbital of VO^{2+} with the π-orbitals of ligands. The lowering of β_2^2 value arises from delocalization of electron onto the ligand with increase in covalent bonding. The values obtained in this study are in agreement with the literature values of VO^{2+} [30, 42–48].

4. Conclusions

We have described the synthesis and spectral characterization of new vanadyl complex of porphyrazine with eight *tert*-butylphenyl groups on the periphery. These compounds have good solubility in many common organic solvents. The presence of bulky *tert*-butyl groups hindered aggregation at higher concentrations (e.g. 10^{-3} M).

The g parameters and hyperfine splittings indicate the presence of one paramagnetic axially symmetric VO^{2+} coordinated by pyrrolic N with axial symmetry for **3**. The values obtained in this study are in agreement with the literature values for VO^{2+} complexes of porphyrinic macrocycles.

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